QUINOLINES

Part II

This is the thirty-second volume in the series

THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

A SERIES OF MONOGRAPHS

ARNOLD WEISSBERGER and EDWARD C. TAYLOR

Editors



QUINOLINES

Part II

Edited by

Gurnos Jones

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KEELE
STAFFORDSHIRE



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The Chemistry of Heterocyclic Compounds

The chemistry of heterocyclic compounds is one of the most complex branches of organic chemistry. It is equally interesting for its theoretical implications, for the diversity of its synthetic procedures, and for the physiological and industrial significance of heterocyclic compounds.

A field of such importance and intrinsic difficulty should be made as readily accessible as possible, and the lack of a modern detailed and comprehensive presentation of heterocyclic chemistry is therefore keenly felt. It is the intention of the present series to fill this gap by expert presentations of the various branches of heterocyclic chemistry. The subdivisions have been designed to cover the field in its entirety by monographs which reflect the importance and the interrelations of the various compounds, and accommodate the specific interests of the authors.

In order to continue to make heterocyclic chemistry as readily accessible as possible new editions are planned for those areas where the respective volumes in the first edition have become obsolete by overwhelming progress. If, however, the changes are not too great so that the first editions can be brought up-to-date by supplementary volumes, supplements to the respective volumes will be published in the first edition.

ARNOLD WEISSBERGER

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Preface

The second part of the volume dealing with the chemistry of quinolines follows the pattern of the first. Every effort has been made to present a comprehensive coverage of the three classes of compound dealt with. A slight departure from the normal procedure has been necessary in Chapter 3, where over 300 references to purely biological properties of the *N*-oxides have been grouped as a bibliography. As in the first part, tabulated compounds are not generally entered in the subject index.

One of the authors (P. A. C.) is indebted to the City University for leave of absence to enable the final stages of the work to be completed in a reasonable time. He, and I, also thank our wives for help given during the preparation of the manuscripts.

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CHAPTER 1

Alkylquinolines and Arylquinolines

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I. Alkylquinolines and Aralkylquinolines

1. Preparation by Pyrolysis and Degradation of Natural Products

Alkylquinoline derivatives, together with quinoline itself, isoquinolines and other organic bases, have been obtained by the thermal degradation of natural organic compounds containing nitrogen. This constitutes an important source of mixed quinoline bases from which individual compounds can frequently be isolated by methods described in Section I.4.H and in the references listed in Table 1.

Petroleum crude oils and distillates and coal tar are the most important source materials for quinoline bases; in other cases, especially the degradation of alkaloids, the isolation of the quinoline bases is important more as an indication of the composition and structure of the original materials. Other natural products from which quinoline bases have been isolated by pyrolysis or other methods of degradation include shale oil, lignite, soot, tea, soya bean cake and tobacco smoke.

Details of the methods involved can be found in the references given in Tables 1 and 2, which constitute a list of the alkylquinolines obtained. Their production from coal tars has been reviewed.[70,1593]

TABLE 1. Alkylquinolines Obtained by Pyrolysis from Petroleum, Coal Tar and Other Natural Sources

Quinoline derivative	Source	References
2-Methyl-	Petroleum (Californian)	1, 5
	Lignite	16
	Coal tar	22, 24, 27, 28, 30, 35, 36, 37, 38, 41, 100, 1592
	Sapropel tar	23, 25, 26
	Black tea aroma	42
	Soya bean	43
	Shale oil	1597

TABLE 1 (*cont.*)

Quinoline derivative	Source	References
3-Methyl-	Petroleum (Californian)	1
	Shale oil	44
	Coal tar	39, 22, 109
	Green coffee	1601
4-Methyl-	Petroleum (Californian)	1, 5
	Coal tar	39, 30, 29, 34, 24, 31, 35, 37, 38, 33, 41, 22, 36, 109
	Sapropel tar	26
	Burley tobacco flavour	45
	Green coffee	1601
5-Methyl-	Coal tar	34, 32, 33, 45, 109
	Sapropel tar	26
6-Methyl-	Coal tar	39, 38, 53, 41, 109
	Sapropel tar	26, 25
	Shale oil	16, 44
7-Methyl-	Petroleum (Californian)	1
	Petroleum (Russian)	46
	Shale oil	44, 47, 16
	Coal tar	39, 34, 38, 33, 41, 36, 109
	Sapropel tar	26, 25
8-Methyl-	Petroleum (Californian)	1
	Shale oil	44, 47, 16
	Coal tar	39, 38, 33, 41, 22, 19, 109
2,3-Dimethyl-	Petroleum	15, 3, 49
	Petroleum (Russian)	48
	Coal tar	39, 18, 21
2,4-Dimethyl-	Petroleum (Californian)	5, 3
	Shale oil	16
	Coal tar	39, 30, 18, 24, 38, 21, 36
2,5-Dimethyl-	Petroleum (Californian)	5
	Tobacco smoke	50
2,6-Dimethyl-	Petroleum (Californian)	5
	Coal tar	39, 38, 21, 41
	Black tea aroma	42
	Tobacco smoke	51
2,7-Dimethyl-	Coal tar	21
2,8-Dimethyl-	Petroleum (Californian)	1, 4
	Shale oil	44, 47, 16
	Coal tar	38
3,5-Dimethyl-	Petroleum (Californian)	5
3,8-Dimethyl-	Petroleum (Californian)	49
4,6-Dimethyl-	Coal tar	38, 36
5,8-Dimethyl-	Coal tar	17
6,8-Dimethyl-	Coal tar	18, 41
2,3,4-Trimethyl-	Petroleum (Californian)	7
2,3,8-Trimethyl-	Petroleum (Californian)	49
	Shale oil	47
2,4,6-Trimethyl-	Coal tar	18
2,4,8-Trimethyl-	Petroleum (Californian)	2
	Petroleum (Russian)	52
	Coal tar	18
2,6,8-Trimethyl-	Coal tar	18
2,3,4,8-Tetramethyl-	Petroleum (Californian)	7
'2,3-Dimethyl-8-alkyl-'	Petroleum (Russian)	48

TABLE 1 (*cont.*)

Quinoline derivative	Source	References
'2,3,4-Trimethyl-8-alkyl-'	Petroleum (Russian)	48
8-Ethyl-	Petroleum (Californian)	12
2-Ethyl-3-methyl-	Petroleum (Russian)	48
8-Ethyl-2-methyl-	Petroleum (Californian)	12
8-Ethyl-3-methyl-	Petroleum (Californian)	15, 6
2,3-Dimethyl-4-ethyl-	Petroleum (Californian)	11
	Petroleum (Russian)	52
2,3-Dimethyl-8-ethyl-	Petroleum (Californian)	15, 6
	Petroleum (Russian)	52, 53
2,4-Dimethyl-8-ethyl-	Petroleum (Californian)	8
4-Ethyl-2,3,8-trimethyl-	Petroleum (Californian)	11
	Petroleum (Russian)	52
8-Ethyl-2,3,4-trimethyl-	Petroleum (Californian)	11, 9
4,8-Diethyl-2,3-dimethyl-	Petroleum (Californian)	14
2,3-Dimethyl-8-propyl	Petroleum (Californian)	7
	Petroleum (Russian)	52, 53
2,4-Dimethyl-8-propyl	Petroleum (Californian)	9
8-Isopropyl-2,3,4-trimethyl-	Petroleum (Californian)	13
8-Propyl-2,3,4-trimethyl	Petroleum (Californian)	9
	Petroleum (Russian)	52, 53
2,4-Dimethyl-6-(1-methyl-propyl)-	Petroleum (Californian)	10
2,4-Dimethyl-8-(1-methyl-propyl)-	Petroleum (Californain)	10
2,3-Dimethyl-4-ethyl-8-propyl-	Petroleum (Californian)	14
'C_{11}-alkyl-' and 'C_2-alkyl-'	Petroleum (Russian)	54
1,2,3,4-Tetrahydroacridine	Coal tar	20
'Alkylquinolines'	Shale oil (Tasmanian)	55
'Methylquinolines, dimethylquinolines and/or ethylquinolines'	Coal soot	40
'Methylquinolines and dimethylquinolines'	Tobacco smoke	56
'Alkylquinolines'	Cane peat	1602
	Shale oil	1598, 1599
	Petroleum (Russian)	1506, 1594
	Deasphaltizate	1595
	Petroleum (Californian)	1596
	Atmospheric pollutants	1600
'Dimethylquinolines'	Petroleum (Russian)	1507
Cycloalkylquinolines	Petroleum (Russian)	1594

2. Synthesis from Compounds Not Containing a Quinoline Ring System

The many methods available for the synthesis of the quinoline ring system (see e.g. Part I, Chapter 2) can be used for the preparation of alkyl- and other substituted quinolines. In particular, the methods of Skraup, Doebner, Von Miller, Friedlander, Pfitzinger, Combes, Beyer, Conrad-Limpach, Knorr and others have been used extensively. Specific references to the use of these methods are given in the Tables of Part I, Chapter 2, Section VI. For example, the reaction of anthranil with ketones, alkenes or alkynes gives a

TABLE 2. Alkylquinolines Obtained by Degradation of Alkaloids

Quinoline derivative	Source	References
2-Methyl-	*P. harmala*	57
4-Methyl-	Cinchona alkaloids	58
	Cinchonine, cinchonidine	59
4-Methyl-6-methoxy-	Quinine, quinidine	59
7-Methyl-	Annotinine	60, 61
	Obscurine	62, 228
	Lycopodine	63
8-Methyl-	Nitramine, *Nitraria schoberi*	64
2-Pentyl-	Angostura bark	65, 66
5,7-Dimethyl-	Lycopodine	63
8-Ethyl-6-methyl-	*Tabernanthe iboga*	67
3-Butyl-6,8-dipropyl-	Ormosia alkaloids	68, 69
6-Butyl-3,8-dipropyl-	Ormosanine and ormojanine	68, 69
3-Pentyl-6,8-dipropyl-	Ormosanine and ormojanine	68, 69
6-Pentyl-3,8-dipropyl-	Ormosanine and ormojanine	68, 69
8-Pentyl-3,6-dipropyl-	Ormosanine and ormojanine	68, 69

variety of 2,3-substituted quinolines in moderate yields (6–39%).[306] The use of cycloaliphatic ketones provides a convenient route to 2,3-polymethylene-substituted quinolines, including tetrahydroacridine. The reaction proceeds by a 1,3-dipolar addition via the quinoline *N*-oxide.

Methods for the preparation of alkyl- and aralkylquinolines from compounds already containing a quinoline ring are given below.

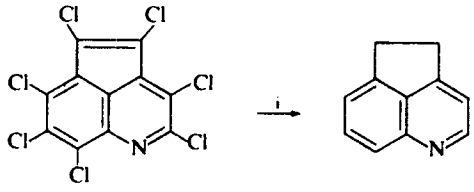
3. Synthesis from Compounds Containing a Quinoline Ring System

A. Reduction Methods

Alkylquinolines (and other substituted quinolines) can frequently be obtained from compounds containing additional functional groups by modification or elimination of these groups, frequently by reductive processes. The most important examples are the removal of hydroxyl groups (or amido-oxygen), frequently present as a result of synthesis by the Conrad–Limpach or Knorr reactions. This can be done directly or after replacement by halogen. The reduction of carbonyl and alkenyl side-chains also provides useful routes to alkyl quinolines.

a. REDUCTION OF HALOGEN DERIVATIVES Halogens attached to the quinoline ring, particularly those at positions 2 and 4, can be replaced by hydrogen by heating with hydrogen iodide in acetic acid; thus 4-chloro-2-methylquinoline at 250–270 °C gave 2-methylquinoline[71] (quinaldine), 2-chloro-3-ethylquinoline at 240 °C gave 3-ethylquinoline[72] and 2-chloro-7-isopropylquinoline[73] at 220–240 °C, 4-chloro-2,3-dimethylquinoline[74] at 275 °C, 2-chloro-3-methyl-4-ethylquinoline[74] at 260 °C and 2-chloro-3,4-diethylquinoline[74] at 295 °C gave the respective alkylquinolines by this method. Similar results have been achieved with hydrogen iodide and red phosphorus, for example 4-methylquinoline (lepidine) was obtained by this method[75] from its 2-chloro derivative at 170 °C and 4-ethylquinoline from 2-chloro-4-ethylquinoline with hydrogen iodide, red phosphorus and potassium iodide.[74] The reduction of 2,4-dichloro-5-methylquinoline with tin and hydrochloric acid[76] gave 5-methylquinoline together

with some 5-methyl-1,2,3,4-tetrahydroquinoline. Catalytic methods have also been used successfully; thus the following have been reduced to alkylquinolines with hydrogen and Pd/C or Ni: 2-chloro derivatives of 4-methyl-, 6-methyl-, 8-methyl, 5,8-dimethyl- and 6,8-dimethylquinolines,[77,495,497] the 4-chloro derivatives of 7-methyl- and 3,5-dimethylquinolines[80] and 4-chloro-2-(dibromomethyl)-3-vinylquinoline[96] (the last compound to 2-methyl-3-ethylquinoline). 4,5-Dihydrocyclopenta[*d,e*]quinoline (**2**) was formed by reduction of the heptachloroacenaphthene (**1**).[79] In this case nuclear-substituted chlorines in positions other than 2 and 4 were reduced. 5-Methylquinoline was obtained in high yield by the catalytic reduction (H_2/Pd, $CaCO_3$) of 5-methyl-8-chloroquinoline.[208]



(1)

(i)

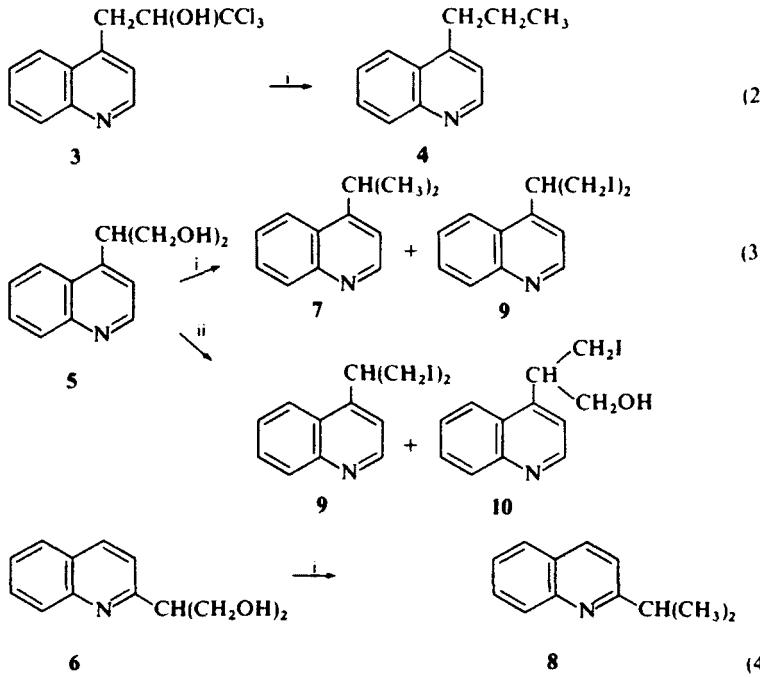
1 **2**

i, H_2/Pd, charcoal, $N(Et)_3$, (68%); ref. 79

Hydrogen and Raney nickel in the presence of a base (methanolic potassium hydroxide) reduced 2-chloro-4-methylquinoline to 4-methylquinoline in 95% yield.[78] Catalytic reduction of a 4-chlorosubstituent has also been used to prepare 3,5-dimethylquinoline and 7-methylquinoline.[80] When a solution of 2-chloro-4-methylquinoline in hydrochloric acid was treated with tin, the double salt was obtained which, on separation and treatment with alkali, gave 4-methylquinoline.[81] Pure 4-methylquinoline can also be prepared from 2-chloro-4-methylquinoline by boiling with hydrazine hydrate and treating the 2-hydrazinolepidine so formed with copper sulphate.[95] Hydrazine hydrate together with palladized charcoal has also been used to reduce chlorine atoms at position 3 of the quinoline ring,[221,222] (see also Scheme 7 and equation 23, Section I.3.H.e). 2-Chloro-4-methylquinoline has also been reduced with zinc and hydrochloric acid (63–75%) and with zinc and 60% acetic acid (60%).[495] 3-Trifluoromethylquinoline can be reduced by sodium borohydride to give 3-methylquinoline (36% yield), but the corresponding 2-, 4- and 6-isomers are unaffected. On the other hand, lithium aluminium hydride will reduce 2-, 4- and 6-trifluoromethylquinolines to give 28.4%, 10.6% and 65.5% yields of the methylquinolines, respectively, but the 3-isomer gave 3-difluoromethyl-1,2-dihydroquinoline. The mechanism suggested involved nucleophilic attack by hydride ion.[496]

b. Reduction of Hydroxy and Amino Derivatives Although these substituent groups can be replaced by hydrogen directly as described below, it is usually better to convert them first to the chloro derivative as the direct methods give less pure products. Heating with zinc dust, for example, a method that has been widely used, can result in the migration of alkyl groups.[82] By heating 4-methyl-2-quinolone with zinc dust under reduced pressure[75,85] 4-methylquinoline was obtained and similarly 3-methyl-2-propylquinoline, together with other products, from 3-methyl-2-propyl-4-quinolone.[74] 4-Methylquinoline was also obtained from 3-cyano-4-methyl-2-quinolone by distillation with zinc dust.[83,84] The following alkylquinolines have been obtained by similar methods: 5-methylquinoline,[76] 6,8-dimethylquinoline,[86,87] 6-methylquinoline[88] and 8-methylquinoline.[88] Reduction has also been reported by distillation over 'glowing' or red hot zinc; in this way 3,4-,[89,90] 4,6-,[89] 4,7-[89] and 4,8-dimethylquinoline[89] were obtained from the respective 2-quinolones, and the last two also by distillation with zinc dust.[91]

Hydrogen iodide alone or with red phosphorus can be used for the reduction of alkylquinolones and hydroxyquinolines, including compounds having a hydroxyl group in a side-chain, to give alkylquinolines, as shown by the following examples. Quinaldine (2-methylquinoline) was isolated when 3-amino-2-methyl-4-quinolone was heated with hydrogen iodide and acetic acid as a result of elimination of the amino group in addition to the carbonyl oxygen.[92] The condensation product of lepidine with chloral (**3**) gave 4-propylquinoline (**4**) when heated with fuming hydrogen iodide ($d = 1.96$) and red phosphorus at 150–160 °C.[93] The corresponding dimethylol derivatives (**5**) and (**6**) formed by condensation of lepidine and quinaldine with 2 mol of formaldehyde gave 4- and 2-isopropylquinoline (**7**) and (**8**), respectively.[93,94] When weaker hydrogen iodide or hydrogen bromide was used, reduction was incomplete and diiodo (**9**), hydroxyiodo (**10**) or hydroxybromo derivatives were formed.[93] See equations 2, 3 and 4.

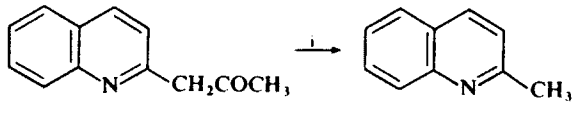


i, HI ($d = 1.96$) + red P (150–160 °C); ii, HI ($d = 1.7$) + red P (150–160 °C)

More recently, 4-methylquinoline has been obtained in 49% yield by refluxing 4-methyl-2-quinolone with red phosphorus and iodine in xylene for 4 h.[95]

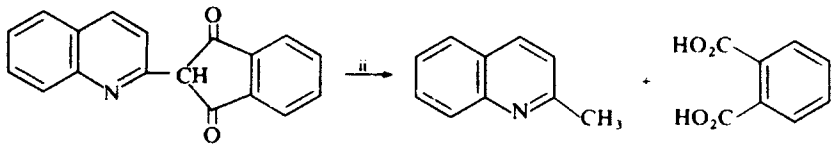
c. Reduction of Carbonyl Compounds Quinoline carbaldehydes and alkyl or aryl quinolyl ketones can be reduced to the alkyl- or aralkylquinolines by the Wolff–Kishner or Clemmensen methods. Quinoline aldehydes on reduction by the Wolff–Kishner method gave methylquinolines[97,1625] and, using the Huang–Minlon modification of the Wolff–Kishner reaction (in which the ketone is heated with potassium hydroxide and 85% hydrazine hydrate in ethylene glycol), all of the benzylquinolines have been prepared from the appropriate phenyl quinolyl ketones.[98] Photolysis of phenyl 3-quinolyl ketone in isopropanol gave 3-benzylquinoline[110] (12%) together with phenyl-3-quinolylmethanol and the expected pinacol. Irradiation of phenyl-3-quinolylmethanol in

isopropanol gave a 44% yield of 3-benzylquinoline and 29% of 3-benzyl-1,2,3,4-tetrahydroquinoline. Quinaldine has also been prepared from carbonyl compounds by the following methods, which involve degradation. 2-Acetonylquinoline(**11**) was heated at 160–170 °C with concentrated hydrochloric acid and 20% sulphuric acid[99] (equation 5), and quinophthalone (**12**) was heated with fuming hydrochloric acid at 240 °C[100] (equation 6).



(5)

11



(6)

12

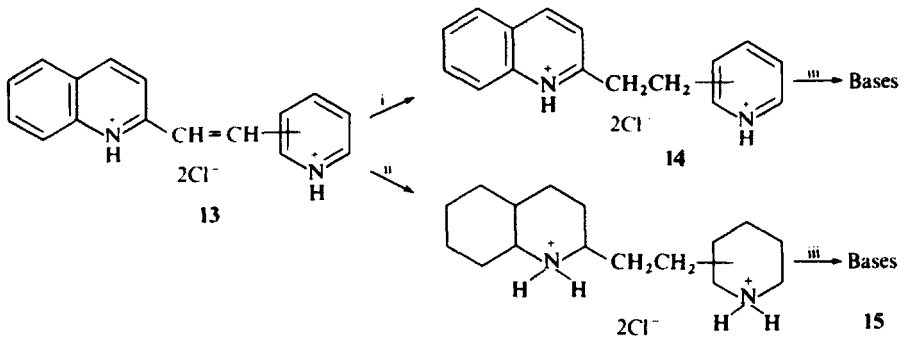
i, HCl (conc.) + H_2SO_4 (20%), 160–170 °C; ii, HCl (fuming), 240 °C

Compounds prepared by the use of Raney nickel as a catalyst for hydrogen transfer reactions include 3-ethyl-5,6,7,8-tetrahydroquinoline from 3-acetylquinoline[1556] with isopropanol as hydrogen donor. Oxidation by one of the methods in Section I.3.G would give 3-ethylquinoline.

d. Reduction of Alkenyl and Aralkenylquinolines Under controlled mild conditions, reduction of these compounds gives the corresponding alkyl- or aralkyl-quinolines. More vigorous conditions result in the further reduction of the heterocyclic ring to give alkyl- or aralkyl-1,2,3,4-tetrahydroquinolines. Hydrogen iodide and red phosphorus has been used for the reduction of 2- and 4-styrylquinolines[101] and of 1-ethyl-2-styrylquinolinium iodide[102] to give the 2- or 4-(2-phenethyl)quinolines, and more recently this has been accomplished in 80% yield by refluxing the bases for 24 h at 200 °C with *p*-methylthiophenol.[202]

Catalytic hydrogenation has been used extensively for the reduction of alkenylquinolines; thus 2-pentylquinoline was obtained by hydrogenation of 1-(2-quinolyl)pent-1-ene in dilute alcoholic solution at 50 °C using a palladized charcoal catalyst,[65] and 1-phenyl-4-(2′-quinolyl)butane was formed by the hydrogenation of 1-phenyl-3-hydroxy-4-(2′-quinolyl)-but-1-ene and of 1-phenyl-4-(2′-quinolyl)-buta-1,3-diene over a palladium sponge catalyst.[103] Hydrogenation of the heteroalkenyl quinolinium salts (**13**)[108,121] gave the 1-(2′-quinolyl)-2-(2″-, 3′- or 4″-pyridyl)ethanes via their quaternary salts (**14**). More vigorous hydrogenation gave the fully saturated bases (**15**) (see Scheme 1). 2-Methyl-4-allylquinoline has been reduced by hydrogen and palladized charcoal to 2-methyl-4-propylquinoline.[125]

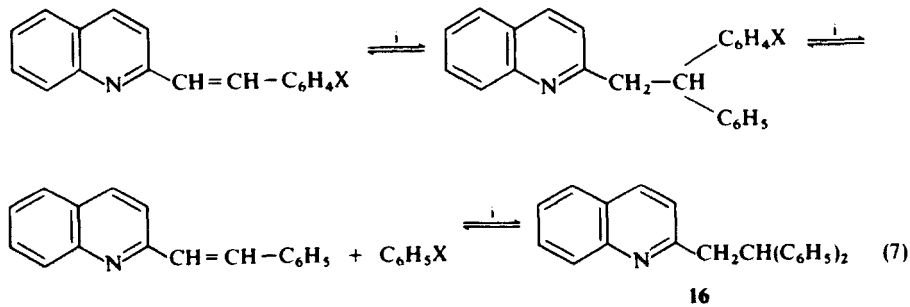
Benzyl alcohol can function both as a reducing agent and as a benzylating agent (see also Section I.3.H.g). When refluxed for 1 h with 2-styrylquinoline, 2-phenethylquinoline (40% yield) was obtained, and when refluxed for 14 h further reduction to 2-phenethyl-1,2,3,4-tetrahydroquinoline occurred.[224] Reduction with sodium and ethanol results in the concurrent reduction of the heterocyclic ring so that 2-styrylquinoline and its 4′-methyl-, 6-methyl-, 4′,6-dimethyl- and 4′-isopropyl- derivatives gave the corresponding 2-(2′-phenethyl)1,2,3,4-tetrahydroquinolines.[104,105]



i, H_2/PtO_2, CH_3CO_2H, 760 mmHg; ii, H_2/PtO_2, HCl, 100 °C, 100 atm; iii, OH^-

SCHEME 1

When treated with benzene, aluminium chloride and hydrogen chloride, styrylquinolines and their *o*-, *m*- and *p*-chloro or -bromo derivatives give 1,1-diphenyl-2-(2'-quinolyl)ethanes (**16**), which has been explained in terms of the reversibility of the Friedel–Crafts reaction[106,107] (see equation 7).

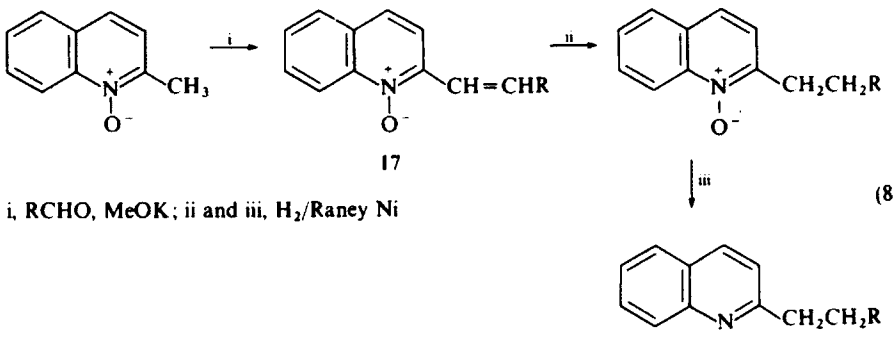


(7)

X = H or *o*-, *m*- or *p*-Cl or Br
i, $AlCl_3$,HCl, C_6H_6

e. REDUCTION OF QUINOLINE-1-OXIDES The reduction of appropriate alkylquinoline-1-oxides can form an important step in the preparation of alkylquinolines. Quinaldine-1-oxide can be reduced with zinc and hydrochloric acid to quinaldine[179] and it will also condense with alkyl, aryl and heteroaryl aldehydes in the presence of potassium methoxide to give the appropriately substituted 2-vinylquinoline-1-oxides (**17**), which can be reduced with hydrogen and Raney nickel to the substituted 2-ethylquinoline-1-oxides and on further hydrogenation to the 2-quinolylethanes[139] (see equation 8).

The 1-oxides can also be reduced by heating at 50–60 °C with phosphoryl chloride or phosphorus trichloride; 2-methylquinoline-1-oxide, for example, gives 2-methylquinoline together with a chloro derivative.[209] 2-Methylquinoline-1-oxide can also be deoxygenated by an acid-catalysed reaction with sulphoxides at elevated temperatures. This is a general reaction of *N*-heterocyclic and other tertiary amine *N*-oxides which are



17

i, RCHO, MeOK; ii and iii, H_2/Raney Ni (8)

reported to form an initial coordination complex by attack of the *N*-oxide oxygen atom on the sulphur atom of the sulphoxide or its conjugate base. This complex, in the case of the heterocyclic *N*-oxides, is then attacked by the nucleophilic sulphoxide oxygen to give a sulphinate and the amine.[210] Lepidine-1-oxide has been converted quantitatively to lepidine by heating for 10 h with Bu_3SnH in the presence of $\alpha\alpha'$-azobisisobutyronitrile.[211]

Many quinoline-1-oxides, including 2-methylquinoline-1-oxide, are reduced by chromium(II) chloride ($CrCl_2$) in acetone, methanol or chloroform at room temperature, in many cases, but under reflux for 2-methylquinoline-1-oxide, to give the deoxygenated products. Reaction times of 20 min may cause dechlorination of 4-chloroquinoline-1-oxides and many nitroquinoline-1-oxides could not be reduced successfully by this method.[1539]

B. Catalytic Alkylation

Direct alkylation by the Friedel–Crafts reaction using Lewis acid catalysts is restricted owing to the deactivating effect of the ring nitrogen towards electrophilic substitutions, although when electron-donating substituents are present alkylation (and acylation) of the carbocyclic ring is possible.[111] Other catalytic methods for the direct alkylation of quinoline have been reported and many are the subject of patents. The vapour phase reaction of quinoline with an approximately 8-fold excess of methanol over a Ni/NiO_2 catalyst in a tubular reactor at 295 °C with a contact time of 10.5 s gave 2-methylquinoline.[1553] 2-Methylquinoline with excess of methanol at 500 °C over an alumina catalyst gave a mixture of 2-ethyl-, 2-isopropyl- and 2-isopropenylquinoline in yields of 10%, 7% and 2%, respectively.[1603] Quinoline is one of the substrates which can be methylated by a carbon monoxide–hydrogen mixture (1 : 2) at 454 °C and 65.5 bar in the presence of a catalyst (Cr_2O_3–ZnO, 22 : 78).[112] The product contained 17.7% of 4-methylquinoline together with 23.6% of unreacted quinoline, 12.5% of a mixture having a b.p. less than that of quinoline, 34.4% of a mixture with a b.p. between those of quinoline and 4-methylquinoline and 11.8% of a mixture with a b.p. higher than that of 4-methylquinoline. Various butyl- and isomeric octylquinolines have been prepared by refluxing alkanols and alkylamines with quinoline in the presence of ruthenium trichloride ($RuCl_3$) and triphenylphosphine (PPh_3).[113] By treating quinoline with benzyl iodide, concentrated sulphuric acid and iron, 2- and 4-benzylquinoline and bibenzyl were obtained.[114] Similarly with isopropyl iodide, sulphuric acid, iron and zinc, 2- and 4-isopropylquinoline and 2- and 4-isopropyl-1,2,3,4-tetrahydroquinoline were obtained.[114] Methylation of quinoline with primary alcohols in the presence of Raney nickel has been reported[115] to give 70% of 2-methylquinoline and 24% of 8-methylquinoline. Alcohols or ethers can also be used as alkylating agents with an Al_2O_3 catalyst

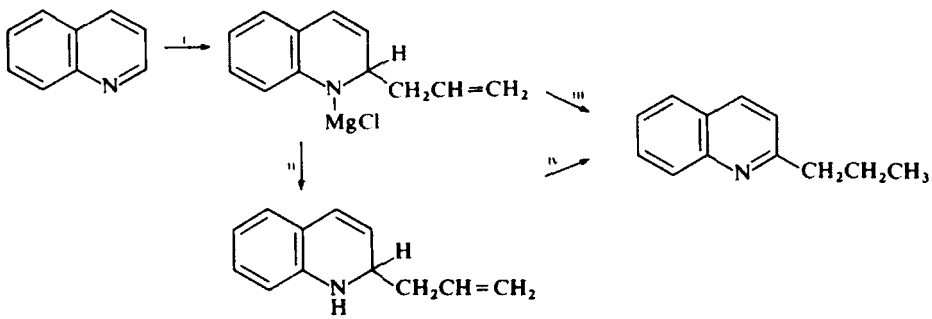
at 450 °C to give 3-substituted quinolines (or 4-substituted isoquinolines). For example, methanol and quinoline gave 41% of 3-methylquinoline and 53% of the quinoline was recovered. Ethanol similarly gave 3-ethylquinoline.[116] Alkenes in the presence of an alumina–silica catalyst gave alkylquinolines; thus ethylene gave 2-ethylquinoline, which could be dehydrogenated at 1000 °F on a chromium(III) oxide–bauxite catalyst to 2-vinylquinoline.[117] Propylene at 250 °C and 2600 lb in^{-2} gave 'monoisopropylquinolines'.[120] When heated with alkenes and sodium, quinaldine is reported to give higher alkylquinolines.[118] By heating lower alkyl or cyclic ethers with quinoline at 150–450 °C (preferably at about 300 °C) in the presence of oxides or hydroxides of Al, Th, Zn, Mg, B, Fe or Si or mixtures of these oxides on inert supports, and preferably using a diluent, 2- and 4-alkyl and 2,4-dialkyl- or cycloalkylquinolines are formed, e.g. 2-isopropylquinoline and 2-cyclopentylquinoline.[119] Ethylene in the presence of aluminium anilide and 1,2,3,4-tetrahydroquinoline gave a 60–70% yield of 8-ethyl-1,2,3,4-tetrahydroquinoline, which was dehydrogenated with sulphur at 220 °C to give 8-ethylquinoline;[227] 2,6-diethylaniline was also formed.

C. Alkylation by Means of Organometallic Reagents

a. NUCLEAR ALKYLATIONS The reaction of quinoline with organolithium reagents and Grignard reagents has been reviewed in Part I, Sections IV.1 and IV.2. As with pyridine, 1,2-nucleophilic addition constitutes the initial reaction and oxidation of the 2-substituted 1,2-dihydroquinolines formed by hydrolysis of the primary addition products gives 2-alkyl(or 2-aryl)quinolines.[122–125,201,187,256,1558,1605]

2-Alkyl- and 2-aralkylquinolines have also been prepared in yields of 8–85% by the action of Grignard reagents in ether or tetrahydrofuran on quinoline-1-oxide. Some 2-alkylquinoline-1-oxide and quinoline were formed concurrently.[1557] Lepidine-1-oxide can be alkylated similarly.[1632] Quinaldylpotassium in liquid ammonia containing potassamide reacts with organic halides; with *p*-chlorotoluene, for example, 2-(*p*-methylbenzyl)quinoline is formed.[1606]

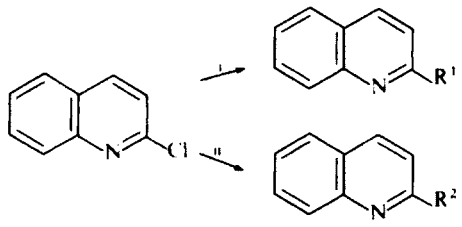
An interesting extension of the use of Grignard reagents for the synthesis of 2-alkylquinolines results from the thermal isomerization of the adducts formed from quinoline and vinyl or allyl Grignard reagents, or the dihydroquinolines formed from them by hydrolysis[126,923] (see Scheme 2).



i, $CH_2=CHCH_2MgCl$; ii, H_2O; iii, heat with quinoline; iv, heat

SCHEME 2

Grignard reagents have also been used in conjunction with a nickel–phosphine complex catalyst to alkylate halogenoquinolines;[127,1262] see equation 9 for 2-chloroquinoline.

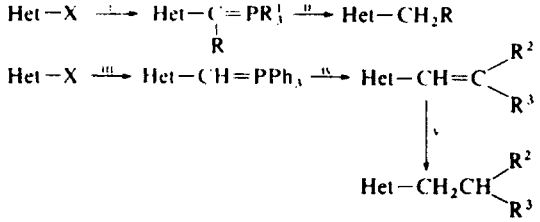


(9)

i, R^1MgCl, $(Ph_3P)NiCl_2$, R^1 = $PhCH_2$, $CH_2{=}CH{-}CH_2$;
ii, R^2MgCl, $(Ph_2PCH_2CH_2PPh_2)NiCl_2$, R^2 = $PhCH_2CH_2$, cyclopentyl, cyclohexyl

The modified catalyst was required in reaction ii, when the potential carbanion of the Grignard reagent had a hydrogen atom bonded to an sp_3 hybridized β-carbon, as in this case the triphenylphosphine–Ni complex induced an alkene-forming elimination together with reduction of the haloquinoline to quinoline. Selective alkylation at position 4 occurred when 4,7-dichloroquinoline was used, and the normally difficultly accessible 3-position of quinoline could be alkylated using 3-bromoquinoline (see also ref. 655).

Wittig reagents can be used for the introduction of alkyl (and alkenyl) groups into heterocyclic systems including quinoline.[128,129] A suitable leaving group on a heterocycle, including chlorine, can be displaced by a Wittig reagent and the resulting heterocyclic ylide converted *in situ* either by hydrolysis into an alkyl derivative of the heterocycle, or by reaction with a carbonyl compound into an alkenyl derivative of the heterocycle. Numerous examples are given in the references cited, including many 2-alkyl-, 2-aralkyl-, 2-alkenyl- and 2-aralkenylquinolines. Scheme 3 illustrates the general procedure. The alkenylquinolines can be subsequently reduced to alkylquinolines.



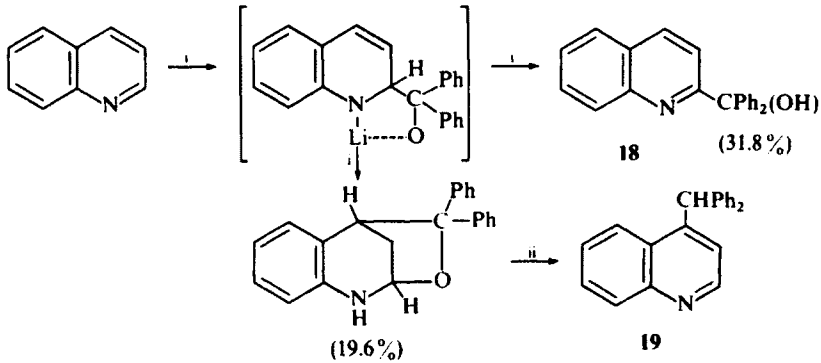
Het = Heterocyclic including 2-quinolyl and substituted 2-quinolyls
X = Good leaving group, including chloro
R^1 = Phenyl or butyl
R^2, R^3 = H, alkyl or aryl

i, $RCH{=}PR^1_3$ (2 equiv); ii, OH^-; iii, $CH_2{=}PPh_3$ (2 equiv);

iv, $\begin{matrix}R^2\\R^3\end{matrix}\!\!>\!C{=}O$, ($-Ph_3PO$); v, H_2/Pd

SCHEME 3

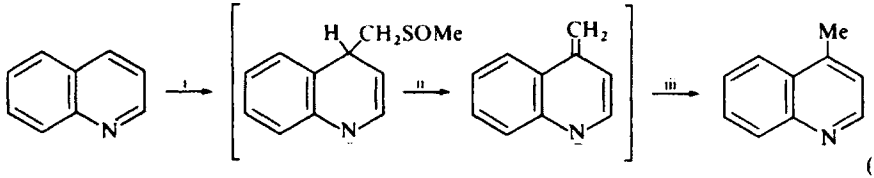
Trialkylboranes[130] react with quinoline-1-oxide to give 2-alkylquinolines and reaction with the quinoline-1-oxide–BF_3 complexes give 4-alkylquinolines, unless the 4-position is already alkylated, when substitution occurs again in the 2-position. Many examples of alkyl, cycloalkyl and aryl substitutions are given. 4-Diphenylmethylquinoline (**19**) and 2-quinolyldiphenylmethanol (**18**) are formed by the reaction of quinoline with benzophenone and lithium in ether[131,132] (see Scheme 4). 2-Methylquinoline, 4-methylquinoline, 2,6-dimethylquinoline and 2-phenylquinoline gave analogous predictable products.



i, Li + Ph_2CO, ether, reflux (N_2); ii, H_2SO_4 ($-H_2O$)

SCHEME 4

Triheteroarylmethanes can be prepared if the sodium salt of a heterocyclic compound having a reactive methyl group, α- or γ- to the heterocyclic nitrogen atom (prepared by the action of sodium in liquid ammonia) and iron(III) nitrate catalyst, is allowed to react with the same, or another, heterocyclic base having a halogen atom in an α- or γ-position to the heterocyclic nitrogen atom. Thus 2-quinolyldi-2-benzothiazolylmethane was prepared from 2-methylbenzothiazole and 2-chloroquinoline.[207] The reaction can also be used for the preparation of di- and polyquinolylmethanes. In the presence of sodium, 2-methylquinoline and 4-methylquinoline add across the double bond of 2-vinylpyridine to give 2- and 4-[3′-(2″-pyridyl)propyl]quinoline.[133] Methylation at position 4 of quinoline can be achieved with high yields (90%) using methylsulphinylmethylpotassium in dimethyl sulphoxide at 70 °C, a reaction which is not given by pyridine[134,199] (see equation 10). A 2-(methylsulphonyl) substituent at position 2 of quinoline can be



(10)

i, $MeSO\bar{C}H_2K^+$, DMSO, 70 °C ($+ MeSO\bar{C}H_2$); ii, $-HOSMe$; iii, $+H^+$ (90% yield)

displaced by nucleophiles.[155,4] The appropriate Grignard reagents gave 2-methyl-, 2-ethyl-, 2-isopropyl-, 2-benzyl-, 2-cyclohexyl- and 2-phenylquinoline. Some 2-quinolyl-2-quinolylmethylsulphone was also formed in some cases.

b. Side-chain Alkylations and Arylations In common with the alkylpyridines, deprotonation at the α-position of the side-chain of 2- and 4-alkylquinolines by a strong base, such as NH_2^-, enables the resulting carbanion to be alkylated by alkyl halides, or other alkyl compounds with a suitable leaving group (e.g. sulphonic or sulphuric esters), resulting in an extension of the side-chain.[135,205,206,559,560] 2-Phenylethylquinoline,[135] 4-propylquinoline,[135] 4-benzylquinoline,[136] 4-diphenylmethylquinoline,[136] 2-triphenylmethylquinoline[136] and 2-heptylquinoline[137] are examples of compounds prepared by this widely used reaction.

Similarly, when quinaldine was treated with a suspension of phenylsodium in toluene for 1.5 h at −15 °C, the addition of propyl and butyl bromide gave 2-butylquinoline and 2-pentylquinoline, respectively.[138] Side-chain alkylations have also been achieved using *n*-butyllithium for the deprotonation, followed by reaction with alkyl halides or deuterio-substituted alkyl halides.[346,347] Side-chain metalation of 3-methylquinoline has been effected by lithium diisopropylamide–HMPA in tetrahydrofuran to give 3-lithiomethylquinoline. This will react with electrophiles to give a variety of side-chain substitution products, including 3-propylquinoline.[676]

Side-chain alkylations resulting from homolytic hydrogen abstraction at the α-position of the side-chains have not been reported, but in non-acidic media only, the methylation of 2- and 4-methylquinolines by di-*t*-butyl peroxide results in the formation of 1,2-di-2′-quinolylethane and 1,2-di-4′-quinolylethane, respectively,[144b] in addition to all possible dimethylquinolines. Presumably the diquinolylethanes were formed by the dimerization of the long-lived benzylic-type intermediate radicals formed by hydrogen abstraction from the side-chains of the methylquinolines. In acidic media the intermediate radicals would be protonated and the cations would not be expected to dimerize.

D. Homolytic Alkylation

Methylation of quinoline with di-*t*-butyl peroxide as the source of methyl radicals in non-acidic media resulted in substitution at all nuclear positions. The relative reactivities of the positions were 8 > 4 > 5 > 2, with some uncertainty concerning positions 3, 6 and 7 as these methylquinolines were not separated by gas chromatography and constituted 19% of the monomethylquinoline fraction. However, in acidic media, 2- and 4-methylquinolines comprised 99% of the monomethylquinolines owing to enhanced reactivity of these positions in the protonated heterocycle.[143,144a] Benzyl radicals gave poor yields of 2- and 4-benzylquinolines in non-acidic media, but the reactivity increased under acidic conditions.[144a]

Alkyl radicals can be generated by the iron(II) ion-catalysed decomposition of hydrogen peroxide in alkyl sulphoxides, and with quinoline they give 2- and 4-methylquinolines.[145] The studies by Minisci and co-workers of the homolytic substitution reactions of heterocyclic compounds[146] included the alkylation of quinoline[147–155] and showed that in acidic solution this reaction is both efficient and selective, giving 2- and 4-alkylquinolines and 2,4-dialkylquinolines in high yields; see Scheme 5 and Table 3.

The reversibility of the addition of acyl radicals to heteroaromatic bases enables 2-acylquinolines to be converted with alkyl radicals to 2-alkylquinolines. Thus the quinolinium salt (**19a**), when treated with pentanoyl or 2-methylbutanoyl peroxide and copper(I) acetate in aqueous acetic acid at 25 °C, gave 2-butyl- or 2-(1-methylpropyl)-4-methylquinoline, respectively. The yields were quantitative when based on the quinoline and 30–35% when based on the peroxides.[1637]

The thermal decomposition of phenyl benzyl ether[140] and β-naphthyl benzyl ether[141] when heated in quinoline for up to 14 days at 260–270 °C gives 2-benzyl- and 4-benzylquinolines among the products. Similarly, the pyrolysis of *N*-benzyltoluidines has

Sources of alkyl radicals

(a) $Hg(CH_2Ph)_2 \rightarrow Hg + 2PhCH_2\cdot$ (ref 143a)

(b) (i) $(RCO_2)_2 \rightarrow 2RCO_2\cdot$

(b) (ii) $(RCO_2)_2 + M^{+} \rightarrow RCO_2\cdot + RCO_2^{-} + M^{2+}$ ($M^{+} = Fe^{2+}$ or Cu^{+}) ·
$RCO_2\cdot \rightarrow R\cdot + CO_2$ (refs. 150, 657)

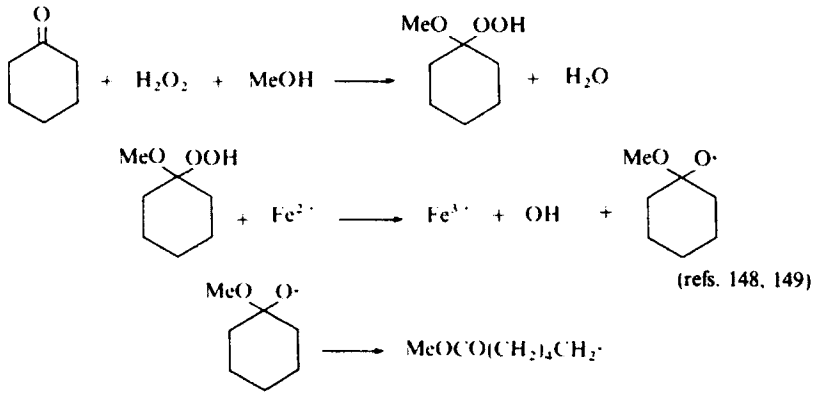
(c) $(Me_3CO)_2 \rightarrow 2Me_3CO\cdot \rightarrow 2Me\cdot + 2Me_2CO$ (refs. 143b, 658, 659)

(d) $S_2O_8^{2-} \rightarrow 2SO_4^{-}\cdot ; RCO_2^{-} + SO_4^{-}\cdot \rightarrow RCO_2\cdot + SO_4^{2-}$
$RCO_2\cdot \rightarrow R\cdot + CO_2$ (ref. 153)

(e) $S_2O_8^{2-} + Ag^{+} \rightarrow SO_4^{-}\cdot + SO_4^{2-} + Ag^{2+} ; SO_4^{-}\cdot + Ag^{+} \rightarrow SO_4^{2-} + Ag^{2+}$
$RCO_2^{-} + Ag^{2+} \rightarrow RCO_2\cdot + Ag^{+} ; RCO_2\cdot \rightarrow R\cdot + CO_2$ (ref. 151)

(f) $Me_3COOH + Fe^{2+} \rightarrow Me_3CO + Fe^{3+} + OH^{-}$
$Me_3CO \rightarrow Me\cdot + Me_2CO$ (ref. 149)

(g)

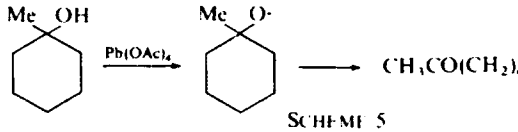


(refs. 148, 149)

(h) $Et_2CO + H_2O_2 \longrightarrow Et_2C(OH)(OOH) \xrightarrow{Fe^{2+}} Et_2C(O\cdot)(OH) + Fe^{3+} + OH^{-}$

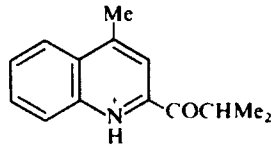
$Et_2C(O\cdot)(OH) \rightarrow Et\cdot + EtCO_2H$ (ref. 149)

(i)



(ref. 153)

SCHEME 5



19a

also been reported to proceed through their homolytic fission to benzyl and toluidine radicals. With quinoline as solvent 2- and 4-benzylquinolines were formed in yields of 5.9% and 10.6% from the *o*- and *p*-tolyl secondary amines, respectively. The isomer ratio was about 43% of 2-benzylquinoline and 57% of 4-benzylquinoline in each case.[1520]

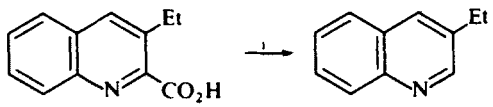
TABLE 3. Products Formed by Homolytic Alkylation of Quinoline or 2- or 4-Methylquinolines

Quinoline compound	Alkyl radical	Radical source (see Scheme 5)	Products: position of alkylation and (proportion formed, %)	Conversion of heterocycle (%)	Yield on heterocycle used (%)	References
Quinoline	$PhCH_2$·	a	2(50); 4(45); 2,4(5)	Low	(347)	143
	$Me_2CH_2CH_2$·	b(ii)	2(25); 4(33); 2,4(42)	70	~100	657 150
	$CH_3(CH_2)_8$·	b(i)	2; 4	Low	(97)	657
	Me·	b(i), reflux	4 (at room temp., *N*-oxide)	10		660
	Me·	c	2(49); 4(50)	Low	(342)	144[a]
	Me·	e	2(23); 4(25); 2,4(52)	97	~100	151
	Et·	e	2(21); 4(25); 2,4(54)	97	~100	151
	Pr·	e	2(28); 4(36); 2,4(36)	87	~100	151 152
	Pr^i·	e	2(13); 4(26); 2,4(61)	99	~100	151
	Bu·	e	2(27); 4(36); 2,4(37)	99	~100	151
	Cyclohexyl·	e	2(24); 4(35); 2,4(41)	100	~100	151
	Bu^t·	e	2	98	95	151
	Me·	f	2(42); 4(38); 2,4(20)	76	~100	149
	$MeO_2C(CH_2)_4CH_2$·	g	2(54); 4(46)	12	~100	148
	Et·	h	2(58); 4(42)	17	~100	149
	$CH_3CO(CH_2)_4CH_2$·	i	2 and 4	—	—	153
2-Methylquinoline	Pr^i·	d	4	98	70	153
	Bu·	e	4	—	—	152
	Me·	e	4	72	90	151
	Cyclohexyl·	e	4	—	—	152
	Et·	e	4	98	~100	151
	Pr·	e	4	98	90	151
	Pr^i·	e	4	100	93	151
	Cyclopropyl·	e	4	30	~100	151
4-Methylquinoline	Bu·	e	2	—	—	152

The reaction between electrochemically generated anion radicals of quinolines and *t*-butyl chloride gives, via an electron transfer reaction and the formation of *t*-butyl radicals, *t*-butylated quinolines in which a large proportion of the substitution is in the carbocyclic ring. Thus 2-methylquinoline gave 3- or 4-*t*-butyl-3,4-dihydro-2-methylquinoline (10.5%), 4-*t*-butyl-1,4-dihydro-2-methylquinoline (15.5%), 5-*t*-butyl-5,6-dihydro-2-methylquinoline (12%), 7-*t*-butyl-7,8-dihydro-2-methylquinoline (14.5%) and 8-*t*-butyl-7,8-dihydro-2-methylquinoline (24%). Quinoline itself gave 2-*t*-butylquinoline, probably as a result of oxidation of the dihydro derivative during work-up.[1604]

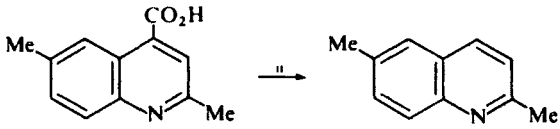
E. Decarboxylation

Alkylquinoline carboxylic acids having the hydroxycarbonyl group in the heterocyclic or carbocyclic ring, but particularly at positions 2 or 4, can be converted into alkylquinolines by thermal decarboxylation (loss of carbon dioxide). Side-chain decarboxylations (e.g. of quinolylacetic acids) have also been reported. The commonest application of this reaction is the decarboxylation of quinoline-4-carboxylic acids (cinchoninic acids) in the final stage of the Pfitzinger synthesis (see Part I, Chapter 2, Section III.D) and numerous references to these reactions can be found in Table 3 at the end of that chapter. The following account has been restricted to giving typical examples to illustrate the many variations in technique which have been reported. Most of the carboxylic acids can be decarboxylated by dry distillation,[156,169] or by heating above their melting point,[157,167] sometimes under reduced pressure.[87] Controlled heating in a bath of Wood's metal[158] is frequently specified. Alternative methods include heating with lime,[159] soda-lime,[160,167] potassium hydroxide[161] or barium hydroxide,[162] or by distillation of the calcium salt[163] or by heating the acid with zinc dust[90,169] or with a trace of copper chromate[164] or with copper powder[165] or copper bronze[166] see also equations 11–18.



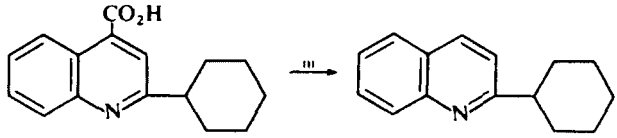
(11)

i, Dry distillation; ref. 156



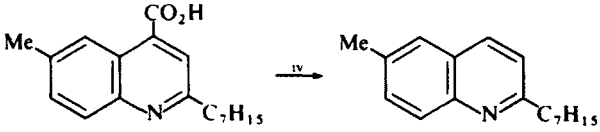
(12)

ii, Heat above m.p.; ref. 157



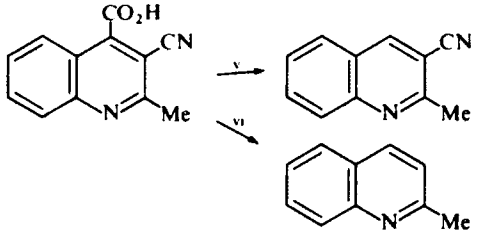
(13)

iii, Heat with soda-lime; ref. 160



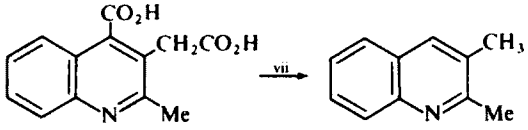
(14)

iv, Heat with copper powder (yield 70–80%); ref. 165



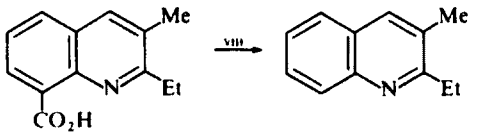
(15)

v, Heat above m.p.; vi, heat with soda-lime; ref. 167



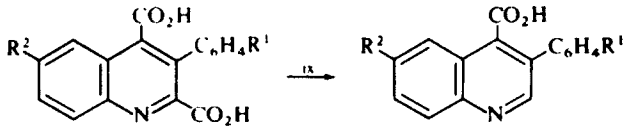
(16)

vii, Heat with soda-lime; ref. 168



(17)

viii, Heat alone or with Zn dust; refs. 90, 169



(18)

R^1 = H, Me, OMe; R^2 = H, Me, Br
ix, Heat to 10–5 °C below decomposition temp.; ref. 170

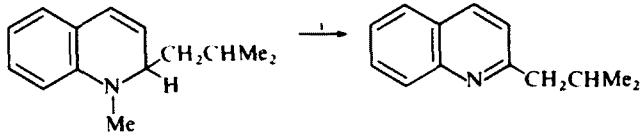
F. Ladenburg Rearrangement

Alkylquinolines are formed by the Ladenburg rearrangement of 1-alkylquinolinium iodides when they are heated in a sealed tube at about 300 °C.[171-177,1538] 1-Ethylquinolinium iodide at 280–290 °C was reported to give a mixture of 2-ethylquinoline, 4-ethylquinoline, 2,4-diethylquinoline and other products.[171-174] 1-Benzyl-2-methylquinolinium iodide at 230 °C gave 4-benzyl-2-methylquinoline.[175] The reaction product from 1-methylquinolinium iodide has been shown to contain 2-, 4-, 5- and 8-methylquinolines, identified by gas chromatography, together with an unresolved mixture believed to contain 6- and 7-methylquinolines, and the presence of a small amount of 3-methylquinoline was not excluded.[178] It is probable that the mechanism of the reaction is analogous to that of the 1-alkylpyridinium iodides, which has been studied in some detail and is believed to involve a seven π-electron radical intermediate.[176-177]

G. Oxidation of Dihydro- Tetrahydro- and Decahydroalkylquinolines

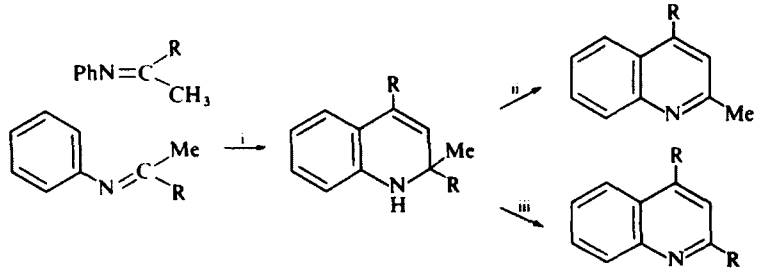
Dihydro-, tetrahydro- and decahydroalkylquinolines can be readily oxidized to alkylquinolines. The following are examples of alkylquinolines prepared by this method. 2-Methyl-,[180] 8-methyl-[181] and 2,4-dimethylquinolines[182] were obtained by the

oxidation of the 1,2,3,4-tetrahydro derivatives with mercury(II) acetate solution. 2,6-Dimethyl-,[183,184] 2,6,8-trimethyl-[183] and 2,5,6,8-tetramethylquinolines[185] were prepared, together with their 1,2,3,4-tetrahydro derivatives, by heating the corresponding 1,2,3,4-tetrahydro-2-quinolones alone or with acid. A study of the oxidation and disproportionation of 1,2-dihydrolepidine[200] to 4-methylquinoline and 4-methyl-1,2,3,4-tetrahydroquinoline is of importance owing to the possible occurrence of such compounds as intermediates in the Skraup and Doebner–Von Miller syntheses. The order of effectiveness of oxidants studied was $FeCl_3 \gg$ disproportionation $\gg O_2$ (autoxidation) > PhCHO ≈ PhCH=NPh > $CH_3COCH{=}CH_2$. 2-Propylquinoline[186] and 2-(2′-methylpropyl)quinoline[187] (see equation 19) were formed with loss of methane by heating the appropriate 1-methyl-1,2-dihydro derivatives. A similar reaction constitutes the final stage of a quinoline synthesis,[188,189,204] first suggested by Riehm,[190–192] whereby the anil of a ketone is heated with acid to give an intermediate 2,2-dialkyl-1,2-dihydroquinoline which loses 1 mol of alkane. Possible mechanisms have been suggested by Knoevenagel[193–195] (equation 20) and by Elderfield for acetone



(19)

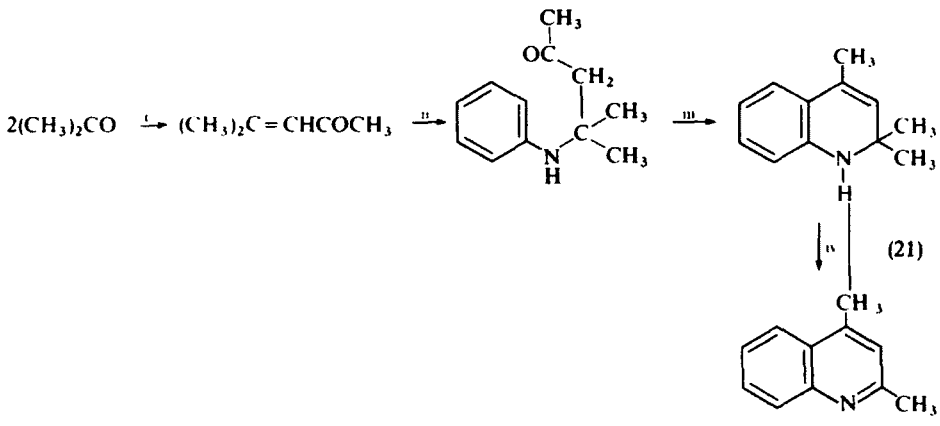
i, Heat



(20a)

(20b)

i, HCl, 180–200 °C; ii, $-RH$; iii, $-CH_4$



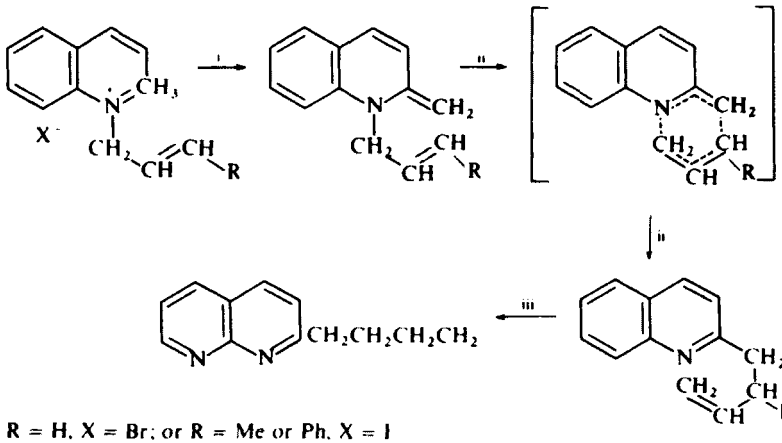
(21)

i, Aldol condensation, $-H_2O$; ii, $+C_6H_5NH_2$, $-H_2O$; iii, ring closure; iv, $-CH_4$

(equation 21).[196] Examples include the synthesis of 2,4-dimethylquinoline[193,197] (equation 20a, R = Me, and equation 21), 2,4,6-trimethylquinoline[193,197] and 4-ethyl-2-methylquinoline[198] by loss of ethane (equation 20b, R = Et). The dehydrogenation of *trans*-decahydro-6-methylquinoline with selenium by heating for 27 h at 160–290 °C gives 6-methylquinoline and 5,6,7,8-tetrahydro-6-methylquinoline.[203]

H. Miscellaneous Methods

a. MOLECULAR REARRANGEMENTS Quinolinium salts with an alkyl substituent in the α-position can be deprotonated by alkali to give the anhydro-bases. The presence of a 1-allyl substituent then provides a structure capable of a Claisen-type rearrangement, which enables the side-chain to be extended in the absence of the strongly basic conditions usually necessary (e.g. NH_2^-/liquid NH_3).[212] The alkenylquinolines so formed can be reduced to alkylquinolines (see equation 22). A similar Claisen-type rearrangement occurs with 4-quinolyl allyl ethers to give an alkenylquinoline, which can be reduced to an alkylquinoline[1054] (see Section II.3.E, Schemes 20 and 21).



(22)

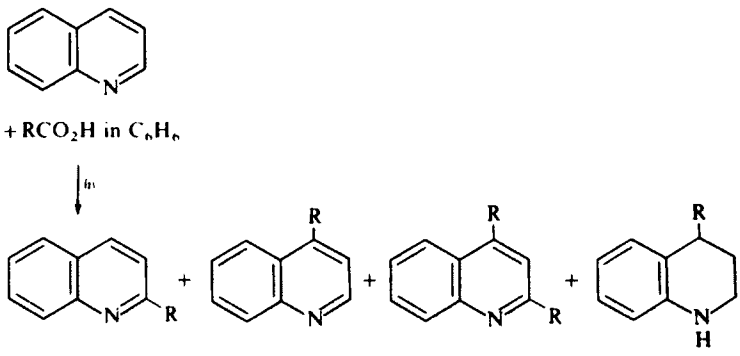
R = H, X = Br; or R = Me or Ph, X = I

i, 1N NaOH; ii, Claisen-type rearrangement; iii, catalytic reduction (R = H). Yields (stages i and ii), R = H (52.5%); R = Me (56.7%); R = Ph (38%). Ref. 212

b. PHOTOCHEMICAL METHODS A review of the photochemistry of carbon–nitrogen double bonds[1552] covers the preparation of alkylquinolines.

Irradiation of quinoline and 8-methylquinoline in acidic ethanol[213,214] gave 2- and 4-ethylquinoline, in 95% ethanol 2-(1-hydroxyethyl)quinoline and 1,2,3,4-tetrahydroquinoline was formed and in *t*-butanol 2-(2-hydroxy-2-methylpropyl)quinoline. The photochemical reaction of quinoline with aliphatic carboxylic acids.[215,216] results in decarboxylation of the acids and formation of 2- and 4-alkylquinolines, 2,4-dialkylquinolines and 4-alkyl-1,2,3,4-tetrahydroquinolines. The products and yields obtained are given in Scheme 6.

Irradiation of 2-, 3- and 4-cyanoquinolines with equimolar amounts of propionic acid in benzene solution for 3–4 h gave the following products:[1551] *from 2-cyanoquinoline*, 2-ethylquinoline (22%), 2-cyano-4-ethylquinoline (20%), 2,4-diethylquinoline (4%) and 2-phenylquinoline (1%); *from 3-cyanoquinoline*, 3-cyano-2-ethylquinoline (9.6%), 3-cyano-



Yields (%):					
R = Me	20	10	5	—
R = Et	23	—	6	16
R = Pr^i	27	20	6	•
R = Bu^t	37	•	•	•

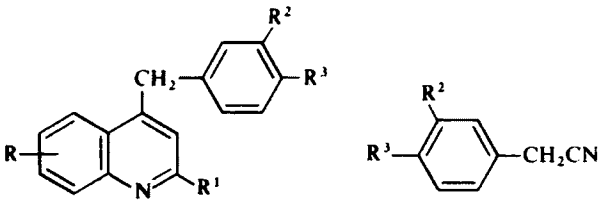
• Detected but not determined

SCHEME 6

4-ethylquinoline (9.7%), 3-cyano-4-ethyl-1,4-dihydroquinoline (10%) and 3-cyano-2,4-diethylquinoline (5%); and *from 4-cyanoquinoline*, 4-ethylquinoline (23%), 2,4-diethylquinoline (10%) and 4-cyano-2-ethylquinoline (12%). The positions of reaction correlated well with Hückel M. O. calculations and the structures of the products were assigned from nmr data.

c. AROMATIZATION A mixture of eight alkylquinolines including 4-ethyl-2-methyl-, 2,4-diethyl-, 2,4-dimethyl-, 2,3,4-trimethyl-, 2,4,5-trimethyl-, 2,4,7-trimethyl and 2,4,8-trimethylquinoline, was obtained by the aromatization of the hydrochloride of 2,2,4-trimethyl-1,2-dihydroquinoline, which was carried out in solution and as the pure molten salt.[217] In solution the reaction was initiated by di-*t*-butylperoxide and catalysed by *β*-naphthalenethiol. A free-radical chain reaction was proposed as the mechanism.

d. NUCLEOPHILIC DISPLACEMENT OF HALOGEN A series of thirteen derivatives of 4-benzylquinoline, see (**20**), were prepared[218] by treating 4-chloroquinoline with the carbanions generated (with sodamide in liquid ammonia) from the appropriate phenylacetonitrile derivative (**21**) and heating the resultant α-4-quinolyl-α-phenylacetonitrile

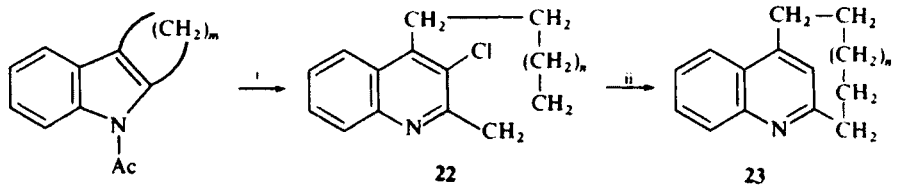


20 **21**

R = H, 6-OMe, 5,8-$(OMe)_2$, 6,7-(—OCH_2O—); R^1 = H, Me; R^2,R^3 = H, OMe, Me

with butanol saturated with hydrogen chloride. The compounds were found to be useful for the treatment of angina pectoris. A similar preparation of 4-benzylquinoline, 7-chloro-4-benzylquinoline and 5-chloro-4-benzylquinoline as potential fungicides has also been described.[219,220]

e. Ring Enlargement of Indoles A synthesis of 1,3-bridged alkylquinolines (**23**) from fused indoles, by ring enlargement with dichlorocarbene, has been described[221] and details are given in Scheme 7.

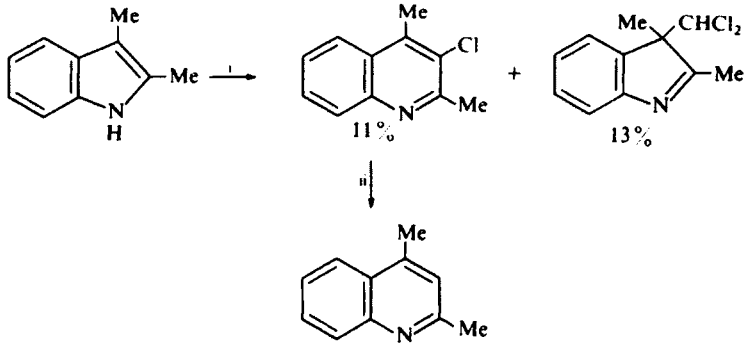


22 **23**

i, $PhHgCCl_3$, C_6H_6, 48 h ($m = 10$, $n = 6$), ($m = 8$, $n = 4$), ($m = 6$, $n = 2$);
ii, N_2H_4, Pd/C ($n = 6$ or 4. When $n = 2$ heterocyclic ring was reduced). Ref. 221

SCHEME 7

A similar ring enlargement of 2,3-dimethylindole with dichlorocarbene[222] gave 3-chloro-2,4-dimethylquinoline together with 3-dichloromethyl-2,3-dimethylindolenine. The chloroquinoline was reduced with hydrazine hydrate and palladized charcoal to 2,4-dimethylquinoline (equation 23).



(23)

i, $CHCl_3$, NaOH–NaOEt, chromatography (Al_2O_3); ii, $N_2H_4 \cdot H_2O$ + Pd/C

f. Catalytic Side-chain Alkylation Side-chain alkylation has been achieved by passing 2- or 4-methylquinoline vapour together with methanol or methyl chloride over alumina at 350–500 °C.[223] 2-Methylquinoline gave 33% of 2-ethylquinoline and 34% of 2-isopropylquinoline; the remaining 33% was recovered unchanged. Similarly, with 4-methylquinoline 48% of 4-ethylquinoline and 11% of 4-isopropylquinoline were formed, 5% was degraded to quinoline and 36% was recovered unchanged.

g. Side-chain Benzylation Quinaldine, lepidine and 2,4-dimethylquinoline have been benzylated at the α-positions of the side-chains by refluxing with benzyl alcohol and

potassium hydroxide and separation of the water formed.[224] Quinaldine gave 2-phenethylquinoline in 78% yield and lepidine and 2,4-dimethylquinoline gave 4-phenethylquinoline and 2,4-diphenethylquinoline, respectively. The latter two compounds were also benzylated further to 4-(1,3-diphenylisopropyl)quinoline and to 2,4-bis(1,3-diphenylisopropyl)quinoline, respectively. 2-Methylquinoline-1-oxide when treated with bromobenzene in the presence of potassamide in liquid ammonia gave 2-benzylquinoline-1-oxide, identical with that obtained by treatment of 2-benzylquinoline with hydrogen peroxide and acetic acid.[225]

h. CONDENSATION WITH QUINOLINE-2-CARBALDEHYDE When quinoline-2-carbaldehyde was heated with benzene below 100 °C in the presence of an acidic dehydrating agent such as sulphuric or phosphoric acid for 15–20 h, 2-diphenylmethylquinoline was formed.[226] Similarly, the condensation of phenol with quinoline-2 or -4-carbaldehyde in the presence of concentrated hydrochloric acid gave bis(4-hydroxyphenyl)-2-(or 4-)quinolylmethane.[1545] Similar reactions are described in a French patent.[1555]

i. ALKYLATION WITH FATTY ACIDS An American patent[645] describes the methylation or ethylation of pyridine or quinoline compounds at position 2 or 4 by heating their solution in the appropriate fatty acid with lead acetate or lead propionate at 120 °C for 1–2 h in the presence of a catalytic amount of an organic active hydrogen compound (e.g. methanol). Red phosphorus and acetic or propionic acid can be used in place of the lead salt.

j. ALKYLATION OF REISSERT COMPOUNDS The Reissert addition compounds in the quinoline series (see Section I.5.G.b) are readily alkylated by alkyl halides and the products can be hydrolysed with aqueous alkali to give the alkylquinolines. 1-Benzoyl-2-cyano-1,2-dihydroquinoline with methyl iodide gave 4-methyl-1,2-dihydroquinoline which, on hydrolysis, yielded 4-methylquinoline. This product in turn was converted via the Reissert compound 1-benzoyl-2-cyano-2,4-dimethyl-1,2-dihydroquinoline into 2,4-dimethylquinoline.[1623]

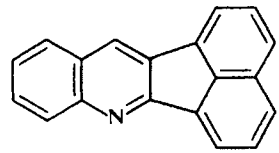
4. Physical Properties, Uses and Methods of Separation

A. General Physical Properties

The alkylquinolines form a family of organic heterocyclic bases whose general characteristics are similar to those of quinoline. Table 39 gives some physical properties of the known alkylquinolines followed by those for cycloalkylquinolines (Table 40), cycloalkenoquinolines (Table 41) and aralkylquinolines (Table 42).

a. MELTING POINTS AND BOILING POINTS As shown in the tables, most of the members of lower molecular weight are liquids or low-melting solids at room temperature. Of the monomethylquinolines, 6-methylquinoline has the lowest m.p. (−22 °C) and 7-methylquinoline the highest (39 °C). Of the dimethylquinolines, the lowest melting is 5,8-dimethylquinoline (m.p. 6 °C) and the highest melting is 3,7-dimethylquinoline (m.p. 80 °C). The boiling points of the mono- and dimethylquinolines range from 247 °C (2-methylquinoline) and 248 °C (8-methylquinoline) to 290 °C (3,4-dimethylquinoline). The low boiling points of the 2- and 8-methylquinolines have been attributed to hydrogen bonding.[229] Vapour pressure/temperature curves have been constructed for a number of methylquinolines[230,231] and the relative volatilities of some compounds concerned with perfumery, including 3-(1′-methylethyl)-, 3-(1′,1′-dimethylethyl)- and 3-(2′-methylpropyl)quinoline, have been determined.[232]

b. DISSOCIATION CONSTANTS Table 4 lists the pK_a values of a number of methylquinolines. The dissociation constants of all of the monomethylquinolines and many of the higher homologues have been determined.[233,234,308,309] Although, as expected, they are stronger bases than quinoline, except for derivatives having methyl substituents at both positions 2 and 8, no striking relationship was observed between the variations of the constants and the locations of the methyl substituents.[233] The effect on the pK_a value of a strained ring system was investigated by a study of acenaphtho[1,2-*b*]quinoline (**24**).



24

The pK_a values of (**24**), quinoline, quinaldine, acridine and the reference compounds 2-phenylquinoline and 2,3-diphenylquinoline were calculated from the half-neutralization potentials (HNP) determined by titration with perchloric acid in acetic anhydride at 25 °C.[235] The acenaphtho substituent resulted in a five-fold decrease in basicity ($pK_a = 3.61$) compared with the reference compounds 2-phenylquinoline ($pK_a = 4.26$) and 2,3-diphenylquinoline ($pK_a = 4.34$). Equilibrium constants for 1:1 adducts of quinoline and 2-methylquinoline with metal halides in ether followed the sequence $BF_3 > GaCl_3 > ZnCl_2$. Alkylquinolines were found to be weaker Lewis bases towards metal halides than pyridines with comparable pK_a values.[236]

TABLE 4. Dissociation Constants of Methylquinolines*

Quinoline substituent	pK_a	Temperature (°C)	Entry No. reference*	Original reference
None	4.89	20	1923	1589
None	4.96	20	1923	234
2-Me	5.71	22±2	2053	1590
2-Me	5.83	20	2053	234
3-Me	5.17	20	2054	234
4-Me	5.67	20	2055	234
5-Me	5.20	20	2056	234
6-Me	5.22	25	2057	234
7-Me	5.34	20	2058	234
8-Me	5.05	20	2059	234
2,3-Me_2	4.94	25	1994	233
2,4-Me_2	5.12	25	1995	233
2,6-Me_2	5.46	25	1996	233
2,7-Me_2	5.02	25	1997	233
2,8-Me_2	4.11	25	1998	233
2,3,8-Me_3	4.42	25	2075	233
2,4,8-Me_3	4.48	25	2076	233
1,2,3,4-H_4-acridine	5.07	20	—	1272

* D. D. Perrin, *Dissociation Constants of Organic Bases in Aqueous Solution*, IUPAC, Analytical Chemistry Division, Commission on Electroanalytical Chemistry, Butterworths, London, 1965.

c. DIPOLE MOMENTS The dipole moments of the monomethylquinolines and some dimethylquinolines have been determined[237-240] and are given in Table 5.

TABLE 5. Dipole Moments of Alkylquinolines

Quinoline derivative	Dipole moment (Debye units)	Temperature (°C)	References
Quinoline	2.16±0.01	—	237
	2.19	—	238
	2.15	25	240
2-Methylquinoline	1.86±0.01	—	237
	1.86	—	238
	1.95	25	239
	1.94	25	240
3-Methylquinoline	2.29	25	240
4-Methylquinoline	2.52	25	239
	2.56	25	240
5-Methylquinoline	2.46	25	240
6-Methylquinoline	2.31	—	238
	2.32	25	240
7-Methylquinoline	2.12	25	240
8-Methylquinoline	1.68	25	240
2,4-Dimethylquinoline	2.30	—	238
2,6-Dimethylquinoline	2.00	—	238
	2.02	25	240
4,8-Dimethylquinoline	2.13	25	240

d. SURFACE TENSION The surface tensions and surface potential variations in aqueous solutions of quinoline and methylquinolines have been measured at various pH values and at concentrations from dilute to saturated.[241] Unlike homologous series of aliphatic compounds, the limiting values of the surface potentials vary with the different values of the vertical component of the electrical moments of oriented molecules. Lowering of the surface tension reaches a maximum in saturated solutions.

e. SOLUBILITY The alkylquinolines are only slightly soluble in water but are soluble in most organic solvents. The solubilities of the bases in water have been studied[242] and also the solubilities of water in the alkylquinolines, which has also given information on the formation of hydrates. The solubilities of the quinoline bases in water were in the order quinoline > isoquinoline > 2-methylquinoline > 4-methylquinoline; they increased with increasing temperature and decreased as the boiling points of the bases increased. The salting-out effect of sodium sulphate and ammonium sulphate was studied on individual compounds and also on mixtures of bases obtained from light–medium coal tar fractions (b.p. 100–248 °C) and from heavy coal tar fractions (b.p. 215–308 °C).[242,1513] Critical solution temperatures of pyridine, quinoline and 2-methylquinoline in normal alkanes (C_5–C_{11}) have also been studied and found to depend on the chain length of the hydrocarbons. A graphical representation is parabolic, with a minimum value for the critical solution temperature (t_c) at chain lengths of C_6 to C_8. In octane the following values for t_c are reported: pyridine 21.7 °C, quinoline 1.6 °C and 2-methylquinoline −31.5 °C.[244,245]

Liquid–liquid equilibrium curves for binary mixtures of quinoline, isoquinoline and 2-, 4-, 7- and 8-methylquinolines with water and their critical solution temperatures (which are in the range 210–306 °C) have been determined.[352a] Methyl substituents were

found to reduce the solubilities of the bases in water. A methyl group at position 8 has the maximum effect as it interferes with the formation of hydrogen bonds between water and the heterocyclic nitrogen atom. A methyl group at position 2 also decreases solubility more than a methyl group at positions 4 and 7 as a result of screening effects.

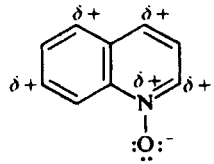
Liquid–solid equilibria of binary systems of 2-methylquinoline with isoquinoline and 4-, 7- and 8-methylquinolines and between binary mixtures of the corresponding hydrochlorides have been studied[352b-354] and the composition and melting points of the eutectics of the mixtures of hydrochlorides determined.[353]

f. MAGNETIC SUSCEPTIBILITY The magnetic susceptibilities of a series of *N*-heterocycles including the 2-, 4-, 6-, 7- and 8-methylquinolines and 2,4-dimethylquinoline have been determined and found to agree with calculated values.[246]

g. ADIABATIC COMPRESSIBILITY The velocity of sound in a number of organic liquids including quinoline and 2-methylquinoline has been used in conjunction with the densities to calculate the adiabatic compressibilities.[247]

B. Acidity of Side-chain Hydrogens

One of the most important properties of alkylquinolines is the increased acidity of the hydrogens attached to α-carbons of the side-chains. In this respect they resemble the alkylpyridines and the effect is strongest for alkyl groups at positions 2 and 4 of the quinoline ring and is enhanced if the nitrogen atom carries a formal positive charge as in quaternary salts or *N*-oxides. This has been explained as the result of electron distributions shown in (**24a**) and is consistent with the observations that hydrogens on 7-methyl substituents are more easily exchanged with deuterium than those at 6-methyl



24a

positions and that corresponding hydrogens of *N*-oxides are intermediate in acidity between those of the free base and a quaternary salt owing to the +M effect of the oxygen lone pairs.[248a] This property is usually studied quantitatively by means of H–D or H–T exchange reactions.[248-252,1620-1622,1635]

In 0.57 N EtOK in EtOD the mobilities of hydrogens in the α-positions of the side-chains were found to decrease as follows: 4-methylquinoline > 2-methylquinoline ≫ 6-methylquinoline (pK_a = 28–37), which overlapped the following series of alkylpyridines: 4-methylpyridine > 2-methylpyridine > 3-methylpyridine (pK_a = 30–37).[249,1621] In ND_3 and ND_3 containing KND_2 the first-order rate constants (min^{-1}) for H–D exchange were reported as 2-methylquinoline 1×10^{-5} (120 °C), 2-methylpyridine 2×10^{-5} (120 °C), toluene 2×10^{-6} (120 °C), Ph_2CH_2 3×10^{-7} (120 °C) and $PhCOCH_3$ 3×10^{-4} (25 °C). Under these conditions MeOH and Ph_2NH exchanged almost instantaneously.[248,1620] The first-order rate constants for H–D exchange in liquid ND_3 at 120 °C ($k \times 10^6 s^{-1}$) have also been reported as 2-methylquinoline 1.8, 4-methylquinoline 1.3, 2-methylpyridine 0.39 and 4-methylpyridine 0.18.[250b]

Various methylated *N*-heterocycles were examined in respect of hydrogen exchange with MeOD in Et_3N; only the H of the methyl group was involved under the conditions

used (130–180 °C). A 79% exchange occurred with 1,2-dimethylquinolinium iodide, the first-order rate constant determined being $3.8 \times 10^{-6}\,s^{-1}$.[1622] H–D exchange rates for α-hydrogens on the methyl groups of a series of *N*-heterocycles including 2-methylquinoline and 4-methylquinoline have been measured in deuterated pyrrolidine.[252] The experimental C–H acidities did not correlate with Hückel M.O., Pariser–Parr–Pople (PPP) or variable βγ(PPP) localization energies.

H–T exchange between methanol and ω-tritium-labelled picolines and methylquinolines gave the rate sequence 2-methylquinoline > 4-methylpyridine > 2-methylpyridine > 3-methylquinoline > 3-methylpyridine.[251] These results were interpreted by M.O. calculations.

C. Stereochemical Properties

As with quinoline itself, hydrogenation of the alkylquinolines gives rise to the expected geometrical isomers such as the *cis* and *trans* forms of decahydroquinoline derivatives and stable conformations of 1,2,3,4-tetrahydroalkylquinolines. In addition, when reduced to the 1,2,3,4-tetrahydro derivatives, alkylquinolines having one alkyl group at position 2, 3 or 4 give a pair of enantiomers and alkylquinolines having alkyl substituents at two of positions 2, 3 or 4 give two pairs of enantiomers. Thus 2,6-dimethyl-1,2,3,4-tetrahydroquinoline[253] and 2-methyl-1,2,3,4-tetrahydroquinoline[254] have been resolved and 2,4-dimethyl-1,2,3,4-tetrahydroquinoline[255] has been resolved into two pairs of enantiomers. Earlier claims that 1-substituted 1,2,3,4-tetrahydroquinolines could form stable enantiomers based on an asymmetrical tervalent nitrogen were shown to be invalid.[256] The stereochemistry and some stereospecific reactions of some 1,3-bridged benzopyridophanes have been studied.[257, 258]

D. Biological and Pharmacological Properties and Medical Applications

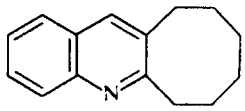
Alkylquinolines are among a number of quinoline derivatives which have been found to affect the growth of plants. Quinoline and 6-methyl-, 8-methyl-, 2,4-dimethyl- and 2,6-dimethylquinolines when applied to the meristems of onion (*Allium cepa*) resulted in the inhibition of mitosis.[259] When potatoes were treated with 2,4-dimethylquinoline, 2,3-dimethylquinoline and a number of other derivatives of quinoline at 0.5–1 $g\,kg^{-1}$ sprouting was prevented but 85–90% of the tubers grew when planted in January.[260] When exposed to the vapours of 5-methylquinoline, 5-isopropyl-8-methylquinoline and 6-butyl-8-methylquinoline germinating barley shoots were stunted and mitosis was abnormal.[261] Herbicidal activity against both broad- and narrow-leaved plants was shown by 8-ethyl-, 4-methyl-, 2-methyl, 4-methyl-3-nitro- and 8-nitroquinoline.[262]

The insecticidal properties of alkylquinolines have been studied and 7-methylquinoline and 8-methylquinoline were found to have high toxicity (100% mortality at 10 p.p.m.) towards the larvae of *Culex quinquefasciatus*.[263] 2-Butylquinoline and a number of tetrahydroalkylquinolines have been shown to have insecticidal properties.[264]

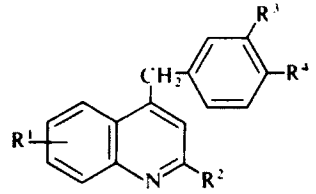
Fungicidal and bacteriocidal activity has been established for tetrahydroalkylquinolines and the *N*-oxides of 2-, 6- and 7-methylquinoline, and the introduction of a nitro group at position 4 increases this activity. The results were based on tests with *Aspergillus niger*, *Escherichia coli* and *Staphylococcus aureus*.[265, 274, 1517] Complex dithiocarbamates, including $(Me_2NCS)_2ZnY$ where Y = 6-methylquinoline, have been found useful as agricultural fungicides and may also be used as vulcanization accelerators.[266] Quaternary halide salts prepared from a C_{8-18}-alkyl halide and a crude tar base fraction (b.p. 230–265 °C) consisting mainly of isoquinoline, 2-methylquinoline and various mono- and dimethylquinolines had bacteriostatic properties effective at concentrations of 15–20 p.p.m. against *Staphylococcus aureus* and *Salmonella typhosa* and with a phenol coefficient of 300.[267]

Quinaldine is an effective anaesthetic and narcotic for fish at concentrations of 10–33 p.p.m. with no lasting toxic effects. Higher concentrations (70–100 p.p.m.) produce deep anaesthesia but are also toxic.[268-275] A concentration of 25 p.p.m. produced anaesthesia in shrimp but was also toxic.[1512] Quinaldine sulphate was found to be active at 2 p.p.m.[1514] The use of 2-methylquinoline and other compounds (metacaine, chlorobutanol and urethane) as narcotics for fish has been reviewed.[274] The identification and determination of 2-methylquinoline residues in fish by gas chromatographic methods[293] and by ultraviolet spectroscopy[294] has been described. The lower limit of sensitivity is 0.01 p.p.m. The distribution of 2-methylquinoline and tricaine methane sulphate (MS222) residues in various areas of fish fillets has also been discussed.[295]

Tumorcidal activity has been reported for the 2-methyl, 2-ethyl and 2-propyl derivatives of 4-nitroquinoline-1-oxide[275] and bis(4-hydroxyphenyl)-2-(and 4-)-quinolylmethane[276,1545] and bis(4-hydroxyphenyl)-(2-quinolyl)methylmethane[277] have been found to possess laxative properties. 2,3-Cyclohexamethylenequinoline[278] (**25**) and a series of thirteen derivatives of 4-benzylquinoline[218] (**26**) have been found to have an action on the heart and to be effective in the treatment of angina pectoris.



25



R^1 = H; 6-OMe; 5,8-$(OMe)_2$; 6,7 = OCH_2O
R^2 = H; Me
R^3, R^4 = H; OMe; Me

26

Quinolylethylpiperazines (see Section II.3.C.b) are reported to have antihypertensive activity and to be useful as antiarrhythmics and depressants and for their ability to lower the blood pressure.[1039,1540] Quinoline, which has recently been reported to be carcinogenic in rats, has also been found to have mutagenic properties. Some known non-carcinogenic quinoline derivatives, e.g. 2-chloroquinoline, do not have mutagenic activity. The possibility of a connection between these properties prompted a study of the mutagenicities of a series of seventeen quinoline derivatives including alkylquinolines not known to be carcinogenic. Twelve of these were found to be mutagenic.[1619]

α-Aminomethyl-2-quinolylethanols are effective as β-adrenergic blocking agents useful in the treatment of angina pectoris and cardiac arrhythmia.[1624]

E. Miscellaneous Properties and Uses

2-Methylquinoline and its quaternary salts are used as levellers and brighteners in nickel electroplating baths.[279-284] 6-Methylquinoline and 8-methylquinoline have been used as solvents for the decarboxylation of oxalic acid[285] and a large number of 8-alkylquinolines are specified as suitable additives to polyethylene for the preparation of insulation material having a high breakdown voltage.[286] Lower alkyl-substituted quinolines (with up to eight carbon atoms in the alkyl groups) have been used to confer water-resisting properties to lubricating greases.[287] Mixed alkylquinoline bases have been found to be effective in the protection of mild steel from corrosive attack by

acids.[288-290,1607,1608] Alkylquinolines have been included among compounds used to stabilize 1,1,1-trichloroethane[291] and a quinoline–methylquinoline fraction acts as an azeotropic agent to improve the separation, by distillation, of mixtures of anthracene, phenanthrene and carbazole.[292] 6-Isopropylquinoline and 2-isobutylquinoline have been used in the cosmetic and perfume industries.[1609]

F. Analysis of Alkylquinolines

In addition to classical methods for the analysis of organic bases of nitrogen by acid–base titrations[1618] by the determination of the nitrogen content and by the thermal decomposition of chloroaurates or chloroplatinates, the picrates of many alkylquinolines, including 2-methylquinoline picrate,[296] may be titrated with perchloric acid in acetic acid or acetic acid–acetic anhydride mixtures with methyl violet as indicator. High-frequency conductomeric titrations with Lewis acids ($AlBr_3$, $GaBr_3$ and BBr_3) in acetonitrile have been described[297] and also a coulometric procedure in acetonitrile.[298]

Polarographic methods for the reduction of 4-methylquinoline[299] and of 2-methylquinoline, 2,8-dimethylquinoline and other derivatives of 2-methylquinoline[300] have been used.

In acidic solution the heterocyclic ring undergoes two reduction equivalents, and in alkaline solution the methyl groups of 2- and 4-methylquinoline undergo 1 reduction equivalent.[524]

Methylquinoline and isobutylquinoline were among the bases which have been determined gravimetrically via their complexes with $H_3P(W_3O_{10})_4$, $H_3P(MoO_{10})_4$, $H_4Si(Mo_3O_{10})_4$ and $H_4Si(W_3O_{10})_4$. The complexes lost water and were stabilized at 200 °C.[1663]

X-ray powder diffraction patterns of solid organic bases including 2,6-dimethylquinoline, 6-phenylquinoline and 2,2′-biquinolyl have been obtained.[301] The decomposition of the tetraphenylborates and chloroaurates of 4-, 6-, 7- and 8-methylquinoline has been studied by differential thermal analysis (DTA)[302] and characteristic and reproducible differences were observed for the various isomers which could be useful for their identification. Quinine and a number of quinoline derivatives, including 2,6-dimethylquinoline, have been determined by measurements of their dielectric constants.[303] A colorimetric method for the determination of quinoline bases in the air of industrial premises has been developed, based on their reaction with violuric acid to form coloured complexes.[417]

A gravimetric method for the determination of 2-methylquinoline in dyes such as Quinoline Yellow WS and Quinoline Yellow SS has been described, based on the separation of the base by steam distillation followed by precipitation from acidic solution as a salt of phosphotungstic acid. The salt can be weighed both before and after incineration at 500–550 °C.[1629]

G. Spectroscopic Properties

The spectroscopic properties of quinoline have been discussed in Part I, Chapter 1, Sections III, 1–6. The following account is limited to the particular influences of alkyl substituents on the spectra.

a. Electronic Spectra The introduction of a methyl group into the quinoline nucleus has little effect on the absorption spectrum of quinoline.[307] The shifts in wavelength and changes in intensity which occur could not be correlated with molecular dimensions, probably because of hyperconjugative effects.[308] The dissociation constants of the monomethylquinolines have been calculated from the ultraviolet absorption

spectra.[233,234,308,309] The electronic absorption spectra of 2-, 4-, 6- and 7-methylquinoline in the vapour phase showed that each had 10–15 broad bands from 280 to 320 nm attributed to ^1L_b–^1A transition.[310]

Spectroscopic studies of the relationships between the stabilities of the iodine charge-transfer complexes and the pK_a values of bases including alkylquinolines[311,312] have shown that the complex with quinaldine is weaker than might be expected apparently because the 2-methyl group interferes more with the bulky iodine than a proton does.[312] Analogies between the absorption spectra of acridine and partially hydrogenated acridines and the corresponding compounds of anthracene in the range 210–400 nm have been observed.[313] The effect of ring size on the positions and intensities of the absorption and fluorescence spectra of 2,3-polymethylene-substituted quinolines has been shown to be related to ring strain and hyperconjugative effects as well as to $n \rightarrow \pi^*$ excitations.[305]

In a study of the electronic spectra of the carbanions formed from methylquinolines[314] by loss of a methyl proton to potassamide in liquid ammonia, absorptions were observed at 450–560 nm and assigned to the $\pi \rightarrow \pi^*$ transitions. With 2-, 3- and 8-methylquinoline doublets were obtained, the intensity ratio of the components being dependent on the amine concentration and time.

Under similar conditions it was also noted that the infrared spectra of 2- and 4-methylquinoline and of 2,6-dimethylquinoline and their 1-oxides showed two bands in the C–H stretching region at 3050–3090 cm^{-1} attributed to the CH_2^- group. The squares of the frequencies of the antisymmetrical vibrations of the CH_2^- groups gave a linear correlation when plotted against the π-electron density at the α-carbon atoms as calculated by the Hückel M.O. and S.C.F. methods.

The phosphorescence spectra of 2-, 4-, 6-, 7- and 8-methylquinoline and 2,4-dimethylquinoline have been measured, analysed and compared with those of quinoline and naphthalene.[341–345] Substituent effects have been examined with the aid of organometallic compounds (e.g. Me_2Hg) as enhancers of spin-forbidden transitions.[343]

b. Infrared Spectra The infrared spectra of all of the monomethylquinolines have been determined.[316–322] The characteristic absorption bands have been correlated with those of similarly substituted naphthalenes and tentative assignments to specific molecular vibrations suggested.[317] The methylquinolines have highly characteristic bands in the fingerprint region which can be used for the analysis of coal tar bases. For example, the high-boiling quinoline and isoquinoline fractions of coal tar bases have been analysed using the key bands at 12.15, 12.47, 13.42 and 12.68 μm for isoquinoline, quinoline, 2-methylquinoline and 8-methylquinoline, respectively.[321]

The far-infrared spectra of a series of substituted quinolines including methylquinolines have been analysed and their absorption frequencies assigned.[322] The intermolecular complexes formed by addition of phenol had a hydrogen-bond stretching mode (OH—N) at 120–130 cm^{-1}. A comparison with similar compounds of pyridine showed similar substituent effects in the two series. Studies of the Raman spectra of methylquinolines and related compounds[323–326] showed that the presence of a methyl group caused changes similar to those noted when toluene is compared with benzene.

c. Nuclear Magnetic Resonance Spectra The introduction of alkyl substituents into the quinoline ring results in changes in the resonances of the remaining nuclei (the substituent chemical shifts, S.C.S.) and also the introduction of additional ^1H and ^{13}C resonances of the substituents themselves. Further possibilities for spin–spin coupling are also provided.[1583] All of these effects are important when analysing particular spectra and are of value in structure determinations. The values of the principal chemical shifts and coupling constants for methylquinolines are given in Tables 6–19. Points of interest arising are discussed below.

TABLE 6. ^{1}H-Nmr Chemical Shifts for Alkyl-, Aralkyl- and Arylquinolines δ p.p.m. downfield from TMS (protons on substituents in parentheses)

Quinoline substituents	Solvent[a]	H-2	H-3	H-4	H-5	H-6	H-7	H-8	Ref.
None	Neat	9.52	7.09	7.83	7.58	7.35	7.60	8.43	1560
	Me_2CO	8.90	7.47	8.29	7.92	7.54	7.74	8.07	1560
	CCl_4	8.81	7.26	8.00	7.69	7.43	7.61	8.05	1560
	TFA	9.11	8.19	9.23	← 8.05–8.40 →				1563
2-Me	TFA	—	8.03	9.01	← 7.95–8.30 →				1563
	THF	(2.72)	7.30	8.09	7.82	7.44	7.67	8.03	1564
	CCl_4	(2.64)	← (7.1–8.3) →						1565
	CCl_4	(2.68)	7.11	7.87	← *m* →				1566
	CCl_4	(2.64)	7.10	7.82	← *m* →			7.99	1587a
	$CDCl_3$	(2.72)	7.21	7.97	← *m* →				1566
	$CDCl_3$	(2.72)	7.24	8.02	← *m* →			8.09	1588a
	DMSO	(2.96)	7.42	8.25					1566
	TFA	(3.13)	7.93	9.00					1566
	CCl_4	(2.64)	7.07	7.82	← *m* →			7.97	1569
3-Me	CCl_4	8.62	(2.38)	7.68	← *m* →			8.03	1569
4-Me	CCl_4	8.62	—	(2.61)	← *m* (7.0–8.2) →				1565
	CCl_4	8.67	7.08	(2.58)	← *m* →			8.08	1587b
	$CDCl_3$	8.75	7.17	(2.68)					1566
	$CDCl_3$	8.73	7.18	(2.67)	← *m* (7.33–7.95) →			8.04	1571a
	DMSO	8.80	7.36	(2.68)	← *m* →				1566
	$CDCl_3$	8.80	7.19	(2.66)	← *m* →				1588b
	TFA	8.90	7.95	(3.17)					1566
	CCl_4	8.61	7.01	(2.54)	7.79	← *m* →		8.03	1569
5-Me[a]	CCl_4	8.70	[b]	8.02	(2.54)	[b]	[b]	[b]	1569
6-Me[c]	CCl_4	8.69	7.13	7.85	7.37	(2.42)	7.37	7.97	1561
	$CDCl_3$	8.78	7.15	7.82	7.29	(2.36)	7.35	7.99	1571b
	TFA	9.02	8.10	9.12	8.20	—	8.20	8.20	1563
7-Me[c]	CCl_4	8.75	7.12	8.00	7.55	7.27	(2.49)	7.83	1561
7-Me[a]	CCl_4	8.79	7.09	7.82	7.48	7.13	(2.40)	7.90	1571c
7-Me	$CDCl_4$	8.80	7.28	8.05	7.66	7.30	(2.57)	7.83	1569
7-Me[a]	CCl_4	8.68	7.07	7.80	7.47	7.08	(2.46)	7.78	1569

Footnotes see p.38.

TABLE 6 (*cont.*)

Quinoline substituents	Solvent[a]	H-2	H-3	H-4	H-5	H-6	H-7	H-8	Ref.
8-Me	CCl_4	8.72	7.12	7.82				(2.77)	1562
	CCl_4	8.79	7.12	7.84	← *m* (7.20–7.60) →			(2.80)	1571d
2,3-Me_2	CCl_4	(2.55)	(2.31)	7.57	← *m* →			7.86	1569
2,4-Me_2[f]	CCl_4	(2.53)	6.79	(2.40)	7.60			7.92	1561
	THF	(2.65)	7.12	(2.65)	7.82	7.40	7.65	8.00	1564
	CCl_4	(2.56)	6.90	(2.50)					1565
	$CDCl_3$	(2.70)	7.14	(2.66)					1568a
	$CDCl_3$	(2.63)	7.02	(2.52)	← *m* (7.30–8.10) →				1571e
	CCl_4	(2.55)	6.85	(2.45)	← *m* →				1569
2,6-Me_2[f]	CCl_4	(2.59)	6.91	7.60	7.19	(2.35)	7.27	7.80	1561
	$CDCl_3$	(2.72)	7.21	7.90	← *m* →	(2.50)	← *m* →	7.90	1568b
	$CDCl_3$	(2.72)	7.23	7.90	← *m* →	(2.51)	← *m* →		
	$CDCl_3$	(2.40)	7.05	7.76[e]	7.33	(2.65)	7.39	7.90[e]	1571f
				7.90				7.76	
	THF	(2.68)	7.22	7.95	7.54	(2.51)	7.46	7.88	1564
2,7-Me_2[f]	CCl_4	(2.59)	6.90	7.40[e]			(2.45)	7.67	1561
	CCl_4	(2.63)	7.04	7.80[d]	7.50[d]	7.15	(2.51)	7.69	1569
	$CDCl_3$	(2.45)	7.00	7.48[e]	7.76[e]	7.11	(2.63)	7.71	1571g
	$CDCl_3$	(2.74)	7.19	7.99	7.81	7.29	(2.58)	7.66	1588d
2,8-Me_2	CCl_4	(2.69)	7.14	7.87	← *m* (centre 8.40) →			(2.76)	1571h
3,4-Me_2	CCl_4	8.46	(2.34)	(2.46)	← *m* →				1569
3,7-Me_2	CCl_4	8.56	(2.45)	7.67	7.47	7.18	(2.52)	7.73	1569
4,6-Me_2[f]	CCl_4	8.56	7.03	(2.59)	7.79	(2.51)	7.39	7.90	1569
4,7-Me_2[f]	CCl_4	8.55	6.94	(2.52)	7.66	7.18	(2.47)	7.78	1569
4,8-Me_2	CCl_4	8.64	7.07	(2.62)	7.69	← *m* →		(2.76)	1569
5,7-Me_2	CCl_4	8.62	7.05	7.91	(2.35)	6.92	(2.43)	7.57	1562
6,7-Me_2	CCl_4	8.64	7.13	7.83	7.38	(2.40)[e]	(2.43)[e]	7.74	1569
2,3,4-Me_3	CCl_4	(2.56)	(2.25)	(2.44)	← *m* →				1569
2,4,7-Me_3	CCl_4	(2.53)	6.81	(2.46)	7.59	7.11	(2.46)	7.66	1569
2,6,7-Me_3	CCl_4	(2.60)	7.00	7.70[d]	7.30[d]	(2.33)[e]	(2.38)[e]	7.67	1569
3,4,7-Me_3	CCl_4	8.43	(2.34)	(2.44)	7.68	7.16	(2.45)	7.69	1569
3,5,8-Me_3	CCl_4	8.61	(2.47)[e]	7.96	(2.54)[e]	7.22	7.07	(2.68)[e]	1569

3,6,7-Me_3	CCl_4	8.51	(2.39)	7.62	7.32	(2.44)[e]	(2.45)[e]	7.71	1569
3,6,8-Me_3	CCl_4	8.54	(2.42)[e]	7.59	7.17	(2.45)[e]	7.17	(2.68)[e]	1569
3,7,8-Me_3	CCl_4	8.58	(2.42)	7.62	7.30	7.14	(2.42)	(2.67)	1569
4,5,7-Me_3	CCl_4	8.50	6.85	(2.73)	(2.73)	6.94	(2.41)	7.60	1569
4,5,8-Me_3	CCl_4	8.54	6.97	(2.80)	(2.77)	7.02	7.24	(2.66)	1569
4,6,7-Me_3	CCl_4	8.48	6.93	(2.54)	7.50	(2.38)	(2.38)	7.71	1569
4,6,8-Me_3	CCl_4	8.56	7.02	(2.57)	7.43	(2.44)	7.25	(2.70)	1569
4,7,8-Me_3	CCl_4	8.60	6.99	(2.60)	7.58	7.20	(2.44)	(2.70)	1569
2,4,6-Me_3[r]	—	—	—	—	—	—	—	—	
2,3,4,7-Me_4	CCl_4	(2.56)	(2.26)	(2.44)	7.64	7.12	(2.48)	7.62	1569
2,4,6,7-Me_4	CCl_4	(2.55)	6.84	(2.51)	7.46	(2.39)	(2.39)	7.63	1569
3,4,6,7-Me_4	CCl_4	8.37	(2.33)	(2.44)	7.50	(2.38)	(2.38)	7.64	1569
2,3,4,6,7-Me_5	CCl_4	(2.54)	(2.25)	(2.43)	7.44	(2.37)	(2.37)	7.55	1569
5-Et	CCl_4			8.14[k]	1.26[f] 2.94[g]				1570
7-Et	CCl_4	8.76	7.21	7.98	7.61	7.28	1.35[f] 2.72[g]	7.83	1570
2-Et-3-Me	CCl_4	1.36[f] 2.88[g]	(2.38)	7.61	←	*m*	→	7.91	1569
4-Et-3-Me	CCl_4	8.46	(2.30)	1.15[f] 2.89[g]	←	*m*	→		1569
2,4-Et_2	CCl_4		7.00						1565
	CCl_4	1.36[f] 2.92[g]	6.96	1.29[f] 2.88[g]	←	*m*	→		1569
2,4-Pr	CCl_4	0.99[f] 1.86[h] 2.92[i]	6.94	0.99[f] 1.75[h] 2.85[f]	←	*m*	→		1569
2,4-Pr^i	CCl_4		6.74						1565
2-Et-3,7-Me_2	CCl_4	1.34[f] 2.86[g]	(2.37)	7.59	7.42	7.12	(2.49)	7.70	1569
3-Pr^i	$CDCl_3$	8.74	1.27[f] 3.11[l]	7.84	←	*m*	→	7.98	1569
4-Phenyl	CCl_4	8.94	7.31	(*m*)	←	*m*	→		1569
4-Phenyl-3-Me	CCl_4	8.72	(2.23)	(*m*)	←	*m*	→		1569

Footnotes see p.38.

TABLE 6 (*cont.*)

Quinoline substituents	Solvent[a]	H-2	H-3	H-4	H-5	H-6	H-7	H-8	Ref.
3-Benzyl-6-Ph	$CDCl_3$	8.80	(4.15)[p] (7.25)[q]	←	*m* (7.20–8.00)	—	(Ph) →	8.15	1571i
3-Benzyl-8-Ph	$CDCl_3$	7.77	(4.12)[p] (7.22)[q]	←	*m* (7.25–7.82)	—	(Ph) →		1571j

[a] Determined using a mixture of 5- and 7-methylquinolines.
[b] Peaks obscured.
[c] These values are probably wrongly assigned in view of those marked [d], which are based on the unequivocal evidence of couplings in 2,6,7-trimethylquinoline.
[d] See [c].
[e] These assignments could be interchanged.
[f] CH_3 protons.
[g] CH_3CH_2 protons.
[h] $CH_3CH_2CH_2$ protons.
[i] $CH_3CH_2CH_2$ protons.
[k] Incorrectly assigned to H-8 in original paper.
[l] Me_2CH protons.
[m] Multiplet (range or centre indicated).
[n] TFA = trifluoroacetic acid; THF = tetrahydrofuran.
[p] $PhCH_2$ protons.
[q] *Ph*CH_2 protons.
[r] For partial spectra see also ref. 1567.

TABLE 7. ^{13}C-Nmr Chemical Shifts of Aromatic Carbons of Methylquinolines
δ p.p.m. downfield from TMS

Methyl substituents	Solvent	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9 C-(8a)	C-10 C-(4a)	Ref.
None	CCl_4	150.9	121.7	136.1	128.5	127.0	129.9	130.5	—	—	1572
									149.3	128.9	328
	$CDCl_3$	150.2	120.9	135.7	127.6	126.4	129.2	129.4	148.3	128.2	1573
											1665
		150.3	121.0	136.0	127.7	126.5	129.4	129.4	148.3	128.3	1664
2-Me[b]		158.7	121.7	135.8	—	—	—	—	147.8	126.3	331
		158.2	121.7	135.6	127.3	125.4	129.1	128.7	147.9	126.4	1573
		158.9	122.0	136.1	127.5	125.6	129.4	128.6	147.9	126.5	1664
3-Me		152.2	130.2	134.4	—	—	—	—	146.5	128.0	331
		152.2	130.1	134.3	127.1	126.3	128.2	129.2	146.6	128.1	1573
		152.3	130.5	134.7	127.1	126.6	128.4	129.2	146.6	128.3	1664
4-Me		149.7	121.6	144.0	—	—	—	—	147.7	128.0	331
		150.2	121.8	144.2	123.8	126.3	129.1	130.1	148.0	128.3	1664
		149.8	121.6	143.9	123.6	126.1	128.8	129.8	147.8	128.0	1573
5-Me[a]		149.9	120.5	132.2	—	126.9	129.0	127.8	—	—	1573, 1574
		149.8	120.5	132.1	134.5	126.9	129.0	127.8	148.5	127.4	1664
6-Me		149.3	120.8	135.0	126.5	135.9	131.4	129.1	147.0	128.2	1573, 1574,
											1665
		149.5	121.0	135.3	126.5	136.3	131.7	129.1	146.9	128.3	1664
7-Me		150.3	120.2	135.6	127.4	128.8	139.6	128.5	148.6	126.3	1573, 1574,
											1665
		150.4	120.3	135.7	127.4	128.5	139.7	128.8	148.6	126.5	1664
8-Me[c]		149.0	120.6	136.0	125.8	126.1	129.5	136.9	147.3	128.1	331
		149.2	120.8	136.2	125.9	126.3	129.6	137.1	147.4	128.2	1664
		149.0	120.6	135.8	125.8	126.1	129.4	137.1	147.5	128.2	1573
2,3-Me_2		158.6	129.7	134.9	—	—	—	—	146.4	127.3	331
		—	—	—	126.6	125.4	128.1[d]	128.2[d]	—	—	1575
2,4-Me_2		158.2	122.3	143.7	—	—	—	—	147.5	126.3	331
		—	—	—	123.4	125.2	128.8[d]	129.0[d]	—	—	1575
		158.5	122.6	144.0	123.5	125.3	129.0	129.2	147.8	126.5	1573, 1574
		158.2	122.6	144.0	123.5	125.3	129.0	129.2	147.8	126.5	1665

Footnotes see p.40.

TABLE 7 (*cont.*)

Methyl substituents	Solvent	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9 C-(8a)	C-10 C-(4a)	Ref.
2,6-Me_2	$CDCl_3$	157.9	121.9	135.4	126.4	135.3	131.5	128.6	146.6	126.5	1664
		157.8	121.8	135.4	126.3	135.2	131.5	128.4	146.5	126.4	1573, 1574
		157.6	121.6	135.2	—	135.0	—	—	146.4	126.3	1578
2,7-Me_2		158.8	121.1	135.7	127.1	127.9	139.5	127.9	148.3	124.6	1664
3,4-Me_2		152.2	129.3	140.7	—	—	—	—	146.7	128.2	331
		—			123.2	126.0	127.7	129.8	—	—	1575
3,6-Me_2		151.4	130.4	134.1	126.0	136.3	130.7	128.8	145.1	128.1	1664
3,7-Me_2		152.3	129.5	134.4	126.8	128.2	138.5	128.7	146.8	126.2	1664
3,8-Me_2		151.2	130.2	135.0	125.3	126.4	128.7	136.7	145.6	128.1	1664
4,6-Me_2		149.3	121.9	148.5	122.8	136.0	131.3	129.7	146.6	128.2	1664
5,8-Me_2		148.3	120.0	131.9	131.8	126.4	128.9	134.8	147.5	127.3	331
		148.6	120.3	132.5	132.1	126.6	129.2	134.9	147.5	127.5	1664
6,7-Me_2		149.5	120.3	134.9	126.9	136.3	139.6	128.8	147.5	126.9	1664
6,8-Me_2		148.2	120.6	135.3	124.6	135.7	131.8	136.5	146.0	128.3	331
7,8-Me_2		149.9	119.6	135.8	124.7	129.3	134.1[e]	136.9[e]	147.3	126.5	331
		149.1	119.9	136.1	124.8	129.4	137.1	134.3	147.4	126.6	1664
2,3,4-Me_3		158.0	128.9	140.1	—	—	—	—	145.7	126.9	331
		—	—	—	123.4	125.2	127.6	129.0	—	—	1575
2,4,7-Me_3		158.3	121.7	143.7	123.2	127.4	138.9	128.3	147.9	124.5	1573, 1574, 1665

[a] Determined on a mixture of 5- and 7-methylquinolines. Quaternary carbon signals not readily discernible.
[b] See also ref. 1576.
[c] See also ref. 1577.
[d] Assignments may be reversed.
[e] Assignments later reversed, see ref. 1664.

TABLE 8. ^{13}C-Nmr Chemical Shifts of Methyl Carbons of Methylquinolines
δ p.p.m. downfield from TMS

Methyl substituent(s)	Solvent	2-Me	3-Me	4-Me	5-Me	6-Me	7-Me	8-Me	Ref.
2-Me	$CDCl_3$	25.2							331
		25.3							1664
		25.1							1573
3-Me			18.5						331
			18.7						1664
			18.4						1573
4-Me				18.2					331
				18.6					1664
				18.2					1573
5-Me					18.5				1573, 1574
					18.5				1664
					18.5				1579
6-Me						21.2			1573, 1665
						21.5			1664
7-Me							21.8		1573, 1574, 1665
							21.9		1664
							21.7		1579
8-Me								18.1	331
								18.1	1664
								18.1	1573
2,3-Me_2		23.4	19.3						331
2,4-Me_2		25.0		18.1					331
		25.1		18.4					1573, 1574, 1665
2,6-Me_2		25.2				21.3			1573, 1665
		25.2				21.4			1664
		25.1				21.1			1578
2,7-Me_2		25.3					21.9		1664
3,4-Me_2			17.1	13.7[a]					331
3,6-Me_2			18.1			21.6			1664
3,7-Me_2			18.6				21.7		1664
3,8-Me_2			18.6					18.2	1664
4,6-Me_2				18.7		21.9			1664
5,6-Me_2					14.0[a]	20.5			1569
5,8-Me_2					18.1			18.1	331
					18.4			18.2	1664
6,7-Me_2						19.9	20.4		1664
6,8-Me_2						21.4		18.0	331

[a] The present authors have observed that the resonances of ^{13}C atoms of methyl groups at positions 4, 5 or 8 (i.e. next to a bridgehead carbon) which also have an *ortho*-methyl substituent (viz. 3,4-, 5,6- and 7,8-dimethylquinolines and appropriate trimethylquinolines such as 2,3,4-trimethylquinoline) are subject to an upfield shift of 4–5 p.p.m. compared with those which do not have an *ortho*-substituent. This is consistent with the resonances of the central methyl carbon of 1,2,3-trimethylbenzene,[1666] if the bridgehead takes the place of the third substituent. The figure of δ = 18.3 p.p.m. for the chemical shift of the 8-methyl carbon of 7,8-dimethylquinoline[1664] is therefore anomalous and could conceivably result from a transcription error for 13.3 p.p.m. See also ref. 334, which discusses a similar effect on ^{1}H resonances.

TABLE 8 (*cont.*)

Methyl substituent(s)	Solvent	2-Me	3-Me	4-Me	5-Me	6-Me	7-Me	8-Me	Ref.
7,8-Me_2	$CDCl_3$						20.5	13.3[a]	331
							20.7	18.3[a]	1664
2,3,4-Me_3		24.7	15.5	14.0[a]					331
2,4,7-Me_3		25.0		18.2			21.6		1573, 1574, 1665

Footnotes see p.41.

TABLE 9. $^3J_{^1H-^1H}$ Ring Proton–Ring Proton Coupling Constants (Hz) for Alkylquinolines[1582]

Substituent	Solvent	$^3J_{2,3}$	$^3J_{3,4}$	$^3J_{5,6}$	$^3J_{6,7}$	$^3J_{7,8}$	Ref.
None	Neat	4.2	8.3	8.1	6.8	8.2	1560
None	CCl_4	4.1	8.2	8.2	6.9	8.6	1560
None	Me_2CO	4.2	8.3	8.0	6.8	8.4	1560
2-Me	Various		8.9				1566
	CCl_4		8.3				1569
3-Me	CCl_4					8.0	1569
4-Me	Various	4–4.3					1566
	CCl_4	4.3					1569
5-Me[a]	CCl_4		8.6				1569
6-Me	CCl_4	4.0	9.0			9.0	1561
7-Me	CCl_4	4.1	9.0				1561
8-Me	CCl_4	4.1	7.9				1562, 1580
2,3-Me_2	CCl_4					8.2	1569
2,4-Me_2	CCl_4					8.0	1561
2,6-Me_2	CCl_4		8.5			9.0	1561
2,7-Me_2	CCl_4		8.3				1569
	CCl_4		8.0				1561
2,8-Me_2	—	4.1					1581
3,7-Me_2	CCl_4			8.4			1569
4,6-Me_2	CCl_4	4.0				8.0	1561
4,6-Me_2	—					8.5	1581
	CCl_4	4.2				8.4	1569
4,7-Me_2	CCl_4	4.2		8.4			1569
4,8-Me_2	CCl_4	4.2		7.8			1569
5,6-Me_2[b]	CCl_4		8.5			8.5	1569
5,7-Me_2	CCl_4	3.9	8.6				1562
	—	4.0	8.4				1581
5,8-Me_2	—	4.1	8.4		7.2		1581
6,7-Me_2	CCl_4	4.2	8.3				1569
6,8-Me_2	—	4.1	8.2				1581
2,4,7-Me_3	CCl_4			8.4			1569
2,5,6-Me_3	CCl_4		8.5			8.5	1569
2,6,7-Me_3	CCl_4		8.2				1569
3,4,7-Me_3	CCl_4			8.5			1569
3,5,8-Me_3	CCl_4				7.1		1569
3,7,8-Me_3	CCl_4			8.3			1569
4,5,7-Me_3	CCl_4	4.2					1569
4,5,8-Me_3	CCl_4	4.2			7.1		1569

TABLE 9 (*cont.*)

Substituent	Solvent	$^3J_{2,3}$	$^3J_{3,4}$	$^3J_{5,6}$	$^3J_{6,7}$	$^3J_{7,8}$	Ref
4,6,7-Me_3	CCl_4	4.3					1569
4,6,8-Me_3	CCl_4	4.2					1569
4,7,8-Me_3	CCl_4	4.2		8.6			1569
2,3,4,7-Me_4	CCl_4			8.6			1569
5-Et[c]	CCl_4		8.7				601
7-Et	CCl_4	4.2	8.2	8.2			601
2-Et-3-Me	CCl_4					8.0	1569
2-Et-3,7-Me_2	CCl_4			8.3			1569
4-Et-3,6-Me_2	CCl_4					8.4	1569
6-Et-2,4-Me_2	CCl_4					8.3	1569
7-Et-2,4-Me_2	CCl_4			8.2			601
3-Pr^i	$CDCl_3$					8.2	1569

[a] Determined on mixture with 7-methyl isomer.
[b] Determined on mixture with 6,7-dimethyl isomer.
[c] Determined on mixture with 7-ethyl isomer.

TABLE 10. ^4J and $^5J_{^1H-^1H}$ Ring Proton–Ring Proton Coupling Constants (Hz) for Alkylquinolines[1582]

Substituent	Solvent	$^4J_{2,4}$	$^4J_{5,7}$	$J_{6,8}$	$^5J_{5,8}$	$^5J_{4,8}$	Ref.
None	Neat	1.7	1.6	1.1	0.3	0.9	1560
	CCl_4	1.7	1.4	1.1	0.5	0.9	1560
	Me_2CO	1.7	1.4	1.1	0.4	0.8	1560
3-Me	CCl_4	2.0					1569
6-Me	CCl_4	2.0					1561
7-Me	CCl_4	1.9					1561
8-Me	CCl_4	1.8					1562, 1580
2,3-Me_2	CCl_4			1.7			1569
2,4-Me_2	CCl_4		2.0				1561
2,6-Me_2	CCl_4		1.9				1561
2,7-Me_2	CCl_4			1.7			1569
2,8-Me_2	—	2.2					1581
3,7-Me_2	CCl_4	2.1		1.7			1569
4,6-Me_2	CCl_4		1.8				1569, 1581
4,7-Me_2	CCl_4			1.8			1569
4,8-Me_2	CCl_4		1.9				1569
5,7-Me_2	CCl_4	1.7			0.8		1562
5,7-Me_2	—	1.6			0.5		1581
5,8-Me_2	—	1.7					1581
6,7-Me_2	CCl_4	1.9					1569
6,8-Me_2	—	1.8					1581
2,4,7-Me_3	CCl_4			1.8			1569
3,4,7-Me_3	CCl_4			1.7			1569
3,5,8-Me_3	CCl_4	2.2					1569
3,6,7-Me_3	CCl_4	2.2					1569
3,6,8-Me_3	CCl_4	2.2					1569

TABLE 10 (*cont.*)

Substituent	Solvent	$^4J_{2,4}$	$^4J_{5,7}$	$^5J_{6,8}$	$^5J_{5,8}$	$^5J_{4,8}$	Ref.
3,7,8-Me_3	CCl_4	2.2					1569
2,3,4,7-Me_4	CCl_4			1.8			1569
5-Et[a]	CCl_4	1.8					601
7-Et	CCl_4	1.7		1.5			601
2-Et-3,7-Me_2	CCl_4			1.7			1569
4-Et-3,6-Me_2	CCl_4		1.8				1569
6-Et-2,4-Me_2	CCl_4		1.8				1569
7-Et-2,4-Me_2	CCl_4			1.8			601
3-Pr[i]	$CDCl_3$	2.1					1569

[a] Mixed with 7-ethyl isomer.

TABLE 11. $^4J_{^1H-^1H}$ Methyl Proton–Ring Proton Coupling Constants (Hz) for Methylquinolines (*ortho*-Benzylic Coupling Constants) Methyl protons given first and indicated by primes (')

Coupling constant	Ref.	Coupling constant	Ref.
$^4J_{2',3} \approx 0$	331	$^4J_{6',7} \approx 0$	331
$^4J_{3',2} \approx 0$	331	$^4J_{7',6} \approx 0$	331
$^4J_{3',4} = 0.85$–0.90	331	$^4J_{5',6} = 0.8$[a]	331
$^4J_{4',3} = 0.90$–0.95	331	$^4J_{6',5} = 0.8$[a]	331
$= 0.95$	330	$^4J_{7',8} = 0.8$[a]	331
$= 1.0$	335b	$^4J_{8',7} = 0.8$[a]	331
		$= (-0.68)$	1566

[a] Sign not established but presumed to be negative.

TABLE 12. $^5J_{^1H-^1H}$ and $^6J_{^1H-^1H}$ Methyl Proton–Ring Proton Coupling Constants (Hz) for Methylquinolines (*meta*- and *para*-Benzylic Coupling Constants) Methyl protons given first and indicated by primes (')

Coupling constant	Ref.	Coupling constant	Ref.
$^5J_{2',4'}$; $^5J_{4',2}$	[a]	$^6J_{5',8'}$; $^6J_{8',5}$	[b]
$^5J_{5',7'}$; $^5J_{7',5}$	[a]		
$^5J_{6',8'}$; $^5J_{8',6}$	[a]	$^6J_{8',4}$[c] $= -0.55$	1566
$^5J_{8',6} = 0.29$	1566		

[a] *meta*-Benzylic coupling does occur but is very weak.[1569]

[b] *para*-Benzylic coupling does occur, it is weaker than *ortho*-benzylic coupling but stronger than *meta*.[1569]

[c] The sense of the original paper indicates that this coupling should be $^6J_{8',5}$.

TABLE 13. $^5J_{^1H-^1H}$ Methyl Proton–Methyl Proton Coupling Constants (Hz) for Methylquinolines (Inter-methyl Coupling Constants)

Coupling constant	Ref.	Coupling constant	Ref.
$^5J_{2',3'}$	[b]	$^5J_{6',7'}$	[b]
$^5J_{3',4'} \approx 0.5$	1569	$^5J_{7',8'}$	
$^5J_{5',6'}$	[a]		

[a] Weak coupling detected but J not determined.[1569]

[b] No coupling detected.[1569]

TABLE 14. $^{1}J_{^{13}C-^{1}H}$ Methyl Carbon–Methyl Proton Coupling Constants (Hz) for Methylquinolines

Substituents	Coupling constant	Refs.
Methyl groups in all positions (with a few exceptions)	$^{1}J_{^{13}C-^{1}H}$ = 126–127	1584, 331, 1573, 1574, 1665

TABLE 15. $^{1}J_{^{13}C-^{1}H}$ Ring Carbon–Ring Proton Coupling Constants (Hz) for Quinoline and Alkylquinolines[1584, 331, 1573, 1574, 1665]

Position	Coupling constant	Position	Coupling constant
2	176–178	6	159–162
3	159–165	7	157–167
4	161–162	8	159–163
5	158–162		

TABLE 16. $^{2}J_{^{13}C-^{1}H}$ Ring Carbon–Methyl Proton Coupling Constants (Hz) for Methylquinolines

Compound[a]	Coupling constant	Ref.
2,4,7-Trimethylquinoline	$^{2}J_{2,2'}$ = 6.4	1569
	$^{2}J_{4,4'}$ = 6.1	1569
	$^{2}J_{7,7'}$ = 6.3	1569
2-Methylquinoline-2-^{13}C	$^{2}J_{2,2'}$ = 6.0	1585

[a] Very few reports of these couplings are available to date.

TABLE 17. $^{3}J_{^{13}C-^{1}H}$ Methyl Carbon–Ring Proton Coupling Constants (Hz) for Methylquinolines
Methyl carbons indicated by primes (′)

Coupling constant	Ref.	Coupling constant	Ref.
$^{3}J_{2',3}$ = 2	331	$^{3}J_{6',5}$ = 5	331
= 1.6	1573	= 4.6	1573
= 2.1	1574	= 4.3	1574
$^{3}J_{3',2}$ = 3	331	$^{3}J_{6',7}$ = 4	331
= 2.4	1573	= 4.6	1573
		= 4.3	1574
$^{3}J_{3',4}$ = 5	331	$^{3}J_{7',6}$ = 4	331
= 4.8	1573	= 4.5	1574
$^{3}J_{4',3}$ = 5	331	$^{3}J_{7',8}$ = 4.5	1574
= 5.0	1573		
= 5.1	1574		
$^{3}J_{5',6}$ = 5	331	$^{3}J_{8',7}$ = 5	331
		= 4.6	1573

TABLE 18. $^3J_{^{13}C-^1H}$ Ring Carbon–Methyl Proton Coupling Constants (Hz) for Methylquinolines
Methyl protons indicated by primes (')

Coupling constant	Ref.	Coupling constant	Ref.
$^3J_{3,2'} = 3.5$	1573, 1574	$^3J_{5,6'} = 5.2$	1573, 1574
$^3J_{2,3'} = 5.5$	1573, 1574		
		$^3J_{6,7'} = 4.8$	1573, 1574
$^3J_{3,4'} = 5.0$	1573, 1574	$^3J_{7,6'} = 5.1$	1573, 1574
$= 6.0$	331		
$^3J_{4,3'} = 5.1$	1573, 1574	$^3J_{7,8'} = 5.2$	1573, 1574
		$^3J_{8,7'} = 5.3$	1573, 1574

TABLE 19. $^3J_{^{13}C-^1H}$ Ring Carbon–Ring Proton Coupling Constants (Hz) for Quinoline and Alkylquinolines

For values of ring carbon–ring coupling constants in quinoline and methylquinolines, see refs. 1573, 1574, 1585, 1587 and 1588.

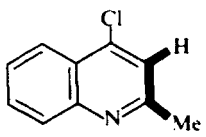
In addition the following values are also available from the spectra of suitably substituted methylquinolines. These couplings involving quaternary bridgehead carbons are too complex to be resolved in the spectrum of quinoline itself:[1573]

$^3J_{10,3} = 7.1$ (from 6,8-dimethylquinoline)[1569]
$^3J_{9,5} = 6.4$ (from 2,4,7-trimethylquinoline)[1569]

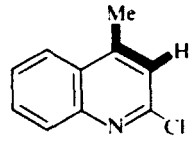
The methyl group of 6-methylquinoline exerts a substituent chemical shift of -1.30 (shielding effect) on the ^{15}N resonance of quinoline.[1586]

The larger shielding effect (negative substituent chemical shift, S.C.S.) for the *para*-methyl substituent compared with those for *ortho*- or *meta*-methyl substituents has been used to confirm the original assignments[327] of the resonances of the two bridgehead carbons in quinoline.[328] Thus C-4a (C_{10}) is shielded by the 2-methyl and 7-methyl substituents, and C-8a (C_9) by the 3-methyl and 6-methyl substituents.

Confirmation of bond fixation, resulting in reduced double bond character of the 2,3- and 6,7- bonds of quinoline, is shown by substituent effects of methyl groups on the chemical shifts of ring protons[329,330,340] and by the reduced values of coupling constants across these bonds (Tables 9, 11, 17 and 18). The lack of benzylic coupling across the 2,3-bond can also be seen from a comparison of the methyl proton peaks in the spectra of 4-chloro-2-methylquinoline (**27**) and 2-chloro-4-methylquinoline (**28**). The former is a singlet and the latter a doublet as a result of benzylic coupling with H-3. In the same spectra the H-3 peak appears as a sharp singlet for (**27**) and as a poorly resolved quartet in (**28**).[331]



27



28

The chemical shifts and coupling constants for a series of methyl- and dimethylquinolines[332] show that ring protons resonate at higher field strengths when alkyl groups are introduced, as a result of inductive and hyperconjugative effects which are stronger for hydrogens in the same ring and which exert the greatest influence at *ortho*-positions. Methyl groups also induce a slight increase in vicinal ^1H (*ortho*) coupling constants, with the exception of $J_{2,3}$, which is not appreciably affected. In studies which included all the monomethylquinolines, semi-empirical S.C.F. calculations of electron charge density and ring current contributions showed that effects that act on the shielding of protons directly attached to heterocyclic systems also act in attenuated form on the ^1H chemical shift of methyl protons in the monomethylquinolines. Vicinal coupling constants were rationalized in terms of π-electron bond order and electronegativities of neighbouring atoms.[333]

In a study of the infrared and ^1H-nmr spectra of quinoline derivatives the chemical shifts of ring protons between two substituents such as methyl, or one substituent and a bridgehead, was correlated with the corresponding deformation energy of the out-of-plane vibrations determined from the infrared absorptions.[334] By the use of dilute solutions in hexane, when magnetic shielding effects are restricted to those caused by electrons in individual molecules, the π-electron densities at ring positions were determined. As expected, positions 2 and 4 were found to be electron deficient and position 3, where the hydrogen had a lower deformation energy, had an electron excess.

Evidence for the existence of enamine forms of 2- and 4-methylquinolines has been deduced from their nmr spectra in $CDCl_3$, DMSO and trifluoroacetic acid (TFA).[335]

In the series of 2,4-bridged polymethylene substituted quinolines and their 3-chloro derivatives (**22**) and (**23**) (see Section I.3.H.e) the non-equivalence of the CH_2 hydrogens, particularly in the 3-chloro compounds, has been demonstrated from their ^1H-nmr spectra.[221]

The plane of the phenyl substituent of 1-phenylquinolinium salts has been shown to be predominantly at right-angles to the plane of the heterocyclic ring by the observed shielding effect on H-2 and on hydrogens of a 2-methyl group. In benzo[*f*]quinolines, H-4 and the hydrogens of a 4-methyl substituent, on the other hand, are deshielded by the benzosubstituent.[336]

From the numbers of quaternary and other carbon atoms deduced from the ^{13}C-nmr spectra of a number of metal complexes with N-donor ligands, and including 8-methylquinoline, the occurrence of cyclometalation has been deduced.[337] Unambiguous evidence of metal-carbon σ-bond formation was also obtained when metal–^{13}C coupling was observed.

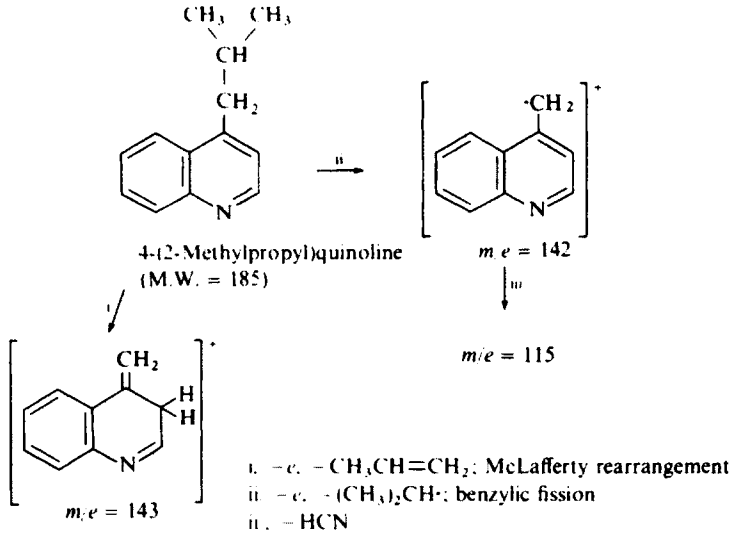
The solvent effects of hexane, acetone and benzene on the ^1H-nmr spectra of a series of dimethylquinolines and 7-ethylquinoline at 5 mol% have been determined and discussed.[338] The benzene-induced solvent shifts ($\Delta = \delta CCl_4 - \delta C_6H_6$ p.p.m.) of the ^1H resonances of quinoline and other heterocycles including methyl- and dimethylquinolines have been shown to accord with the orientation of the benzene solvent molecules by the solute dipoles. The shifts were found to be sufficiently characteristic in sign and magnitude to be useful in structure determinations. Methyl substituents cause a decrease in Δ relative to quinoline.[339]

ESR spectra of the negative ions of quinoline and some methylquinolines have been investigated in order to obtain information about hyperfine interaction of the aromatic ring nuclei. Spectra of the methyl derivatives were not analysed completely owing to the complexity of the spectra.[1633]

d. Mass Spectra The mass spectrometric examination of many alkylquinolines (and isoquinolines) has shown that azatropylium ion intermediates are formed in the pathway leading to the $[M-(H+HCN)]^+$ ion.[346] Studies of deuterium-labelled methylquinolines

indicated that all hydrogens were randomized prior to hydrogen loss and the formation of ring-expanded intermediate molecular ions was proposed to account for this;[350b] dimethylquinolines may give two possible ring expanded ions.[350a] Ring expansions involving methyl groups attached to the carbocyclic ring are favoured relative to expansions involving methyl groups on the heterocyclic ring.

Alkylquinolines having three or more carbons in the side-chains fragment by β-cleavage and McLafferty rearrangement. The relative amounts of these cleavages can be correlated with the electron density at the position of substitution. Alkyl chains at positions 4 and 8 undergo facile γ- and δ-cleavage probably because the resulting radicals can be stabilized by cyclization to the *peri*-position.[346] The fragmentation of methylquinolines, dimethylquinolines, ethylquinolines and propylquinolines and their deuterium-labelled analogues has been studied[347] and found to be closely related to that of the corresponding alkylbenzenes. Rearrangements of molecular ions appear to precede the fragmentation process of many compounds. The proximity of the heterocyclic nitrogen atom influences the fragmentation of 2- and 8-ethyl- and -propylquinolines.[347] A study of 4-(2-methylpropyl)quinoline did not reveal any *peri* interactions.[348] The base peak at $m/e = 143$ results from the McLafferty rearrangement, the peak at $m/e = 142$ from benzylic fission and that at $m/e = 115$ from the further loss of the elements of HCN (see Scheme 8).



SCHEME 8

The mass spectra of dihydrocyclopenta- and dihydrocyclobuta[*b*]quinolines[349] exhibit a prominent $(M-1)^+$ peak which is followed by loss of the elements of HCN, and the cyclobuta derivative shows a prominent 2-3-quinolyne fragment.[304]

The distribution of pyridine- and quinoline-type bases in petroleum distillates has been examined by mass spectrometric methods.[351]

H. Methods of Separation

a. Distillation, Crystallization and Counter-current Extraction As indicated in Section I.1, the main natural sources of quinoline bases are from coal tars and

crude petroleum, both of which are fractionated by distillation processes. The mixtures of bases are usually obtained from the appropriate fractions (b.p. 230–240 °C for quinoline itself or up to 300 °C for the alkylquinolines) by extraction with acids such as sulphuric, hydrochloric or phosphoric acid. The neutral and acidic components are completely removed by washing the acid extracts with hydrocarbon solvents and the bases are finally liberated with alkali such as 20% sodium hydroxide solution. Individual bases can then be isolated by crystallization of suitable salts such as phosphates, bisulphates, nitrates, picrates or complexes with urea, cresols or metal salts (e.g. $CuCl_2$). Counter-current liquid–liquid or liquid–solid partition methods can also be used. Final purification is usually by distillation at atmospheric or reduced pressure. The references in Table 1 give details of the many combinations of these procedures which have been used. Some further examples are given below.

As a result of the greater stability of its complex with urea, 2-methylquinoline has been isolated from mixtures of coal tar bases by treatment with urea.[355-357]

The relative solubilities of the phosphate and bisulphate salts have been investigated in connection with the separation of individual alkylquinolines from mixed coal tar bases.[358-363] Thus isoquinoline forms a readily water-soluble phosphate compared with those of 2-methylquinoline and quinoline[358,359] and the bisulphate of quinoline is more soluble in 85% ethanol at 10 °C than that of 2-methylquinoline by a factor of 3.8.[359] Although 4-methylquinoline could not be isolated from mixtures by the use of phosphoric acid alone,[364] a combination of phosphoric and sulphuric acids was successful.[363] 2-Methylquinoline has also been separated from mixtures of bases as its hydrochloride.[365]

Partition studies have been carried out, leading to the separation of alkylquinolines and other bases by counter-current extraction methods using cyclohexane or chloroform as the non-polar or weakly polar solvent and water or citrate–phosphate buffered solutions as the polar solvent.[366,367] Counter-current separations have also been investigated using the following solvent pairs: (I) dinitriles, $(NCAlk)_2X$, where X = O, S, NH or NR and Alk = any lower alkylene radical, e.g. $(NCCH_2CH_2)_2O$, and (II) any saturated hydrocarbon chosen on the basis of its boiling point.[368] Weakly polar solvents such as cyclohexane and chloroform have also been used to extract bases from strongly acidic solutions in sulphuric, hydrochloric, hydrobromic and perchloric acids.[369]

The formation of complexes with various esters of boric acid has been investigated for the separation of alkylquinolines,[370] and the purification of 2-methylquinoline has been achieved via the formation of a complex with *o*-cresol or some other 'tar acid' with a vacant *para*-position. The base is finally recovered by distillation of the complex which separates out on cooling to 10–25 °C.[371] Mixtures of alkylquinolines have been separated by oxidation to the 1-oxides followed by fractional distillation and recovery by reduction of the oxides with phosphorus trichloride.[372] The formation of insoluble salts with β-resorcylic acid by aliphatic and heterocyclic amines enables them to be separated from aromatic amines, most of which do not react. The β-resorcylates have sharp melting points (quinoline = 128 °C, 2-methylquinoline = 145 °C) which are suitable for identification purposes.[373] The purification of 4-methylquinoline to better than 99% by vacuum distillation has been reported.[1505] The formation of an easily purified solid 2 : 1 complex between the hydrochlorides of quinaldine or substituted quinaldines and zinc chloride has been used successfully to isolate the main product from Doebner–Von Miller syntheses of alkylquinolines.[1536]

b. Chromatographic Methods Most of the chromatographic methods have been used for the separation of alkylquinolines for purposes of purification and identification. In column chromatography alumina and silica gel are the usual stationary phases, used

in combination with a variety of solvent mixtures for elution. Pretreatment of silica gel with quinoline or phenanthroline is reputed to improve the adsorption characteristics for alkylquinolines.[374] An antimony microelectrode system has been used as a detector during the separation of quinoline bases after elution by non-conducting solvents from columns of alumina or $CaCO_3$.[375] Good separations of 2-methylquinoline, quinoline and isoquinoline have been achieved on chromatographic-grade alumina (activated at 160 °C for 6 h) with ether as eluent. The sequence of elution did not follow that of the pK_a values of the bases.[376] In a similar study using alumina treated with $CoCl_2$, 2-methylquinoline was eluted first by light petroleum followed by quinoline, while isoquinoline remained on the column.[377] Preparative liquid chromatography using acetonitrile–chloroform (1:9) as solvent followed by vacuum distillation has enabled commercial samples of 2-methylquinoline and 2,4-dimethylquinoline to be purified to better than 94% purity, and 8-methylquinoline was similarly purified to 99% purity using chloroform containing 1% of ethanol as solvent.[1505] Methylquinolines were separated by elution from γ-Al_2O_3 at 9–12 atm using dioxan–isooctane (5:95). The order of elution was dependent on the degree of steric hindrance of the substituents adjacent to the ring nitrogen atom.[1610,1611] A theoretical study of the extraction process based on a mathematical model has been published.[1612] Nitrogenous bases including alkylquinolines in heavy gas oil have been identified by a combination of column chromatography on alumina, followed by a two-step paper chromatographic technique employing toluene–methanol–water (1:10:1) and heptane saturated with methanol as developing solvents.[378] Paper electrophoresis was also used.[378] Molecular sieves [Type X zeolite, metalloaluminosilicates (British Patent 777,233), preferably CaNaAl silicate, pore size 10 Å] can be used for the separation of alkylquinolines and also pyridines and isoquinolines.[379]

There are many examples of the use of thin-layer chromatography (TLC) for the separation of alkylquinolines. Silica gel is the usual adsorbent and is used in conjunction with a variety of solvent mixtures for development.[380–387] Detection of the spots has been achieved with Dragendorff's reagent,[381,383,390] potassium permanganate,[381] iodine[382] and 2,4,7-trinitro-9-fluorenone[384] or by the use of a fluorescent indicator.[381] Quinolines substituted at position 8 are the least strongly adsorbed.[381]

Separations have also been made using paper chromatography,[388–396,1613] for example on Whatman No. 4 paper impregnated with an acetone solution of formamide containing various amounts of formic or citric acid. The solvents used included heptane, carbon tetrachloride and chloroform.[388,389] In another study,[390] twenty different water immiscible solvents were used. Reversed-phase chromatography has also been used with decalin, *m*-xylene or amylacetate as the organic phase with the aqueous phase buffered at pH 1.7–7.[391] As with TLC, 8-methylquinoline had a higher R_f value than the other methylquinolines.[394]

Gas chromatography has been used extensively for the separation and analysis of quinoline bases,[143,293,397–415,1617] and the use of the technique has been reviewed.[397] The method has proved valuable for the identification of the basic components of coal tars,[409–415] and by the direct injection of aqueous solutions to the study of water pollution involving heterocyclic compounds, including 2-methylquinoline.[1616] The principal materials used as stationary phases include in the non-polar category silicone elastomers SE-301, SE-52, DC-710, GESF-96, Igepal CO-880 and Apiezon L grease. More polar materials used are Reoplex 400, polyethylene glycol 400, polyethylene adipate, diglycerol and hexakis(cyanoethyl)melamine. The complexing property of 2,4,7-trinitrofluorenone[404] has been used, and also eutectic mixtures of inorganic salts.[406] The combined use of gas chromatography with infrared and nmr spectroscopy has also been described.[405] The formation of the pentafluoropropionic amide derivatives[407] has been used to identify the basic components in shale oil naphtha. In this method the

hydrochlorides of the bases are first hydrogenated using Adams catalyst and the resulting secondary amines treated with pentafluoropropionic anhydride.

Of the monomethylquinolines the 3-, 6- and 7-isomers are particularly difficult to separate.[143,403-405] As with alkylpyridines, compounds having substituents next to the heterocyclic nitrogen atom have shorter retention times on polar stationary phases than other compounds with comparable boiling points.[408] High-performance liquid chromatography (HPLC) has been used for the analysis of air samples in a study of environmental pollution. Among the compounds detected at limits of 0.2–0.25 ng per injection were *N*-heterocyclic bases including 2-methylquinoline. A Zipax support impregnated with silver was used on a 1-m column with a uv monitor.[416] A similar account of the use of HPLC and its application to the study of air pollution has been reported.[1615]

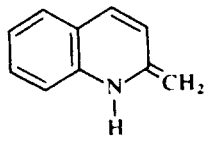
5. Chemical Properties and Reactions

Most of the reactions of alkyl- and aralkylquinolines can be attributed to the quinoline ring structure and have been discussed under that heading (see Part I, Chapter 1). The present account is limited to the reactions of the side-chains themselves or to the influences of the side-chains on the course of nuclear reactions.

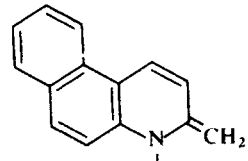
A. Isomerization and Dealkylation

When passed over alumina at 350 °C, 2-methylquinoline is partly converted into 4-methylquinoline.[418] Quinoline is converted by a glow discharge into an unsaturated open-chain nitrile, or into a polymer of the nitrile.[419] Under similar conditions, 2-methylquinoline behaves in a different manner and gives unidentified products. 1-Allylquinolinium salts having an α-alkyl substituent, on conversion to the anhydro base with alkali, are capable of isomerization by a Claisen-type rearrangement[212] to give a 2-alkenylquinoline (see Section I.3.H.a and equation 22). The aromatization of 2,2,4-trimethyl-1,2-dihydroquinoline on heating its hydrochloride salt (or in solution catalysed by di-*t*-butyl peroxide and β-naphthalenethiol) results in the migration of one of the methyl substituents[217] to other ring positions or to a side-chain (see Section I.3.H.c). In the Riehm synthesis of quinolines, however, similar 2,2-dialkyl-1,2-dihydroquinolines are aromatized by elimination of an alkane.[420,421]

In a study of tautomerism in 2-methyl-*N*-heterocycles by nmr spectroscopy,[335a] the evidence for the existence of the methylene structure (**29**) of 2-methylquinoline was assessed. The deprotonated 2- and 4-alkylquinolinium salts can be formulated as methylene bases; these are highly reactive enamines, but unlike the corresponding pyridine compounds they can usually be isolated, e.g. (**30**).[422]



29

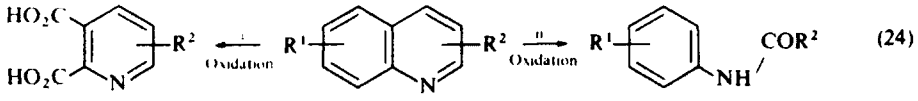


30

B. Oxidation

a. Oxidations Leading to Ring Opening Vigorous oxidation of quinoline and its derivatives usually results in ring opening, in which either or both rings may be

disrupted. Alternatively, under milder conditions, oxidation may be restricted to the substituents such as alkyl side-chains, or to the formation of an *N*-oxide. Ring opening can occur with potassium permanganate in neutral,[427] alkaline[424b,425,426,429] or acidic[428] solution, with nitric acid[1651] or by ozonolysis as described below. Chromic acid usually results in the oxidation of side-chains to the carboxylic acid stage. The carbocyclic ring is normally attacked in preference to the more electron-deficient heterocyclic ring, but electron-donating substituents, including alkyl groups, can increase the reactivity of either ring whereas electron-withdrawing substituents such as NO_2 have the opposite effect. Quinoline itself gives pyridine 2,3-dicarboxylic acid (quinolinic acid) as a result of the opening of the carbocyclic ring. Alkylquinolines having substituents in this ring[424b-429] or at position 4[424b,426] behave in a similar manner. With alkyl or aryl substituents at position 2, however, it is the heterocyclic ring that is opened preferentially[428,430] to give acyl- or aroylanthranilic acids (equation 24).

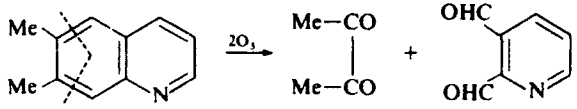


(24)

i, R^1 = H or alkyl, R^2 = H or 4-alkyl; ii, R^1 = H, R^2 = 2-alkyl or 2-aryl

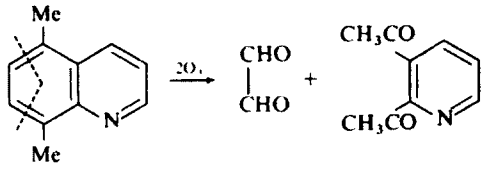
An alkyl substituent at position 3 may result in the opening of both rings to give oxalic acid, carbon dioxide and ammonia.[423,428,431b,432]

b. Ozonolysis The ozonolysis of quinoline homologues[433,434] follows a course similar to that for quinoline itself. The main reaction is an attack on the carbocyclic ring to form a monoozonide, which is rapidly converted to the (5,6-),(7,8)-diozonide, which in turn reacts slowly to form the (3,4),(4a,8a),(5,6),(7,8)-tetraozonide. A slower initial attack at the 3,4-bond of the heterocyclic ring leads to the same product, but there is no evidence for addition of ozone to the 2,3- or 6,7-bonds which have less double-bond character or to the C=N bond.[434] Boer and Wibaut's ozonolyses[433] were carried out at −30 to −40 °C with a controlled supply of ozonized oxygen; the results can be summarized as follows for 6,7-, 5,8- and 2,3-dimethylquinolines (see equations 25, 26 and 28, respectively).



(25)

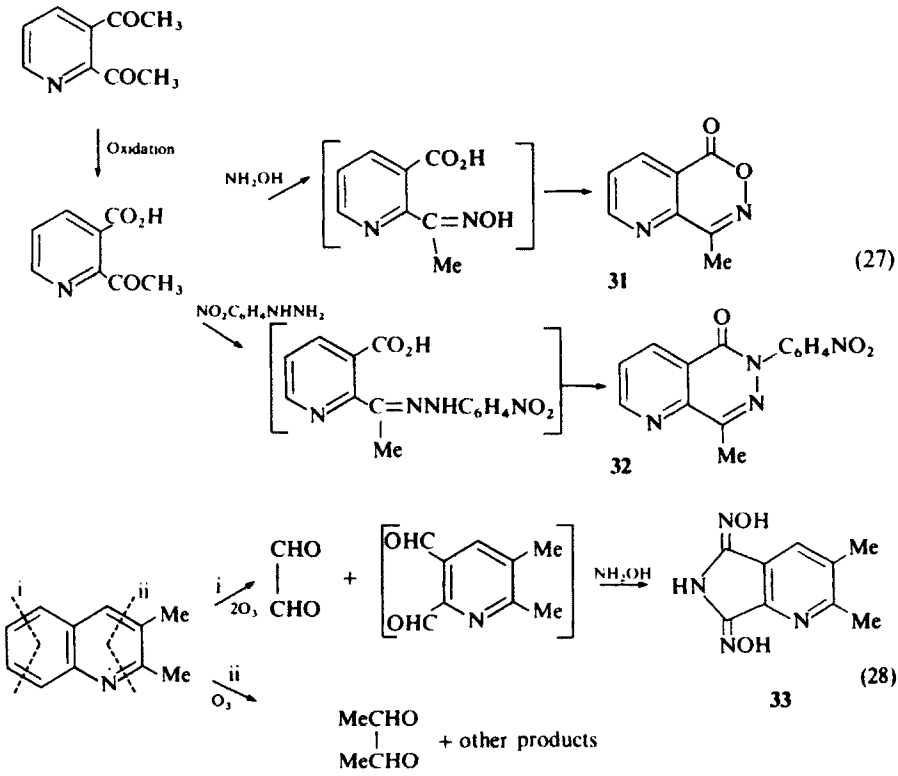
The pyridine 2,3-dicarbaldehyde (2%) was isolated as its bis-*p*-nitrophenylhydrazone and the dimethylglyoxal (13%) as its dioxime and as the bis-*p*-nitrophenylhydrazone.



(26)

The glyoxal was isolated as its dioxime (8%) and also as the bis-*p*-nitrophenylhydrazone (12%). The 2,3-diacetylpyridine was not isolated as such, but its formation as

the primary ozonolysis product was inferred from the isolation of derivatives (**31**) and (**32**) of 2-acetylpyridine-3-carboxylic acid formed from the diacetyl pyridine by oxidation (equation 27).



The product from the ozonolysis of 2,3-dimethylquinoline after treatment with hydroxylamine was shown by infrared analysis to contain a mixture of the dioximes of glyoxal and dimethylglyoxal and a compound $C_9H_{10}O_2N_4$, which was considered to be (**33**), derived from 2,3-dimethylpyridine-5,6-dicarbaldehyde. The dioxime of dimethylglyoxal was considered to have been formed in a secondary reaction in which the heterocyclic ring was attacked by ozone at the 3,4-bond to form a monoozonide.

Under less vigorous conditions the quinoline ring structure remains intact but alkyl side-chains can be oxidized either to hydroxycarbonyl (carboxylic acid) groups or to an intermediate carbonyl state in which methyl groups become formyl (aldehyde) and higher alkyl groups may give quinolyl alkyl ketones. With peracids such as an acetic acid and hydrogen peroxide mixture (peracetic acid) *N*-oxides are formed, a reaction characteristic of quinoline itself and other tertiary amines.

c. Oxidation of Side-chains Alkylquinolines can be oxidized to quinoline carboxylic acids by a variety of reagents, of which chromic acid or potassium dichromate in sulphuric acid are the most widely used. The latter is reported[435] to be the more effective as a result of catalysis by the potassium bisulphate present; it is also effective for oxidizing ethyl substituents on the carbocyclic ring to the methyl quinolyl ketones. Other

oxidizing agents which have been used successfully include potassium permanganate[438] (preferably neutral or in acidic solution), manganese dioxide,[439,440] nitric acid and oxides of nitrogen,[441-443] hydrogen peroxide on a $PdCl_2$ complex of the base[436] and air or oxygen[444] with or without a catalyst. Catalysts used for air oxidation are V_2O_5, $V_2O_5MoO_3$, $Ca(VO_3)_2$, $Cd(VO_3)_2$ and $Cd(VO_3)_2$ on pumice.[437] In the absence of the $PdCl_2$ complex, hydrogen peroxide gives the *N*-oxide.

The results obtained by these methods are listed in Table 20, from which it will be seen that alkyl groups attached to the carbocyclic ring, particularly at position 8, are more readily oxidized than those attached to the heterocyclic ring, where substituents at position 2 are the most difficult to oxidize. Higher yields of 8-carboxylic acids containing other alkyl substituents can be obtained by using an excess of the alkylquinoline, which can be recovered and recycled.[435]

TABLE 20. Products Obtained by the Oxidation of Alkylquinolines to Carboxylic Acids and Alkyl Quinolyl Ketones

Alkyl-quinoline	Reagent	Product (quinoline substituents)	Reference
2-Me	$K_2Cr_2O_7$, H_2SO_4 (dil.)	2-CO_2H	432
	CrO_3, H_2SO_4 (dil.) (4–5 days)	2-CO_2H	459
	Air, or air + V_2O_5 or other catalyst	2-CO_2H + 2-CHO	437
	O_2 + alkali (aqueous), 100–275 °C 20–100 kg cm^{-2}	2-CO_2H	444
3-Me	CrO_3, H_2SO_4 (dil.)	3-CO_2H	431b, 445
4-Me	CrO_3, H_2SO_4	4-CO_2H	426, 446
5-Me	CrO_3, H_2SO_4 (dil.), 150 °C (sealed tube)	5-CO_2H	447, 448
6-Me	$KMnO_4$, H_2SO_4 or CH_3CO_2H	6-CO_2H	438
7-Me	CrO_3, H_2SO_4 (dil.), 150 °C (sealed tube)	7-CO_2H	449
	CrO_3, H_2SO_4 (42%)	7-CO_2H	450
2-Et	CrO_3, H_2SO_4	2-CO_2H	172
3-Et	CrO_3, H_2SO_4 (dil.)	3-CO_2H	452
4-Et	CrO_3, H_2SO_4 (dil.)	4-CO_2H	172, 174, 173
8-Et	$K_2Cr_2O_7$, H_2SO_4	8-CO_2H (40%) + 8-$COCH_3$ (40%)	435
2,3-Me_2	CrO_3, H_2SO_4	2-Me, 3-CO_2H	455
2,4-Me_2	CrO_3, H_2SO_4	2-Me, 4-CO_2H	429, 456
2,5-Me_2	CrO_3, H_2SO_4	2-Me, 5-CO_2H	459, 90
	HNO_3	2-Me, 5-CO_2H (3.2%)	442
2,6-Me_2	CrO_3, H_2SO_4	2-Me, 6-CO_2H	90
2,8-Me_2	CrO_3, H_2SO_4 (4–5 days)	2-Me, 8-CO_2H	90
3,4-Me_2	CrO_3, H_2SO_4	3-Me, 4-CO_2H	90
3,7-Me_2	CrO_3, H_2SO_4 (50%), reflux	3,7-$(CO_2H)_2$	445

TABLE 20 (*cont.*)

Alkyl-quinoline	Reagent	Product (quinoline substituents)	Reference
4,6-Me_2	CrO_3, H_2SO_4 (boiling)	4-Me, 6-CO_2H	90
5,8-Me_2	HNO_3 (22%), 170 °C	8-Me, 5-CO_2H (*sic*)	443
2-Me, 4-Et	CrO_3, H_2SO_4 (dil.) (boiling)	2-Me, 4-CO_2H	193
2-Me, 6-Et	CrO_3, H_2SO_4 (100 °C)	2-Me, 6-CO_2H	460
2-Me, 6-Et	$K_2Cr_2O_7$, H_2SO_4	2-Me, 6-$COCH_3$ (75%)	435
2-Me, 8-Et	$K_2Cr_2O_7$, H_2SO_4	2-Me, 8-$COCH_3$ (75%)	435
3-Me, 2-Et	CrO_3, H_2SO_4	3-Me, 2-CO_2H	431b, 458
3-Me, 8-Et	$K_2Cr_2O_7$, H_2SO_4	3-Me, 8-$COCH_3$ (75%)	435
5-Me, 2-Ph	CrO_3, H_2SO_4	2-Ph, 5-CO_2H	450
3-Et, 2-Pr	CrO_3, H_2SO_4	3-Et, 2-CO_2H	156
3-Pr^i, 2-Bu^i	CrO_3, H_2SO_4	3-Pr^i, 2-CO_2H	454
2,3,6-Me_3	CrO_3, H_2SO_4 (dil.)	2,3-Me_2, 6-CO_2H	90
2,3,8-Me_3	CrO_3, H_2SO_4	2,3-Me_2, 8-CO_2H (85%)	435
2,6,8-Me_3	CrO_3, H_2SO_4 (dil.)	2,8-Me_2, 6-CO_2H	451
2,3-Me_2, 8-Et	CrO_3, H_2SO_4	2,3-Me_2, 8-CO_2H (56%) + 2,3-Me_2, 8-$COCH_3$ (12%)	435
2,3-Me_2, 8-Et	$K_2Cr_2O_7$, H_2SO_4	2,3-Me_2, 8-CO_2H (50%) Recovered base (50%)	435
2,4-Me_2, 6-Et	$K_2Cr_2O_7$, H_2SO_4	2,4-Me_2, 6-$COCH_3$ (30%) Recovered base (60%)	435
2,4-Me_2, 8-Et	CrO_3, H_2SO_4	2,4-Me_2, 8-$COCH_3$ (36%)	435
2,4-Me_2, 8-Et	$K_2Cr_2O_7$, H_2SO_4	2,4-Me_2, 8-CO_2H (30%) Recovered base (60%)	435
3,6-Me_2, 2-Et	CrO_3, H_2SO_4 (dil., hot)	6-Me, 2-Et, 3-CO_2H + 6-Me, 2-Et, 3-CHO	453
3,8-Me_2, 2-Et	CrO_3, H_2SO_4 (conc.)	3-Me, 2-Et, 8-CO_2H	90
2,3-Me_2, 8-Pr	CrO_3, H_2SO_4	2,3-Me_2, 8-CO_2H (83%)	435
2-Me,3,8-Et_2	$K_2Cr_2O_7$, H_2SO_4	2-Me, 3-Et, 8-CO_2H (10%) + 2-Me, 3-Et, 8-$COCH_3$ (55%)	435
3-Me, 2,6-Et_2	$K_2Cr_2O_7$, H_2SO_4	3-Me, 2-Et, 6-$COCH_3$ (85%)	435
2,3,4,8-Me_4	CrO_3, H_2SO_4	2,3,4-Me_3, 8-CO_2H (86%)	435
3,6,8-Me_3, 2-Et	CrO_3, H_2SO_4	3,6-Me_2, 2-Et, 8-CO_2H	90
2,3,4-Me_3, 8-Et	$K_2Cr_2O_7$, H_2SO_4	2,3,4-Me_3, 8-$COCH_3$ (50%) + 2,3,4-Me_3, 8-CO_2H (25%)	435
Various Me	MnO_2	CO_2H	439
Various Alkyl	MnO_2, H_2SO_4	CO_2H	440, 457
2-Me	$PdCl_2$ complex + H_2O_2	2-CO_2H	436
3-Me	$PdCl_2$ complex + H_2O_2	3-CO_2H	436
4-Me	$PdCl_2$ complex + H_2O_2	4-CO_2H	436

TABLE 20 (*cont.*)

Alkyl-quinoline	Reagent	Product (quinoline substituents)	Reference
4-Me	$KMnO_4$	4-CO_2H [(21%)]	1288
3-Me-2-Ph	CrO_3, MnO_2, H_2SO_4 (30%)	2-Ph-3-CO_2H (66%)	1287
8-Me-2-Ph	$K_2Cr_2O_7$, H_2SO_4	2-Ph-8-CO_2H	1286
2-*p*-Tolyl	CrO_3, MnO_2, H_2SO_4 (40%)	2-$C_6H_4CO_2H$(*p*) (70%)	1287
	CrO_3, AcOH	2-$C_6H_4CO_2H$(*p*) (70%)	1178

d. Oxidation of Methyl Substituents to Aldehydes Methylquinolines can be oxidized to the intermediate aldehyde stage by selenium dioxide[460-478] or by catalytic vapour-phase methods.[159,479,480] Selenium dioxide is the reagent most frequently used, with *m*-xylene or dioxan as solvent. Further oxidation to the carboxylic acids to various extents has been reported,[465,466,471,473,476] bimolecular products of the quinaldoin or quinaldil type are sometimes formed[469,470,475] and one report describes the quantitative conversion of 4-methylquinoline by selenium dioxide to 1,2-bis(4-quinolyl)ethene.[1091] In the course of the reaction the selenium dioxide is reduced to selenium, which is removed by filtration. The aldehydes can be separated by steam distillation and purified as their bisulphite addition compounds.[460]

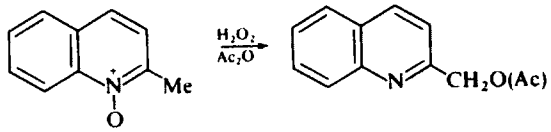
The preparation of the reagent appears to be an important factor. Kaplan[469] emphasizes that the selenium dioxide used should be freshly prepared and sublimed. A particularly reactive form of the oxide can be prepared by treatment with benzoic anhydride and hydrolysis of the dibenzoyloxyselenium dioxide ($C_{14}H_{10}O_5Se$) formed, by passing moist air through its solution in benzene. The precipitated selenium dioxide so formed is reported to oxidize 2-methylquinoline at room temperature.[468]

In contrast to the reaction with chromic acid, methyl groups at position 2 of the quinoline ring are the most easily oxidized by selenium dioxide, and this property enables the 2-aldehyde to be prepared with other alkyl groups unaffected.[472-474,476,477] A methyl group at position 3 is particularly resistant to oxidation[467] and, apart from this substituent, methyl groups at all the other positions have been converted to aldehyde by selenium dioxide.[460-466,478] 3-Methylquinoline, however, has been reported to react violently with selenium dioxide at 130 °C and on heating for 10 min at 260–270 °C 41% of the aldehyde was formed.[1070] 2-Methylquinoline, 4-methylquinoline and their 1-oxides have also been converted to the aldehydes in about 33% yields by treatment with sodium, a small amount of iron(III) chloride and amyl nitrite in liquid ammonia.[1634]

In the gas phase, methylquinolines have been oxidized by passing a mixture of steam, air and the methylquinoline over MoO_3 catalyst at 250–450 °C.[480,159] Using air and a V_2O_5–MoO_3–WO_3 catalyst at 450–480 °C quinaldoin was formed from 2-methylquinoline.[479]

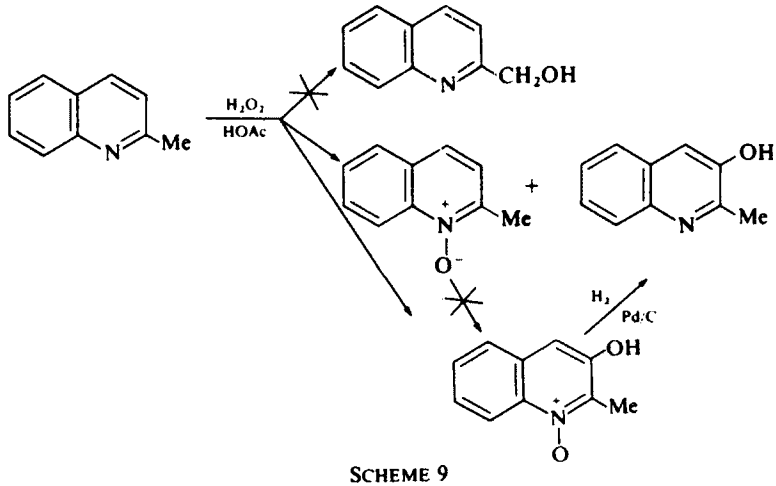
e. Dehydrogenation of Tetrahydroacridines 1,2,3,4-Tetrahydroacridine has been dehydrogenated to acridine by distillation with litharge in a current of carbon dioxide,[481] and when heated in a stream of hydrogen with palladized charcoal it is converted into 9,10-dihydroacridine (56%) and acridine (17%).[483] On heating for 20 min at 250 °C with palladized charcoal 4-phenyl-5,6,7,8-tetrahydroacridine gave 4-phenylacridine (61%).[482]

f. OXIDATION TO *N*-OXIDES When oxidized with peracids (usually hydrogen peroxide and glacial acetic acid as a convenient form of peracetic acid), alkylquinolines are converted to the *N*-oxides, although the presence of alkyl substituents may result in additional side-reactions. Further oxidation of 2-methylquinoline *N*-oxide with hydrogen peroxide followed by acetic anhydride was reported to give the acetate ester of 2-quinolylmethanol in 57% yield[484] (equation 29).



(29)

The conversion of 2-methylquinoline to the *N*-oxide with hydrogen peroxide and acetic acid has also been reported to be accompanied by the formation of small amounts of 3-hydroxy-2-methylquinoline and its *N*-oxide, but no 2-hydroxymethylquinoline could be detected.[485] The 3-hydroxy-2-methylquinoline-1-oxide was readily reduced to 3-hydroxy-2-methylquinoline with hydrogen and Pd/C but it could not be prepared directly from 2-methylquinoline-1-oxide. It was therefore assumed that it was formed directly from 2-methylquinoline (see Scheme 9).



SCHEME 9

The preparation of 4-methylquinoline-1-oxide by the action of hydrogen peroxide and acetic acid is accompanied by the formation of a small amount of 3-hydroxy-4-methyl-2-(1*H*)-quinolone.[486] Quinoline-1-oxides are oxidized by lead tetraacetate to quinoline-hydroxamic acids [derivatives of 1-hydroxy-2-(1*H*)-quinolone], and in the course of this investigation it was reported that quinolines with an 8-methyl substituent could not be oxidized to 1-oxides with hydrogen peroxide and acetic acid.[487,1124,1125] However, in a previous paper it was reported that the main product from this oxidation is 3-hydroxy-8-methylquinoline and that 8% of the 1-oxide is also formed.[488] Nitration of 2-methylquinoline-1-oxide gives a good yield (73.5%) of 2-methyl-4-nitroquinoline-1-oxide.[489] 2-Methylquinoline can be oxidized to the 1-oxide with *t*-amyl hydroperoxide in the presence of $MoCl_5$ in 95–100% yield. The method is claimed to be superior to the peracid route.[490]

g. MISCELLANEOUS OXIDATION REACTIONS Photochemical oxidations of alkyl- and mixed alkylarylquinolines have been reported in which the alkyl, but not the aryl, groups were converted in low yields (3–8%) to the carboxylic acid group.[491,492] In the organism of the dog quinolines were oxidized by opening the carbocyclic ring to give a pyridine derivative, but with 2-methylquinoline the heterocyclic ring was opened to give *N*-acetylanthranilic acid.[493] 8-Methylquinoline can be oxidized at pH 7 to 2-hydroxy-8-methylquinoline by dehydrogenase obtained from rabbit liver.[494]

When heated with degassed rhodium on carbon at their boiling points, quinoline and 6-methyl-, 7-methyl-, 4-phenyl- and 4-benzylquinolines gave 2,2'-biaryls in 15–50% yields. The methylquinolines also underwent demethylation and 2-methylquinoline also formed bis-2-quinolylmethane, tris-2-quinolylmethane and 1,2-bis-2-quinolylethane.[1072]

C. Reduction

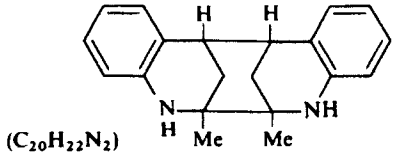
Quinoline and the alkylquinolines can be reduced by a variety of methods. One important method already discussed (see Section I.3.C.a) is the formation of 2-alkyl(or 2-aryl)-1,2-dihydroquinolines by the hydrolysis of the addition products formed by the action of organolithium reagents or Grignard reagents.[122–125,201] Other methods widely used include electrolytic reduction, catalytic hydrogenation and chemical reagents such as sodium metal and alcohol, tin or zinc with acids, lithium aluminium hydride, sodium borohydride and dialkylaluminium hydrides. The products formed may consist of dihydroquinolines or their dimers or polymers, tetrahydroquinolines, of which 1,2,3,4-tetrahydroquinolines (or Py-tetrahydroquinolines) and 5,6,7,8-tetrahydroquinolines (or Bz-tetrahydroquinolines) are the most important, decahydroquinolines and, under drastic conditions, products of ring-opening reactions. Hexahydro derivatives of 7-methyl and 8-methylquinoline have also been reported[498] and stereoisomers of many of the products have been isolated. The extensive literature on this subject has been reviewed in connection with the reduction of quinoline itself (see Part I, Chapter 1, Section IV.1), but the presence of alkyl substituents can influence the course of the reaction and the stability of the products formed.

a. DIHYDROALKYLQUINOLINES The 1,2-dihydroquinolines have been studied most extensively, although 1,4- and 5,8-isomers have been recorded. The following 1,2-dihydromethylquinolines were prepared in high yields by the reduction of the methylquinolines with lithium aluminium hydride:[499] 4-methyl-, 94%, m.p. 58 °C; 1-methyl, 30%, b.p. 118 °C (10 mmHg); 3-methyl-, 94%, m.p. 87 °C; 6-methyl-, 89%, m.p. 61 °C; 7-methyl-, 91%, m.p. 75 °C and 8-methyl, 72%, oil. The action of diethyl- and diisobutylaluminium hydride (R_2AlH) on quinoline or 2-methyl- or 4-methylquinoline in dry air-free benzene under argon at temperatures below 100 °C gave the 1,2-dihydro-derivatives.[500] The reaction with quinoline was carried out at 0–10 °C, with 4-methylquinoline at 40 °C and with 2-methylquinoline at 60–70 °C. Above 100 °C (e.g. at 130–160 °C) ring opening of the heterocyclic ring occurs to give the appropriate *o*-alkylanilines (see Section I.5.D). The reduction of quaternary alkylquinolinium salts by lithium aluminium hydride and sodium borohydride has been shown by Elderfield and Wark[525] to result in the formation of mixtures of the 1,2-dihydro- and 1,2,3,4-tetrahydroalkylquinolines with the dihydro compound predominating. The exact ratios of the two products were dependent on the reaction temperature, the solvent and the nature of the anion (Cl^-, Br^-, I^- or HSO_4^-).

Reductive alkylation of quinoline and 2-, 3-, 4- and 8-methylquinolines has been reported by the action of alkylating agents (e.g. Me_2SO_4) with lithium in liquid ammonia to give yields (~88%) of 1-alkyl-1,4-dihydroquinolines.[1631]

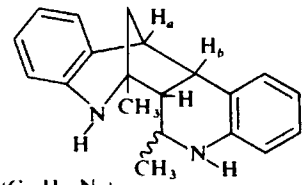
In a study of the electrolytic reduction of 2-methylquinoline in acidic solution, Levchenko[501b] obtained a trimer of a 2-methyldihydroquinoline (23.8%) previously obtained by Ahrens[502] together with a smaller yield (7.1%) of a dimer of 2-methyldihydroquinoline ($C_{20}H_{22}N_2$) (m.p. 177–178 °C) previously obtained by Heller and Sourlis[503] by reduction with zinc and hydrochloric acid. In a later study using a mercury cathode with continuous renewal of the mercury surface, 2-methylquinoline under both acidic and alkaline conditions was found to give 2-methyl-1,2-dihydroquinoline (monomer) in 55–60% yield together with trace amounts of a 2-methyltetrahydroquinoline.[504a] 8-Methylquinoline under similar conditions gave 8-methyl-1,2-dihydroquinoline (70%). Further examination of the product from the electrolytic reduction in alkaline medium[504b] led to the isolation of a dimeric methyldihydroquinoline (up to 12.6%), m.p. 119–120 °C, different from that described by Heller and Sourlis,[503] which had also been obtained electrolytically in acidic conditions.[501b] The main product in this case was a white amorphous material (42.7%) similar to Ahren's trimer.[502] Similar electrolytic reductions of 4-methylquinoline, in both acidic[505a] and alkaline[505b] media, with a mercury cathode having a continuously renewed surface gave a dimer of a 4-methyldihydroquinoline, m.p. 279 °C (7.6%). This dimer could not be obtained by reduction with tin and hydrochloric acid, which gave 1% of a dimer, m.p. 187 °C.[506] Chemical reduction of 4-methylquinoline in alkaline solution with sodium or potassium amalgam gave a 4-methyldihydrolepidine dimer (6.7%, m.p. not given), together with oxygenated products.[506]

On the basis of its infrared, ultraviolet and particularly its ^{1}H-nmr spectrum, the structure of Heller and Sourlis's dimeric 2-methyl-1,2-dihydroquinoline prepared in this case by a slightly modified method (m.p. 183.5–184 °C) was believed to be that shown in (**34**),[507a] which is consistent with an unsplit methyl proton signal at 8.82τ, a doublet–quartet pattern [7.15–7.93, 8.13, (8.80), 9.00τ] assignable to two ABX groups,



($C_{20}H_{22}N_2$)

34



($C_{20}H_{22}N_2$)

35

the NH proton signal at 6.27τ and the aromatic proton multiplet at 2.55–3.63τ. This structure has since been confirmed,[508a] and with the additional use of dipole moment measurements and Dreiding models to calculate theoretical moments by vector addition, it has been assigned the head-to-head *trans*-configuration. The isomer prepared by electrolysis at the mercury cathode has been assigned structure (**35**) with an *endo*-configuration from the application of the Karplus equation to the coupling constants of H_a and H_b of formula (**35**). A later paper described an X-ray crystallographic study of this dimer obtained by catalytic reduction of the product ($C_{20}H_{20}N_2$) formed by the electrolytic reduction of quinaldine at a mercury cathode in a strongly alkaline medium[508b] (see also Section I.5.H).

The electrochemical reduction and alkylation of quinoline in liquid ammonia has also been investigated and differences in the nature of the products from those of chemical reduction were discussed.[839]

b. TETRAHYDROALKYLQUINOLINES Quinoline compounds can be reduced to tetrahydro derivatives by controlled catalytic hydrogenation or by reducing agents such as

sodium and alcohol or by tin or zinc and acids. More vigorous conditions in the catalytic process, e.g. higher temperatures and hydrogen pressures, result in the formation of progressively more decahydro products[509,510] or of the products of ring opening.[511,512] In unsubstituted quinoline it is normally the more electron-deficient heterocyclic ring that is attacked preferentially by nucleophilic reducing agents, although high yields of the 5,6,7,8-tetrahydro derivatives have been reported by hydrogenation with PtO_2 catalyst from quinoline and from 2-, 3-, 6- and 8-methylquinolines and 2-isopropylquinoline[513] and by reduction with hydrogen iodide of quinoline, 2- and 8-methylquinolines and 2,4-, 2,6-, 2,7- and 2,8-dimethylquinolines and 2,4,6-, 2,4,7- and 2,4,8-trimethylquinolines.[498] 3,6-Dimethylquinolinium chloride was also reduced with hydrogen and a platinum catalyst at 50 lb in^{-2} to 5,6,7,8-tetrahydro-3,6-dimethylquinoline.[1519]

The electron-donating character of alkyl substituents, however, does result in the deactivation towards chemical reducing agents of the ring to which they are attached, so that alkylquinolines substituted in the carbocyclic ring may be reduced almost exclusively to 1,2,3,4-tetrahydroquinolines (Py-tetrahydroquinolines), whereas alkyl substitution of the heterocyclic ring leads to increased formation of 5,6,7,8-tetrahydroquinolines (Bz-tetrahydroquinolines). Alkyl substituents at positions 3 and 4 on the heterocyclic ring are more effective in this respect than those at position 2. These influences can be seen from Table 21, which gives the results of catalytic hydrogenations by Von Braun and coworkers[514–516] with a nickel catalyst.

The results of other reductions giving 1,2,3,4-tetrahydroalkylquinolines are listed in Table 22.

TABLE 21. Effect of Alkyl Substituents on the Relative Extents of Reduction of the Heterocyclic and Carbocyclic Rings of Substituted Quinolines Using a Reduced Ni catalyst with no Solvent or with decalin or tetralin[514,516]

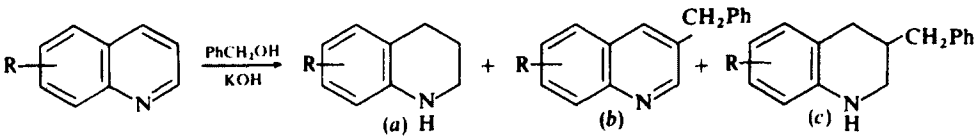
Quinoline substituents	Temperature (°C)	1,2,3,4-Tetrahydro-derivative (%)	5,6,7,8-Tetrahydro-derivative (%)
None	210	100.0	0.0
2-Me	110–150	96.0	4.0
3-Me	190	66.7	33.3
4-Me	160	66.7	33.3
6-Me	120	100.0	0.0
7-Me	150	100.0	0.0
8-Me	120	100.0	0.0
3-Et	180–190	67.0	33.0
2-Pr	170	65.0	35.0
3-Pentyl	180–190	50.0	50.0
2,3-Me_2	156	56.0	44.0
2,4-Me_2	140	20.0	80.0
2,6-Me_2	105	98.5	1.5
2,3,4-Me_3	155–160	—	>80.0
2,4,5,8-Me_4	160–170	96.0	4.0
2,3-Me_2-7,8-$(CH_2)_4$	—	100.0	0.0
2-Ph	150	100	0.0
3-Ph	160	67.0	33.0
2-Me-4-Ph	170–180	16.0	84.0
2,3-CH_2CH_2-	—	51.0	49.0
2,3-CH_2-CH_2-CH_2-	—	52.0	48.0

TABLE 22. Reduction of Alkylquinolines to the 1,2,3,4-Tetrahydro Derivatives

Reagent	Alkylquinoline substituents	Refs.	Reagent	Alkylquinoline substituents	Refs.
Sn, HCl	2-Me	459	Na, EtOH	2-Me	536
	4-Me	528		6-Me	523
	6-Me	529		2,3-Me_2	517a, 537–538
	7-Me	530, 535		2,4-Me_2	255, 517b, 537–539
	8-Me	529, 531		3,4-Me_2	517b, 539
	2,3-Me_2	517a		5,7-Me_2	520
	2,4-Me_2	517b		6,8-Me_2	86, 87
	2,6-Me_2	521, 459		2,6,8-Me_3	183
	2,8-Me_2	521, 459		2,4,6-Me_3	543
	3,4-Me_2	517b		Various 2-alkyl	123
	5,8-Me_2	532			
	6,8-Me_2	529	Formic acid[a]	6-Me	527
	2-Pr	533		8-Me	527
	3-Me-2-Et	458		2,4-Me_2	527
	2,6,8-Me_3	451			
	5,6,8-Me_3	534	Ni, NaOH	2-Me	519
	3,6-Me_2-2-Et	453			
	3,8-Me_2-2-Et	453	Raney Ni, 180°C, pressure	2-Me	526
	3,6,8-Me_3-2-Et	90		6-Me	540, 541
	2-Bu^t	187, 99			
			Ni, Pt, or Ag on pumice (gas phase)	6-Me	522
Pt black, CH_3CO_2H	2-Cyclohexyl	160			
			Raney Ni, 10% NaOH, EtOH	7-Me	518
Zn, HCl	7-Me	535			
	2,3-Me_2	517a			
	2,4-Me_2	517b	Electrolytic	2-Me	542
	2-Et	172		3,4-Me_2	517b

[a] 1-Formyl-1,2,3,4-tetrahydroalkylquinoline formed, which gives the tetrahydro derivative quantitatively on acid hydrolysis.

Attempts to effect benzylation of the heterocyclic ring at position 3 of 6- and 8-methyl- and -phenylquinolines[544] resulted in reduction in addition to as benzylation (see Scheme 10).



		(a)	(b)	(c)
Yields (%):	R = 6-Me	10	19	26
	R = 8-Me	14	34	3
	R = 6-Ph	—	5	43
	R = 8-Ph	17	20	17

SCHEME 10

The oxidation of 2-methyl-1,2,3,4-tetrahydroquinoline with hydrogen peroxide and acetic acid did not give the 1-oxide but resulted in dehydrogenation to 2-methylquinoline followed by oxidation to 2-methylquinoline-1-oxide.[545]

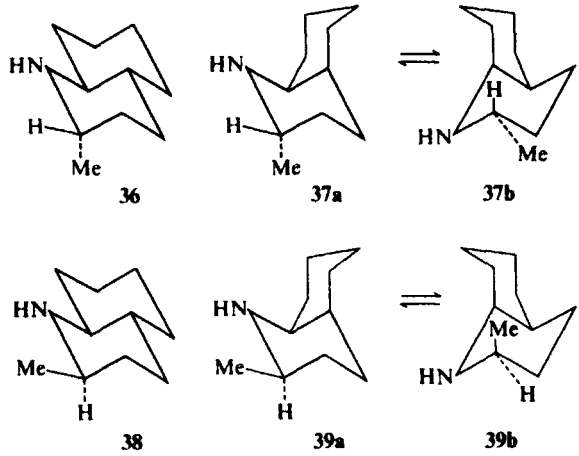
The reduction of 3,4-dimethylquinoline with tin and hydrochloric acid, sodium and ethanol, zinc and ethanolic hydrochloric acid or electrolytically gave only one form of 3,4-dimethyl-1,2,3,4-tetrahydroquinoline, but similar reductions of 2,4-dimethylquinoline gave both geometrical isomers of the tetrahydro derivative but in varying proportions depending on the reducing agent.[517b]

A one-step reduction–alkylation of quinolines (and isoquinolines) with sodium borohydride–RCO_2H mixtures has been reported.[1626] Quinoline gave 1-(CH_2R)-1,2,3,4-tetrahydroquinoline (where R = H, Me, Et and F_3C) in 17–79% yields; 2- and 4-methylquinoline were similarly reduced and alkylated on the nitrogen atom. With sodium borohydride and acetic acid in acetone quinoline gave 1-isopropyl-1,2,3,4-tetrahydroquinoline as the main product. $NaBH_3CN$ in acetic acid gave tetrahydro derivatives without alkylation.

c. DECAHYDROALKYLQUINOLINES The four racemic stereoisomers of decahydroquinaldine (**36**) to (**39**) have been prepared by the Wolff–Kishner, Huang–Minlon reduction of the α- and β-isomers of 2-methyl-4-oxodecahydroquinoline.[546] their conformations were assigned by the Auwers–Skita rule and from considerations of their infrared and nmr spectra. It was found that hydrogenation of quinaldine on a nickel catalyst gave 16% of (**36**), 46% of (**38**) and 34% of (**39a**⇌**39b**). The *N*-methyl derivatives of all of the stereoisomers were also prepared by the action of aqueous formaldehyde and formic acid on the bases at 100 °C.

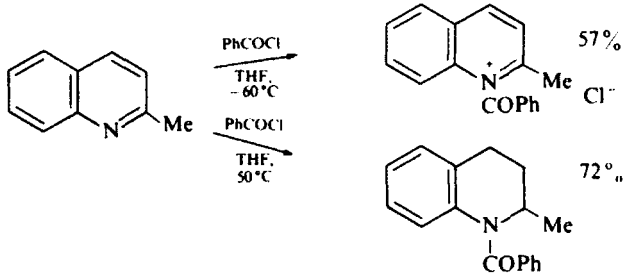
In a conformational study of decahydroquinolines,[1504] the ^{13}C nmr spectra of *cis*-decahydroquinoline and its epimeric 3-, 6- and 8-methyl derivatives, the 10-methyl derivative and the 3α,10-, 3β,10- and 8α,10-dimethyl derivatives and the corresponding 1-methyl derivatives have been recorded. The study included detailed accounts of the catalytic hydrogenation (using Pt and Raney Ni catalysts) of quinoline itself, and 3-, 6- and 8-methylquinoline and some partly hydrogenated intermediates to the decahydro-state.

In a similar study the preferred conformations of fourteen C-2, C-3, C-4, C-4a and C-8a substituted *cis*- and *trans*-methyldecahydroquinolines were established by variable-



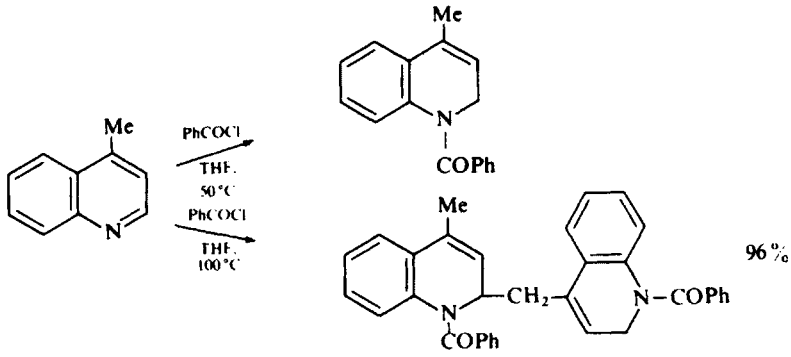
temperature ^{13}C and ^{1}H nmr spectroscopy. The conformational preference for the equatorial position of a C-4 methyl substituent of *cis*-decahydroquinoline approximates to that of a methyl group of cyclohexane but the equatorial preference of a C-2 or C-8a methyl substituent is greater. Full details were included of the reduction of the various methylquinolines to decahydro derivatives and the proportions and conformations of the products obtained.[1638] In general, the fully hydrogenated alkyl quinolines can be prepared by vigorous hydrogenation of the aromatic bases[526,547,1504,1638,1650] and also by further reduction of the 5,6,7,8-tetrahydroalkylquinolines with sodium and alcohol.[498,515,516]

d. Miscellaneous Reductions Catalytic hydrogenation of 1,2,3,4-tetrahydroacridine in methanol at room temperature with a Pd–Pt–C catalyst gave a high yield of the 1,2,3,4,4a,9,9a,10-octahydroacridine, although quinoline and some simple alkylquinolines were not reduced under these conditions.[551] Earlier examples of the reduction of tetrahydroacridines have been reported.[548-550] The action of benzoyl chloride in tetrahydrofuran on 2- and 4-methylquinolines formed quaternary salts initially but gave reduction products or dimers at temperatures of 50–100 °C, as shown in equations (**30a**) and (**30b**).[553]



(30a)

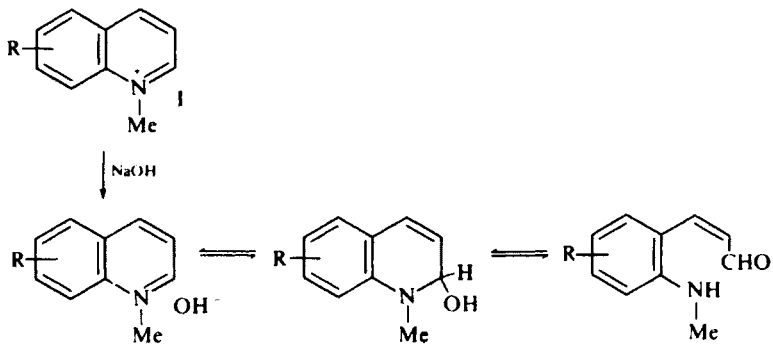
A kinetic study of the hydrogenation of a variety of compounds including quinoline and quinaldine, in acetic acid at 40 °C and 2.5 atm absolute pressure of hydrogen with PtO_2 as catalyst showed that reaction to be first order with respect to hydrogen and zero order with respect to the hydrogen acceptor.[552]



(30b)

D. Ring-opening Reactions

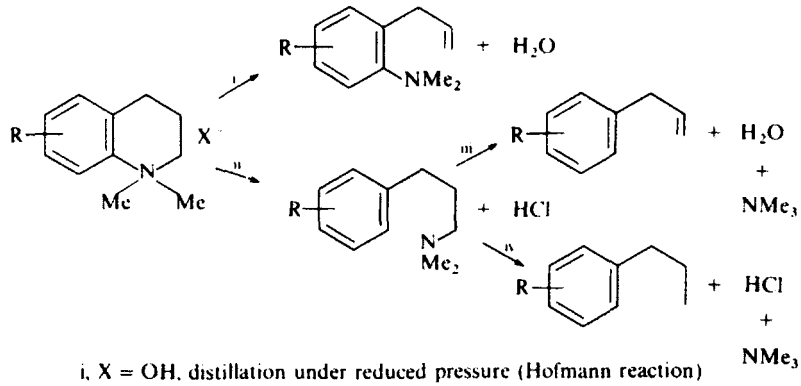
Either the heterocyclic or the carbocyclic ring of quinoline can be opened by oxidation,[424-432] including ozonolysis[433,434] and by reduction,[511,512] and the course of the reaction is influenced by the presence of alkyl substituents which increase the reactivity towards oxidizing agents but decrease the reactivity towards reducing agents. These processes have been discussed above (see Section I.5.B and I.5.C). Other ring-opening reactions characteristic of quinoline will also be applicable to alkylquinolines, such as the ring-chain tautomerism of the carbinolamine bases to give derivatives of *o*-aminocinnamaldehyde (see equation 31).



(31)

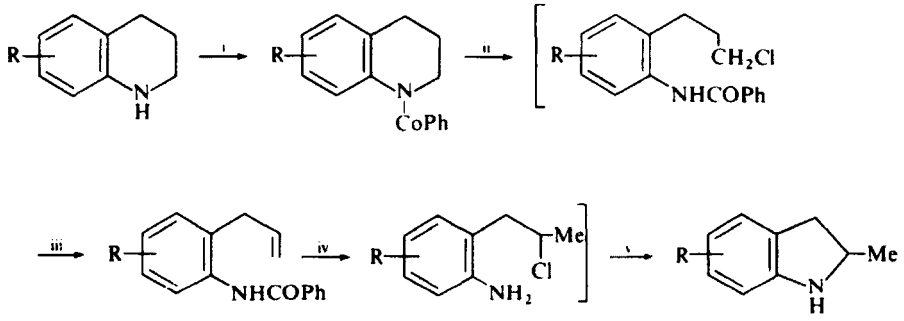
Spectroscopic evidence is also available for the formation of 2-benzamidocinnamaldehydes (in low yield) by the action of benzoyl chloride and sodium hydroxide on quinoline and some substituted quinolines,[554] but 4-methylquinoline was found to be among a number of derivatives which were resistant to ring opening by this method.

The Hofmann and Emdé exhaustive methylation procedures may be used for structural determinations of the alkylquinolines after reduction to the 1,2,3,4-tetrahydro compounds, although the first stage of the Hofmann method requires distillation under reduced pressure to remove the 2-allylaniline derivative formed.[555] As shown in Scheme 11, the Hofmann reaction opens the 2,3-bond of the heterocyclic ring and the Emdé reaction opens the 1,8a-bond between the nitrogen atom and the carbocyclic ring. Under the conditions of the Von Braun reaction,[556] with benzoyl chloride and phosphorus pentachloride, the 1,2,3,4-tetrahydroalkylquinolines undergo ring contraction to an indole, presumably by way of ring opening (Scheme 12).



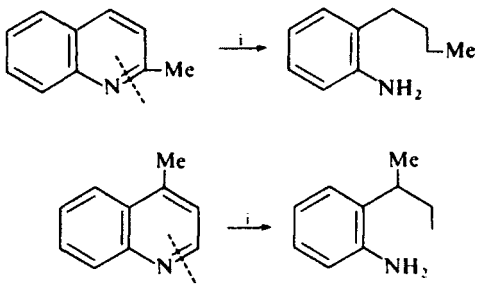
i, X = OH, distillation under reduced pressure (Hofmann reaction)
ii, X = Cl, Na/Hg reduction (Emdé reaction)
iii, 2nd stage Hofmann exhaustive methylation
iv, 2nd stage Emdé exhaustive methylation

SCHEME 11



i, PhCOCl; ii, PCl_5, 200 °C; iii, −HCl; iv, +HCl, hydrolysis; v, −HCl, ring closure

SCHEME 12



(32)

(33)

i, $(Bu^t)_2AlH$, dioxan, 130–160 °C

The action of diethyl- or diisobutylaluminium hydride on quinoline and alkylquinolines gives 1,2-dihydro derivatives at temperatures below 100 °C (see Section I.5.C.a), but at higher temperatures ring opening occurs with the formation of an *o*-alkylaniline. 2-Methylquinoline gives *o*-butylaniline and 4-methylquinoline gives *o*-(1-methylpropyl)aniline in each case, together with a hydrocarbon (isobutylene plus some isobutane from the isobutylaluminium hydride)[500] (see equations 32 and 33).

E. Side-chain Substitutions

a. DEUTERIUM AND TRITIUM EXCHANGE Exchange of hydrogen for deuterium or tritium, particularly at the α-position of the side-chains of alkylquinolines, occurs readily in CH_3OD, CH_3OT or liquid ND_3 and has been discussed in Section I.4.B in connection with the acidities of the protons involved.[248-252,1620-1622,1635] The preparation of deuterated alkylquinolines is included in a review of this subject.[557] Deuterium exchange at the 2- and 4-benzylic positions has also been studied in an acidic medium (CD_3CO_2D), when exchange occurred even in the presence of hydrochloric acid.[558]

b. SIDE-CHAIN METALATION AND ALKYLATION The deprotonation of alkyl side-chains and the alkylation of the resulting carbanions has been discussed above (see Section I.3.C.b) as a method for the preparation of alkylquinolines.[135-138,205,206,346,347,559,560,676]

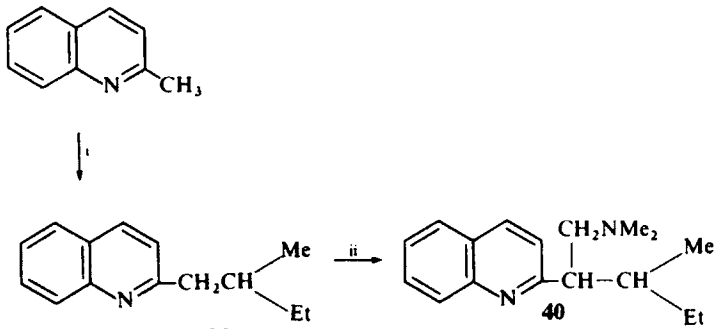
Selective metalation of the methyl groups of 2,4-dimethylquinoline has been shown to depend upon the metalating reagent employed, the reaction time and nature of the solvent.[646-648] The reaction is reversible and subject to kinetic or thermodynamic control depending on the conditions.[648] With butyllithium in tetrahydrofuran (THF)–hexane for short reaction times 2,4-dimethylquinoline gave exclusively 2-lithiomethyl-4-methylquinoline, but longer reaction times gave the isomeric 4-lithiomethyl-2-methylquinoline, but in ether–hexane lithiation occurred only at position 2 and the 4-lithiomethyl derivative isomerized to the 2-isomer if the THF was replaced by ether. Metalation of 2,4-dimethylquinoline with alkali metal amides in liquid ammonia or by lithium diisopropylamide in ether–hexane gave exclusively the 4-metalated derivative; 2,6- and 2,7-dimethylquinolines were metalated only at position 2. Preference for metalation at position 2 was considered to be partly due to prior coordination of the metal to the nitrogen atom, which could be hindered by solvent effects. *Peri* interactions were also considered to interfere with the bulky lithium diisopropylamide reagent at position 4. Confirmation of the formation of the various anions was made by subsequent condensation with benzophenone to give the appropriate quinolyl diphenyl carbinols and by self-condensation to give diquinolylethanes,[647] also prepared from the anions by reaction with molecular oxygen.[650]

The pmr spectra of the carbanions of quinaldine and various methyl derivatives of quinaldine showed that the two methylene protons are not equivalent at room temperature[649] and that the α-carbon atom in these carbanions is in a near-sp^2 configuration. Further examples of side-chain metalation[651-653] and Claisen-type condensations with esters have been reported.[654]

Metalation of 2-methylquinoline by means of a Grignard reagent (isopropylmagnesium chloride) gave quinoline-2-CH_2MgCl with evolution of propane. Treatment with benzophenone then gave an 85% yield of diphenyl quinaldinyl carbinol, which was readily dehydrated to the aralkenylquinoline 1,1-diphenyl-2-(2′-quinolyl)ethene.[635]

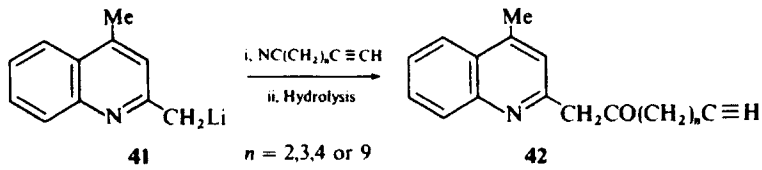
Reactions similar to those above have been used to prepare dialkylaminoquinolines. The anion formed from 4-methylquinoline by sodamide gave with $Et_2NCH_2CH_2Cl$

4-(3'-diethylaminopropyl)quinoline,[561a] and the compound (**40**) was formed from 2-methylquinoline by alkylation followed by a Mannich reaction[562] (see equation 34).



i, $NaNH_2$, liq. NH_3; $\begin{matrix}Me\\Et\end{matrix}\!\!>\!CHBr$; ii, $Me_2NH.HCl$, $(CH_2O)_3$, pentanol (34)

The anion from 2-methylquinoline and sodamide with benzophenone gave 1,1-diphenyl-2-(2'-quinolyl)ethanol.[561b] Benzyl alcohol and very strong (or molten) potassium hydroxide have been used to replace one or two hydrogens from the methyl groups of 2- or 4-methylquinoline or 2,4-dimethylquinoline to give the appropriate phenylethyl- or dibenzylmethylquinolines.[224] A series of 2-quinolylethinyl ketones (**42**) was prepared from 2,4-dimethylquinoline by treating the lithium derivative (**41**) with the appropriate acetylenic nitrile[563] (equation 35).



41 n = 2,3,4 or 9 **42** (35)

c. Side-chain Halogenation Halogenation with chlorine or bromine occurs by displacement of hydrogen from the α-position of the side-chains of alkylquinolines. Methyl groups at positions 2 and 4 are the most readily chlorinated or brominated and, unless conditions are carefully controlled, the substitution proceeds to the trichloro- or tribromomethyl stage. One report, however,[588] indicates that 4-methylquinoline is not readily converted directly to 4-trichloromethylquinoline but this derivative can be prepared in 60% yield by the action of phosphorus pentachloride on the hydrazide of quinoline-4-carboxylic acid.[589] Methyl groups at position 3 are resistant to direct halogenation, but the presence of a 2- or 6-nuclear halogen substituent enables the 3-methyl group to be brominated.[564] Methyl groups in the carbocyclic ring give mainly the chloromethyl or bromomethyl product together with some disubstitution product. Further substitution may then occur in the nucleus at position 3,[565] presumably by the addition–elimination mechanism.[566] Homolytic bromination with *N*-bromosuccinimide (NBS) occurs at α-positions of the side-chain (benzylic positions) and is normally initiated by dibenzoyl peroxide or irradiation with ultraviolet[567] or visible radiation (tungsten).[568] In moderately polar solvents ($CHCl_3$ or ether) the reaction may proceed even without specific initiation to give mainly dibromomethyl derivatives. In non-polar

solvents (C_6H_6 or CCl_4) the reaction is slower and requires initiation to give the bromomethyl derivatives as the main product.[567]

The chloromethyl- and bromomethylquinolines have a reactive benzylic halogen substituent and readily polymerize in the liquid state or in solution by intermolecular quaternization. They can be stabilized by dilution in a non-polar solvent[569] or as their crystalline hydrochloride or hydrobromide salts. 2-Ethylquinoline is brominated to the 2-(1,1-dibromoethyl)quinoline, which can be hydrolysed by sulphuric acid to give 2-acetylquinoline.[570] Tribromomethyl substituents can be hydrolysed to hydroxycarbonyl.

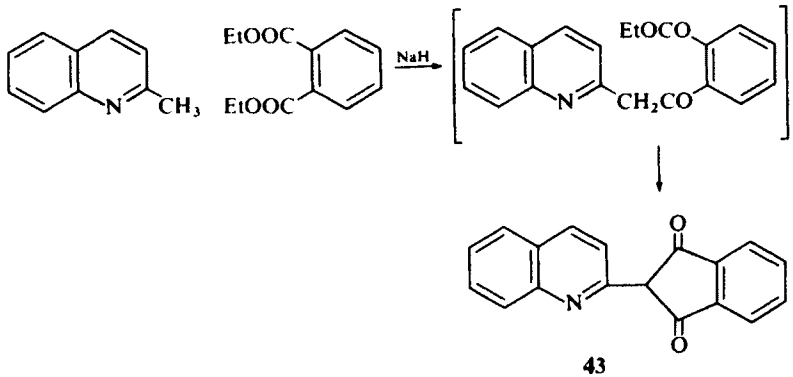
2-Methylquinoline was one of a number of methyl heterocycles which underwent rapid chlorination of the side-chain to $-CCl_3$ when heated with thionyl chloride, presumably as a result of electrophilic attack on the deprotonated species; 6- and 8-methylquinolines did not react.[1659]

2-Methyl, 4-methyl- and 2,4-dimethylquinoline were iodinated in the side-chain when mixed with iodine monobromide and pyridine at room temperature. The products were isolated as *N*-quinolylmethylpyridinium salts as a result of quaternization with the solvent. At room temperature only the 2-methyl group of 2,4-dimethylquinoline reacted, but at 100 °C for 5 h both methyl groups were iodinated.[1549]

Table 23 gives examples of chlorinations and brominations of alkylquinolines from which the generalizations above have been derived.

d. Miscellaneous Side-chain Substitutions Vinylation of 2-methylquinoline to give 2-allylquinoline has been achieved by the addition of acetylene at 35–40 atm with potassium hydroxide in an autoclave at 200 °C.[591] The Vilsmeier–Haack reaction with $ClCH{=}\overset{+}{N}Me_2Cl^-$ in dimethylformamide enables 2- or 4-methylquinoline to be formylated to give 2-(2'- or 4'-quinolyl)malonodialdehyde.[592]

Quinaldine and lepidine were among the compounds which could be acylated with benzoate, trifluoroacetate, nicotinate, oxalate and phthalate esters using sodium hydride as condensing agent to give the appropriate 2- or 4-quinolymethyl ketones, ethyl 2- or 4-quinolylpyruvate or 2-(2' or 4'-quinolyl)-1,3-indanedione (**43**), respectively (e.g. see equation 36).[593]



(36)

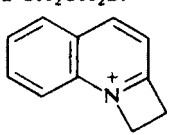
43

With sodium hydride as condensing agent, 2-acetonylquinoline (from 2-methylquinoline and ethyl acetate) will react with aryl esters to give the 1,3-diketones (**44**). When heated with hydrazine (**44**) gives 3-(2'-quinolylmethyl)-5-arylpyrazoles (**45**), and when heated with urea (**44**, Ar = Ph) gives 2-hydroxy-4-phenyl-6-(2'-quinolylmethyl)-pyrimidine (**46**, Ar = Ph) (see equation 37).[594]

TABLE 23. Products Formed by Side-chain Halogenation of Alkylquinolines

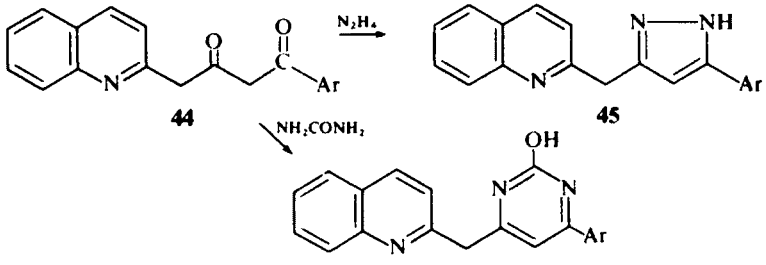
Alkylquinoline substituent	Reagent[a,b] and reaction conditions	Product (quinoline substituents)	Ref.
2-Me	Br_2, AcOH, AcONa	2-(CBr_3), quantitative	571
	Product + Cl_2	2-(CCl_3)	571
	Product + (i) NaSH (ii) $Et_4N^+Cl^-$	(i) 2-$(CS_2)^-$ (ii) 2-$CS_2^-.N^+Et_4$	590
2-Me	Cl_2, CCl_4 (or $CHCl_3$ or Cl_2 = CHCl), Na_2CO_3, 40–80 °C	2-(CH_2Cl), 60% + 2-($CHCl_2$)	572 573
2-Me	Cl_2, CCl_4, Na_2CO_3	2-(CH_2Cl), 86% + 2-($CHCl_2$), 3.8%	574
2-Me	Cl_2, Ac_2O (or P_2O_5), AcOH AcONa	2-(CCl_3), 102% (88.3% pure) = 90% yield	575
2-Me	Br_2(3 mol), AcONa, AcOH	2-(CBr_3), 78%	576
2-Me	NBS, *polar solvent* ($CHCl_3$ *or* ether)	2-($CHBr_2$) + some 2-(CBr_3)	567
2-Me	NBS, non-polar solvent (C_6H_6 or CCl_4), 80–90 °C uv irradiation	2-(CH_2Br) main product + some 2-($CHBr_2$) and 2-(CBr_3)	567
2-Me	NBS	2-(CH_2Br)	577
2-Me	IBr, *(pyridine)*, room temp.	2-$CH_2Py^+I^-$	1549
2-Me-5-NO_2	Br_2 (3 mol), AcONa, AcOH, hot	2-(CBr_3)-5-NO_2	578
2-Me-8-NO_2	Br_2 (3 mol), AcONa, AcOH, hot	2-(CBr_3)-8-NO_2	578
2-Me-8-NO_2	Br_2 (2 mol), AcONa, AcOH, hot	2-($CHBr_2$)-8-NO_2	578
3-Me	Bromination under various conditions	No 3-bromomethyl derivative	564
2-X-3-Me (X = Cl, Br, I or O)	NBS, CCl_4 + $(PhCO_2)_2$ (trace)	2-X-3-CH_2Br	564
4-Me	Br_2 (3 mol), AcONa, AcOH	4-(CBr_3), 72%	576
4-Me	IBr, (pyridine), room temp.	4-$CH_2(Py)^+I^-$	1549
4-Me	NBS, CCl_4, 60 °C	4-(CH_2Br), decomposed in 4 h to give high m.p. solid	579

TABLE 23 (*cont.*)

Alkylquinoline substituent	Reagent and reaction conditions	Product (quinoline substituents)	Ref.
4-Me	NBS, Bz_2O_2, CCl_4, heat	4-(CH_2Br)[a]	569, 580
4-CH_2OH	HBr, 130–140 °C, CCl_4	4-(CH_2Br)[a]	569
4-Me-8-NO_2	Br_2	4-(CBr_3)-8-NO_2	93
6-Me	HBr, Br_2(2 mol), $CHCl_3$, 2 stages, heating to 170–180 °C	6-$(CHBr_2)$ + some 6-$(CHBr_2)$-3-Br	565a
6-Me-2-Ph	NBS, CCl_4, Bz_2O_2	6-(CH_2Br)-2-Ph	581
6-Me-2-$C_6H_4F(p)$	NBS, CCl_4, Bz_2O_2	6-(CH_2Br)-2-$C_6H_4F(p)$	581
6-Me-2-$C_6H_4Cl(p)$	NBS, CCl_4, Bz_2O_2	6-(CH_2Br)-2-$C_6H_4Cl(p)$	581
6-Me-2-thienyl	NBS, CCl_4, Bz_2O_2	6-(CH_2Br)-2-thienyl	581
8-Me	NBS, CCl_4, Bz_2O_2 (trace), reflux for ½h (or 60-W tungsten lamp irradiation)	8-(CH_2Br)	568
	Product + dil. HCl	8-(CH_2Cl)	568
8-Me	NBS, Bz_2O_2, CCl_4, reflux for 4 h	8-(CH_2Br), 62%	582
	Product + KSH	8-(CH_2SH)	582
8-Me	HBr, Br_2, $CHCl_3$, product heated	8-(CH_2Br), 39% + some 8-$(CHBr_2)$	583
8-Me	HBr, Br_2, 180 °C	8-$(CHBr_2)$ + 8-$(CHBr_2)$-3-Br	565b
2,6-Me_2	Cl_2, Na_2CO_3, 60 °C	2-(CH_2Cl)-6-Me	584
2,6-Me_2	Br_2	2-(CBr_3)-6-Me	585
	Product + tetralin, 100 °C, 12 h	2-$(CHBr_2)$-6-Me	585
2,4-Me_2	IBr (pyridine), room temp.	2-$CH_2(Py)^+ I^-$, 4-Me	1549
2,4-Me_2	IBr (pyridine), 100 °C	2,4-bis$(CH_2)(Py)^+ I^-$	1549
2-Et	(i) Br_2, AcONa, AcOH, 90 °C	2-CBr_2CH_3	570
	(ii) Product + H_2SO_4	2-$COCH_3$	570
2-CH_2CH_2OH	(i) HBr	2-CH_2CH_2Br	586
	(ii) Product on heating		586

Alkylquinolines	Cl_2, vapour phase, quartz tube empty or packed with SiC + steam, 220–280 °C (packed), > 500 °C (unpacked)	Chloroalkylquinolines	587

[a] High dilution with CCl_4 prevents polymerization.[569] [b] NBS = *N*-Bromosuccinimide



44 45 46 (37)

2,6-Dimethylquinoline reacts with diethyl ammonium chloride in 45% formaldehyde and alcohol at 50 °C ($\frac{1}{2}$ h) to give 2-(2'-diethylaminoethyl)-6-methylquinoline in 16.5% yield.[584]

Alkylquinolines can be nitrated at the α-position of a side-chain on the heterocyclic ring by an alkyl nitrate and alkali metal amide in liquid ammonia. The relative reactivities of the methyl groups were found to be 4- > 2- > 3-.[595] If the side-chain is an aralkyl group, nitration with nitric acid and sulphuric acid will occur in the side-chain aryl group in preference to even the carbocyclic ring of the quinoline. 4-Benzylquinoline gives 4-(*p*-$NO_2C_6H_4CH_2$)quinoline[615] and 2-phenethylquinoline gives 2-(*p*-$NO_2C_6H_4CH_2CH_2$)quinoline.[616] Arylquinolines behave similarly[656] (see also Table 24).

Methylquinolines with active hydrogens (e.g. 2-methylquinoline) react with aromatic azo compounds in liquid ammonia, or (as their lithium derivative) in tetrahydrofuran, to form substituted hydrazobenzenes by addition across the —N=N— double bond.[1627] 2-Methylquinoline with azobenzene gave 1,2-diphenyl-1-(2'-quinolylmethyl)hydrazine.

On treatment with ethyl nitrite and potassamide in liquid ammonia, 2,4-dimethylquinoline was nitrosated on the 4-methyl group to give the oxime of 2-methylquinoline-4-carbaldehyde.[1660]

F. Nuclear Substitutions

The remaining nuclear hydrogens of alkylquinolines are subject to substitution as in quinoline itself, and the reactions involved have been reviewed (Part I, Chapter 1, Section IV). The following account is concerned with the influences of the alkyl substituents on the course of these substitutions. In general, alkyl groups have an activating effect towards electrophilic reagents and a deactivating effect towards nucleophilic reagents, consistent with their effect towards oxidizing agents and reducing agents. In quinoline itself electrophilic reagents attack the carbocyclic ring preferentially at positions 5 and 8; nucleophilic reagents attack the heterocyclic ring preferentially at positions 2 and 4. In neutral media radical attack may occur at all positions with 8, (4, 5) and 2 as the most reactive, in that order, with some uncertainty about the relative reactivities of positions 3, 6 and 7 owing to the difficulty of separating the products. In acidic media, however, attack on the protonated base by radicals having nucleophilic character occurs more readily, is highly specific at positions 2 and 4 and is of synthetic importance.

Alkyl substituents in the carbocyclic ring direct electrophilic reagents to remaining positions in that ring which are fully conjugated with them (i.e. *ortho* or *para*), taking account of the lack of double bond character of the 6,7-bond. Thus a 7-alkyl substituent directs to position 8 rather than 6 and a 6-alkyl substituent directs to position 5 rather than 7, at least for reactions such as nitration which are kinetically controlled, although at higher temperatures sulphonation may take a different course owing to the reversible

nature of the reaction. A 4-alkyl substituent deactivates position 5 owing to a *peri* steric effect.

a. DEUTERIUM EXCHANGE The exchange of hydrogen for deuterium from nuclear positions of quinoline, 2-methylquinoline and their 3-hydroxy derivatives with D_2SO_4 has been studied by nmr spectroscopy over 65–70 h at 145 °C. The hydrogens of the carbocyclic ring were the most active and the rate of exchange was accelerated by the presence of the methyl or hydroxyl substituents in the heterocyclic ring.[1550]

b. NITRATION The results of nitration of a number of alkylquinolines are given in Table 24 and provide the principal evidence for the generalizations above. Thus 2- and 3-methylquinolines nitrate at positions 5 and 8 as for quinoline. In 4-methylquinoline, position 5 is deactivated, probably by the *peri* steric effect. 5-Methylquinoline is nitrated both at position 6 and position 8 (conjugated *ortho* and *para*), but 6- and 7-methylquinolines nitrate only at the *ortho*-positions 'fully' conjugated with them, namely positions 5 and 8, respectively. Data for the nitration of 8-methylquinoline are scarce and only nitration at position 5 seems established, although position 7 is fully conjugated. The deactivating effect of the heterocyclic nitrogen atom is clearly shown in the mononitration of phenyl-, benzyl- and phenethylquinolines (see Table 24). The phenyl ring in the side-chain is attacked in preference to even the carbocyclic ring of the parent heterocycle.[614,656] The further effect of quaternization is also apparent from the exclusive direction of the nitro substituent to the *meta*-position of the phenyl side-chain of 1-methyl-2-phenylquinolinium methosulphate, whereas with 2-phenylquinoline itself, which is incompletely protonated under the conditions employed, some *para*-substitution also occurs.[656]

TABLE 24. Products of Nitration of Alkylquinolines

Alkyl-quinoline substituent	Position of nitration	Yield (%)	Reagent and conditions	Ref.
2-Me	5	59	HNO_3, H_2SO_4,	617
	+8	33	60 °C, 20 min	617
2-Me	5			458, 578
	+8			
2-Me-*N*-O	4	73.5	HNO_3, H_2SO_4	489
3-Me	5	50.7	HNO_3, H_2SO_4,	618
	+8	25.4	10 °C, 7 h	
4-Me	8	52		619
4-Me	8	Main product	HNO_3 (fuming), H_2SO_4 100 °C, 15 min	93
	+5?	Trace	HNO_3 (fuming), H_2SO_4 100 °C, 15 min	596–599
2-Cl-4-Me	8		H_2SO_4, 100 °C, 15 min	596
	+6			
5-Me	8	64	HNO_3 (fuming)	601
	+6	24	H_2SO_4, 5 °C, 30 min	
6-Me	5		HNO_3, H_2SO_4	602–603
7-Me	8	99	HNO_3 (fuming) H_2SO_4, 5 °C, 30 min	601
7-Me	8	67	HNO_3, H_2SO_4	604
	+another			601
2-Cl-7-Me	8		HNO_3, H_2SO_4	604
8-Me	5		HNO_3, H_2SO_4	603

TABLE 24 (*cont.*)

Alkyl-quinoline substituent	Position of nitration	Yield (%)	Reagent and conditions	Ref.
5-Et	8	[a]	HNO_3 (fuming) H_2SO_4, 5 °C, 30 min	601
7-Et	8	>61[a]	HNO_3 (fuming), H_2SO_4, 5 °C, 30 min	601
2-Et-*N*-O	4		HNO_3, H_2SO_4	605
2,4-Me_2	8	54.7	HNO_3 (fuming),	606
	+6	18.2	H_2SO_4, 0 °C,	
	+5	1.8	2 h	
2,4-Me_2	8	8- to	KNO_3, H_2SO_4,	607
	+6	6- ratio = 3:1	100 °C, 5 h	
2,4-Me_2	6,8-$(NO_2)_2$		Fuming HNO_3 + KNO_3	607
2,4-Me_2	8		HNO_3 (fuming),	608
	+6		H_2SO_4, 5 °C	
2,4-Me_2	8	Major	KNO_3, H_2SO_4	613
	+5	Minor		
6-Cl-2,4-Me_2	5		HNO_3, H_2SO_4	609
7-Cl-2,4-Me_2	8		HNO_3, H_2SO_4	609
8-Cl-2,4-Me_2	5		HNO_3, H_2SO_4	609
5,8-Cl_2-2,4-Me_2	6		HNO_3, H_2SO_4	609
2,6-Me_2	5	86	HNO_3, H_2SO_4	608
	5		KNO_3, H_2SO_4	610
2,7-Me_2	8	88, 92	KNO_3, H_2SO_4	610
4,6-Me_2	5		HNO_3, H_2SO_4, −5 °C	600
6,7-Me_2	5	Major		611
	+8	Minor		
6,8-Me_2	5		HNO_3, H_2SO_4	603
2,3,8-Me_3	5			472
2,4,6-Me_3	5		HNO_3, H_2SO_4, −5 °C	600
2,5,8-Me_3	6		KNO_3, H_2SO_4	610
2,6,8-Me_3	5 (or 7?)		HNO_3 (fuming), H_2SO_4	451
2,3-Me_2-8-Et	5	83	HNO_3, 100 °C, 5 h	612
2,3-Me_2-8-Pr	5	93	HNO_3, 100 °C, 5 h	612
4-CH_2Ph	*p*-Ph		HNO_3, H_2SO_4	615
2-CH_2CH_2Ph	*p*-Ph	99		616
2,3-$(CH_2)_4$	8		HNO_3, H_2SO_4, heat, 2 h	614
	+5			
2,3-$(CH_2)_3$	8		HNO_3, H_2SO_4, heat, 2 h	614
	+5			
2-Ph	*m*-Ph + *p*-Ph		HNO_3 (sp. gr. 1.5), 0 °C, 24 h	656
[2-Ph-1-Me]$^+$ $(CH_3SO_4)^-$	*m*-Ph		HNO_3 (sp. gr. 1.5) 0 °C, 24 h	656

[a] See ref. 601.

c. SULPHONATION Sulphonation of quinoline can result in the formation of all the monosulphonic acids with substituents in the carbocyclic ring. At sulphonation temperatures up to 100 °C the 8-isomer predominates, together with the 5-isomer. The

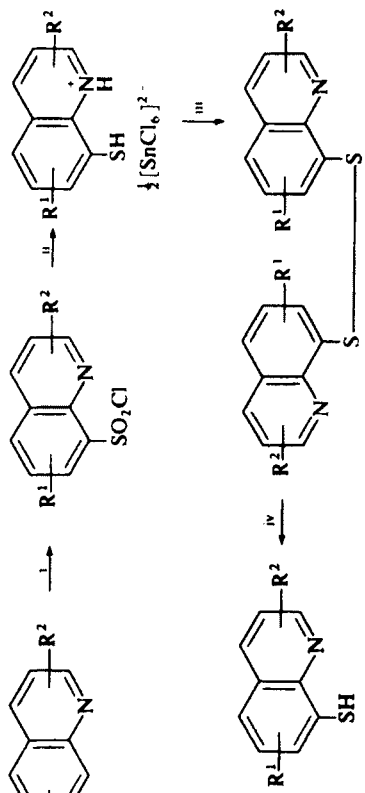
proportion of the 5-sulphonic acid increases up to about 170 °C. At higher temperatures (250–300 °C), owing to the reversibility of the sulphonation reaction, the thermodynamically favoured 6-sulphonic acid is the main reaction product, and other isomers rearrange to the 6-sulphonic acid at these temperatures. No direct sulphonation of the heterocyclic ring (other than at the nitrogen atom) has been reported. Much of the early work reviewed by McCasland[620] is confusing owing to uncertainties in the characterization of the acids formed and of derivatives made from them, although in many cases the experimental work can be reinterpreted. The influence of alkyl substituents on the sulphonation of alkylquinolines must be considered against this background. Table 25 gives the results reported.

TABLE 25. Products of Sulphonation of Alkylquinolines

Alkylquinoline substituent	Sulphonation condtions	Positions sulphated (mono-substitution)	Ref.
2-Me	Fuming H_2SO_4	5+6+8	458, 621
4-Me	Conc. H_2SO_4, 300 °C	6	
	Longer heating	Another also (8?)	622
6-Me	Fuming H_2SO_4 (25% SO_3), 90 °C	5 (main product)	603
6-Me	Fuming H_2SO_4 (sp. gr. 1.89), 135–140 °C	8	623
8-Me	Fuming H_2SO_4 (sp. gr. 1.89), 135–140 °C	5	623–625
4-Et	Fuming H_2SO_4, 260 °C	Not characterized	172
2,4-Me_2	Fuming H_2SO_4 100–130 °C	Not characterized	429
5,8-Me_2	Fuming H_2SO_4, warm	6	626
6,8-Me_2	Fuming H_2SO_4, 160–170 °C	5 (or 7)	627
2,6,8-Me_3	$H_2S_2O_7$, 120–130 °C	5 (or 7)	451
3,6-Me_2-2-Et	Fuming H_2SO_4 (20% SO_3), 100 °C	Not characterized	453
3,6,8-Me_3-2-Et	$H_2S_2O_7$, 100 °C	5 (or 7)	90

A series of alkylquinolines have been chlorosulphonated at position 8. Reduction with tin(II) chloride and hydrochloric acid gave the chlorostannate salt of the quinoline-8-thiol. Oxidation with alkaline hydrogen peroxide followed by reduction with hypophosphorous acid gave the disulphide and finally the 8-mercaptoquinoline[633,634] (see Scheme 13).

d. HALOGENATION Direct halogenation of alkylquinolines, particularly in the presence of a halogen acid acceptor such as sodium acetate or sodium carbonate, gives side-chain substitution products (see Section I.5.E.c and Table 23). In the absence of a suitable base, perhalides may be formed, which decompose on heating to give mainly side-chain substitution products. In addition to side-chain substitution some nuclear halogenation may occur at position 3[565] by the addition—elimination mechanism.[566] Examples of halogenations where the products have not been characterized, but which are presumably side-chain substitution products, include a monobromo derivative of 6-methylquinoline by the action of S_2Br_2 and dibromo and diiodo derivatives by the action of bromine or iodine and fuming sulphuric acid (50% SO_3).[628] Similarly, a dihalogen derivative is formed from 8-methylquinoline with iodine and fuming sulphuric acid (50% SO_3).[629] With bromine and carbon disulphide, 3,6-dimethyl-2-ethylquinoline gives an

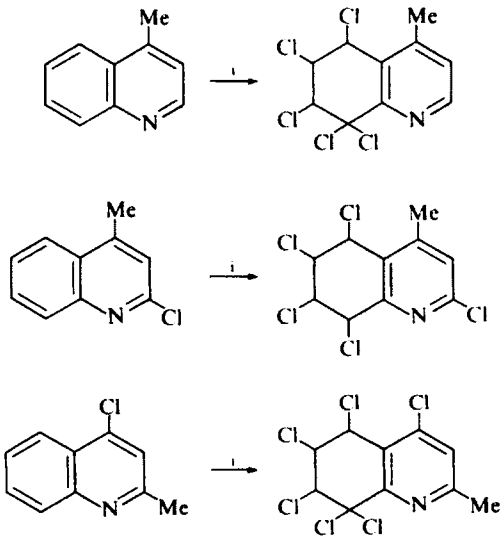


(i), HSO_3Cl; (ii) $SnCl_2$, HCl; (iii) H_2O_2, NaOH; (iv) H_3PO_2
(a) R^1 = 6Me, R^2 = H (ref. 633); (b) R^1 = H, R^2 = 2,3-Me_2 (refs. 634a, b); (c) R^1 = 6-Me, R^2 = 2-Me (ref. 634c);
(d) R^1 = 7-Me, R^2 = 2-Me (ref. 634d); (e) R^1 = 6-Me, R^2 = 2,4-Me_2 (ref. 634e); (f) R^1 = H, R^2 = 2-Pr^i (ref. 634f)

SCHEME 13

addition compound which, on heating to 130 °C, forms a dibromoderivative.[453] When treated with bleaching powder and water, 6,8-dimethylquinoline forms a chloro derivative.[87]

More recently, treatment of the 1-benzoyl derivatives of 2,6-dimethyl-1,2-dihydroquinoline and of 2,6,8-trimethyl-1,2-dihydroquinoline with chlorine or bromine in carbon tetrachloride was found to give dichloro or dibromoderivatives. On boiling with 50% sulphuric acid for 30 min the dichloro compounds gave the 3-chloro substitution products, 2,6-dimethyl-3-chloroquinoline and 2,6,8-trimethyl-3-chloroquinoline, and the dibromo derivatives gave the corresponding quinoline bases 2,6-dimethyl- and 2,6,8-trimethylquinoline.[630] 4-Methylquinoline with chlorine in carbon tetrachloride was found to give 5,6,7,8,8-pentachloro-5,6,7,8-tetrahydro-4-methylquinoline and 2-chloro-4-methylquinoline and 4-chloro-2-methylquinoline gave 2,5,6,7,8-pentachloro-5,6,7,8-tetrahydro-4-methylquinoline and 4,5,6,7,8,8-hexachloro-5,6,7,8-tetrahydro-2-methylquinoline, respectively. The unmethylated 2-chloro- and 4-chloroquinolines did not react in this way[631] (see Scheme 14).



i, Cl_2, CCl_4

SCHEME 14

e. MERCURATION The action of mercury(II) acetate on quinoline and 2-, 6-, 7- and 8-methylquinolines has been investigated by Ukai.[632] The procedure used consisted in heating the quinoline or alkylquinoline with mercury(II) acetate on a water bath or in methanolic solution. The initial products were coordination complexes containing either 1 or 2 mol of the quinoline base with mercury(II) acetate, together with some substitution products, consisting of acetoxymercuriquinolines. The coordination complexes were heated at 160 °C and treated with sodium chloride solution to give chloromercuriquinolines. These could also be formed from the acetoxymercuri derivatives by treatment

with sodium chloride solution. In some cases the chloromercuriquinolines were treated with bromine to give bromoquinolines, which served for their identification.

The final conclusions can be summarized as follows. Quinoline itself is substituted at positions 8 and 3. 8-Methylquinoline is substituted at position 5 and 7-methylquinoline gave two chloromercuri derivatives after treatment with sodium chloride, one of which was identified as 5-chloromercuri-7-methylquinoline. The other derivative was not characterized apart from its m.p. (197–198 °C) and that of its bromo derivative (24–26 °C; hydrochloride salt, 210–216 °C). 6-Methylquinoline similarly gave two mercurichloride derivatives, one of which was identified as 8-chloromercuri-6-methylquinoline; the other was not characterized apart from its m.p. (180 °C) and that of its bromo derivative (53 °C). 2-Methylquinoline, on the other hand, was mercurated in the side-chain to give 2-acetoxymercurimethylquinoline, which with sodium chloride solution gave 2-chloromercurimethylquinoline; the latter, with bromine, gave 2-bromomethylquinoline (m.p. 55–56 °C), which was oxidized to quinoline-2-carboxylic acid (quinaldinic acid) (m.p. 155 °C) with nitric acid.

f. Friedel–Crafts Substitutions Friedel–Crafts alkylation and acylation reactions are rare in the quinoline series of compounds owing to the deactivation effect of the heterocyclic nitrogen atom. It has been reported that 6- and 8-methylquinolines and 6,8-dimethylquinoline could not be acylated with either acetyl chloride or acetic anhydride with an aluminium chloride catalyst in carbon disulphide, but that 5,7-dimethylquinoline with acetyl chloride under these conditions gave a low yield (about 5%) of 6-acetyl-5,7-dimethylquinoline.[635] Arylations are possible in which 2- or 4-chloro- or -bromoquinolines are used as reagents with an aromatic compound as substrate (see Section V.1.D.f).

g. Amination The direct amination of quinoline by means of alkali metal amides or barium amide, in liquid ammonia or *NN*-dimethylaniline as solvents (Chichibabin amination reaction), has been reviewed by Leffler.[636a] The reaction has been applied to alkylquinolines with varying degrees of success. 4-Methylquinoline in *NN*-dimethylaniline gave 2-amino-4-methylquinoline,[636b] although no product was obtained in liquid ammonia.[637] 5-Methylquinoline with sodamide in *NN*-dimethylaniline after working up gave only the product of hydrolysis, 3,4-dihydro-5-methyl-2-(1*H*)-quinolone.[638] 6-Methylquinoline with barium amide in liquid ammonia (30 days) gave a 59% yield of liberated hydrogen and 17% of 2-amino-6-methylquinoline,[640] but with sodamide in *NN*-dimethylaniline 3,4-dihydro-6-methyl-2-(1*H*)-quinolone and 6,6′-dimethyl-2,3′-biquinolyl were formed in addition to the 2-amino-6-methylquinoline.[638] With barium amide in liquid ammonia, 7-methylquinoline gave an 85% yield of liberated hydrogen but no amino compound was isolated,[640] and with sodamide in *NN*-dimethylaniline 2-amino-3,4-dihydro-7-methylquinoline was formed, which was separated with difficulty and hydrolysed to 3,4-dihydro-7-methyl-2-(1*H*)-quinolone.[641] 8-Methylquinoline gave a 35% yield of the 2-amino derivative with barium amide in liquid ammonia (22 days)[640] and with sodium in liquid ammonia the 2-amino-8-methylquinoline was accompanied by some 2-amino-3,4-dihydro-8-methylquinoline.[639] Barium thiocyanate, $Ba(CNS)_2$, has been used in conjunction with barium amide, and potassium nitrate with an excess of potassium nitrite has been used, presumably as an oxidizing agent, to assist in the removal of the hydride ion.[640]

h. Hydroxylation The direct hydroxylation of quinoline to carbostyril has been described by Chichibabin[642,643] by heating the base with carefully dried potassium hydroxide, potassium hydroxide containing added barium oxide or barium hydroxide containing added barium oxide. Sodium hydroxide was ineffective at temperatures at

which potassium hydroxide reacted easily. The reaction has been extended to alkylquinolines with some success but with the notable exception of 2-methylquinoline. 4-Methylquinoline[642,643] 6-methylquinoline[644] and 8-methylquinoline[644] all gave the appropriate methyl-2-(1*H*)quinolones with evolution of hydrogen when heated with dry fused potassium hydroxide at 250–260 °C for 3–5 h. 2-Methylquinoline on the other hand reacted in a different manner. When heated with dry potassium hydroxide containing added barium oxide for 8 h at 226–260 °C no hydrogen was evolved and no hydroxyquinoline or quinolone was detected, only tarry products believed to contain indoles.[642,643]

i. Alkylation and Arylation Alkyl and aryl organolithium compounds and Grignard reagents form 1,2-addition compounds with quinolines, which on hydrolysis give 1,2-dihydro derivatives; these in turn may be oxidized (e.g. with nitrobenzene) to 2-alkyl- or 2-arylquinolines. This constitutes an important method for the preparation of these compounds and is discussed in Sections I.3.C.a and V.1.B. Some metalated quinolines cannot be made directly, but are available by halogen–metal exchange reactions. Thus, position 3 of quinoline is difficult to metalate and quinolines with a 2-methyl substituent are metalated directly only in the side-chain,[655] and 2-methylquinoline with phenyllithium in tetrahydrofuran gave dimeric reduction products containing azepine and diazocin ring systems[680] (see Section I.5.H). The following examples of reactions of alkyl quinolines with organometallic reagents have been reported. 4-Methylquinoline with phenyllithium gave 4-methyl-2-phenylquinoline (54%),[497] and 5-methylquinoline similarly gave 57% of a phenyl derivative reported as a 'mixture of isomers'. The most likely composition of the product would be 5-methyl-2-phenylquinoline containing some 1,2-dihydro and 1,2,3,4-tetrahydro derivatives.[256] When the magnesium salt of 2-allyl-2-methyl-1,2-dihydroquinoline, from 2-methylquinoline and allylmagnesium bromide, was heated, the product isolated contained 4-allyl-2-methylquinoline and its 1,2- and 1,4-dihydro derivatives. Similar treatment of the lithium salt of 2,2-diphenyl-1,2-dihydroquinoline gave 2-phenylquinoline with elimination of one phenyl group. This led to the interpretation of the allylic rearrangement also as a 1,2-elimination, followed in this case by a 1,4-addition.[126b] Butyllithium and phenyllithium form addition products with 4-methylquinoline, which on hydrolysis give 2-butyl(or 2-phenyl)-1,2-dihydro-4-methylquinoline. This was considered originally to result from the rearrangement of an initial 4-butyl (or 4-phenyl)-1,4-dihydroquinoline addition product,[675] but subsequent investigations have shown that the 1,2-addition products were formed directly.[126b,c,840] The benzylation of 6- and 8-methylquinolines at position 3 by benzyl alcohol and potassium hydroxide[544] has been described above (see Section I.5.C.b and Scheme 10).

j. Homolytic Nuclear Substitutions Homolytic alkylations and arylations of quinoline have been discussed in Sections I.3.D and V.1.C as methods for the preparation of alkyl- and arylquinolines (see in particular Scheme 5 and Table 3). The remaining vacant nuclear positions of alkylquinolines are subject to further homolytic attack in the same way as quinoline itself and other heterocycles. In addition to alkylation and arylation, the principal substitutions involved have been reviewed by Minisci and Porta,[146] and consist of acylation,[147,661,662] including formylation,[663] oxyalkylation,[142,664,665] aminoalkylation,[666] amidation [667,668] and arylation. The last type is considered in Section V.1.C.

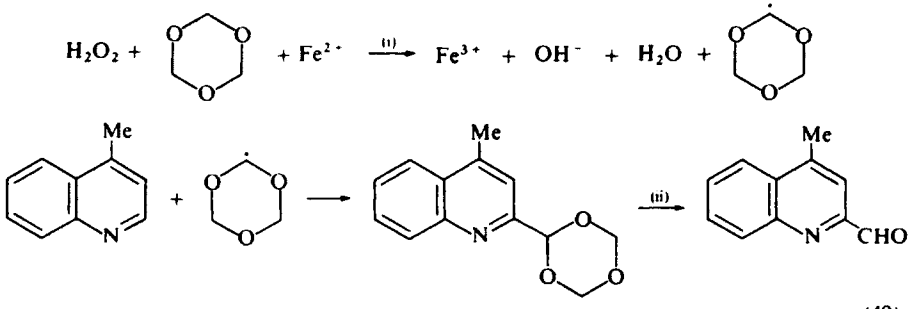
Acylation. Acyl radicals can be obtained by redox reactions from either aldehydes or keto-acids (equations 38 and 39). Under these conditions quinoline gives 2- and 4-acyl

$$\left.\begin{array}{l} Me_3COOH + Fe^{2+} \rightarrow Me_3CO\cdot + Fe^{3+} + OH^- \\ Me_3CO\cdot + RCHO \rightarrow Me_3COH + RCO\cdot \end{array}\right\} \quad (38)$$

$$S_2O_8^{2-} + Ag^+ \rightarrow SO_4^{-\cdot} + SO_4^{2-} + Ag^{2+}; SO_4^{-\cdot} + Ag^+ \rightarrow SO_4^{2-} + Ag^{2+}$$
$$RCOCO_2H + Ag^{2+} \rightarrow CO_2 + H^+ + Ag^+ + RCO\cdot \quad (39)$$

derivatives and 2-methylquinoline gave 4-acetyl-2-methylquinoline in 40% yield by the method in equation 39.

Formylation. Formylation can be achieved by homolytic substitution with the trioxanyl radical followed by hydrolysis.[663] 4-Methylquinoline gave 32% of 2-trioxanyl-4-methylquinoline, which was hydrolysed (93%) by 2 N hydrochloric acid to the aldehyde (equation 40). 2-Methylquinoline similarly gave the 4-aldehyde.



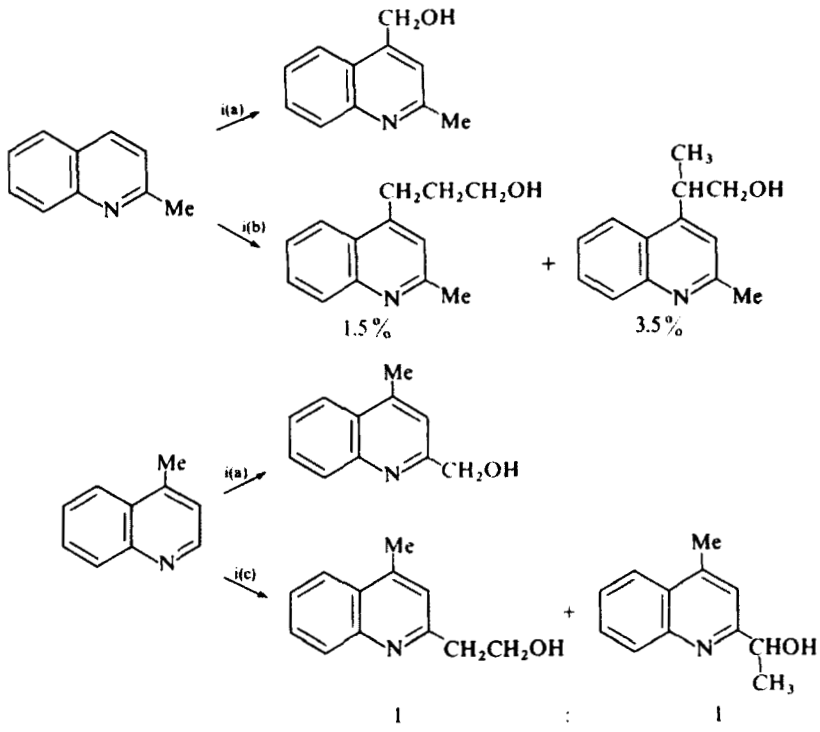
(40)

i, H_2SO_4, 3%; ii, 2 N HCl

Oxyalkylation. Oxyalkylation results from the generation of a radical by hydrogen abstraction from the α-position of methanol or a primary alcohol by oxidation with peroxydisulphate,[670] sulphamic acid,[142] perborate, peroxydicarbonate, hydrogen peroxide and Cr^{2+} *t*-butyl hydroperoxide and Fe^{2+}[669] or by photochemical methods[671] (see Scheme 15).

Hydroxyalkylation was also achieved by irradiation of *N*-alkoxyquinaldinium or lepidinium perchlorate in alcohol to give 4- or 2-hydroxyalkylated methylquinolines together with small amounts of the 8-alkoxymethylquinoline.[1636]

Amidation. Hydrogen abstraction by an electrophilic radical from formamides gives carbamoyl radicals, and from *N*-alkylformamides or other *N*-alkylamides α-amidoalkyl radicals can also be formed. The relative proportion of the two possibilities depends on the primary radical source and different mechanisms operate.[674] Di-*t*-butyl peroxide or *t*-butyl hydroperoxide and Fe^{2+} ions form Me_3CO radicals, which abstract the formyl hydrogen to give amido radicals (equation 41). The $SO_4^{-\cdot}$ radical ions from peroxydisulphate ions ($S_2O_8^{2-}$) engage in an electron-transfer process followed by deprotonation to give α-amidoalkyl radicals (equation 42). The products formed are given in Table 26, p. 82.



i, 30% H_2O_2 + Fe^{2+}: (a) + MeOH; (b) + PrOH; (c) + EtOH

SCHEME 15

$$Me_3CO\cdot + HCONMe_2 \rightarrow Me_3COH + \cdot CONMe_2 \quad (41)$$

$$SO_4^{-}\cdot + Me_2NCHO \rightarrow SO_4^{2-} + Me_2\overset{+\cdot}{N}CHO$$
$$Me_2\overset{+\cdot}{N}CHO \rightarrow \cdot CH_2N(Me)CHO + H^+ \quad (42)$$

Protonated aromatic heterocycles including 2-methylquinoline have been amino-alkylated by radicals obtained by intramolecular hydrogen abstractions from trialkyl-amine-*N*-oxides.[666]

G. Addition Reactions

a. GENERAL ADDITION REACTIONS The following addition reactions of quinoline and alkylquinolines have been covered in previous sections: additions of organometallic compounds (Sections I.3.C.a and I.5.F.i); direct addition of hydrogen by catalytic hydrogenation and by chemical reduction (Section I.5.C); addition reactions occurring as the first stage of an eventual nuclear substitution [Sections I.5.F.b (nitration), I.5.F.d (halogenation); I.5.F.e (mercuration), I.5.F.g (amination) and I.5.F.h hydroxylation)]. Other addition reactions which result in the formation of new ring structures are discussed below in Section I.5.H; these include the addition of dimethylacetylene dicarboxylate and dimethylketen.

TABLE 26. Products of Homolytic Amidation of Alkylquinolines

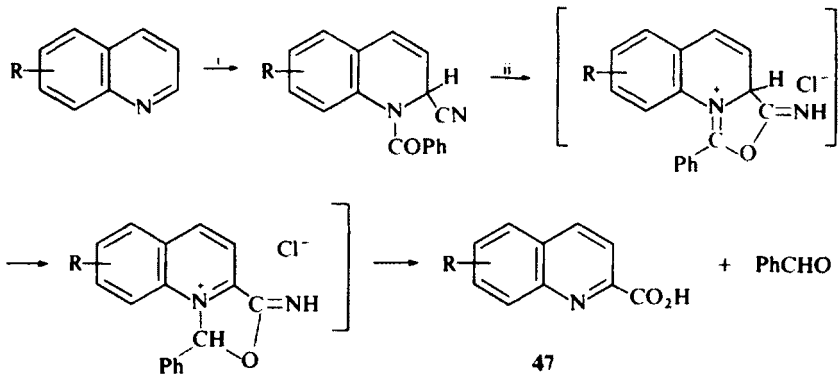
Alkyl-quinoline sub-stituent	Amide	Initiating radical source	Position of sub-stituent	Type of product	Yield (%)	Ref.
2-Me	$HCONH_2$	*t*-BuOOH	4	Amido	80	672
	HCONHMe	*t*-BuOOH + Fe^{2+}	4	Amido	67	668
	CH_3CONMe_2	$S_2O_8^{2-}$	4	α-Amidoalkyl	92	668
	CH_3CONMe_2	$(t\text{-BuO})_2$	4	α-Amidoalkyl	81	668
	Cyclohexyl-acetamide	$(t\text{-BuO})_2$	4	α-Amidoalkyl	36	668
	Cyclohexyl-acetamide	$(S_2O_8)^{2-}$	4	α-Amidoalkyl	51	668
	N-Acetyl-piperidine	$(t\text{-BuO})_2$	4	α-Amidoalkyl	37	668
4-Me	$HCONH_2$	*t*-BuOOH	2	Amido	87	673
	HCONHMe	*t*-BuOOH + Fe^{2+}	2	Amido	45	668
	$CH_3CONHMe$	$(t\text{-BuO})_2$	2	α-Amidoalkyl	71	668
	$CH_3CONHMe$	$S_2O_8^{2-}$	2	α-Amidoalkyl	65	668
	CH_3CONMe_2	$S_2O_8^{2-}$	2	α-Amidoalkyl	44	668
	CH_3CONMe_2	$(t\text{-BuO})_2$	2	α-Amidoalkyl	85	668
	NN-Dimethyl-urea	$(t\text{-BuO})_2$	2	α-Amidoalkyl	38	668
	Caprolactam	$(t\text{-BuO})_2$	2	α-Amidoalkyl	59	668

b. REISSERT REACTION The Reissert addition compounds of quinoline with acyl halides and potassium cyanide have been reviewed in Part I, Chapter I, Section IV.1 and by Popp,[677] and many alkylquinolines participate in this reaction.[584,678,1630] No Reissert compound could be obtained from 2-methylquinoline[678] and attempts to prepare one from 8-methylquinoline have resulted in conflicting reports.[678,1630] With the exception of the addition compound from 4,6-dimethylquinoline, the Reissert compounds could be hydrolysed by concentrated hydrochloric acid in the usual way to give the 2-carboxylic acids and an aldehyde. Scheme 16 illustrates the results achieved using benzoyl chloride as the acyl halide.

The Reissert reaction between benzoyl chloride, potassium cyanide and 2,3-substituted quinoline-*N*-oxides has also been investigated.[1534] *N*-Oxides with a phenyl substituent at position 2 gave the 3-benzoyloxy-4-cyano-2-hydroxy compounds (**47a**) together with the benzoyloxyquinolines (**47b**) and (**47c**). With an alkyl substituent at position 2, the *N*-oxides gave 2-α-benzoyloxyalkylquinolines, e.g. (**47d**) from 2,3-dimethylquinoline-1-oxide. The replacement of benzoyl chloride by furoyl chloride, *p*-anisoyl chloride, nicotinoyl chloride and *p*-nitrobenzoyl chloride resulted in the formation of analogous products.

The reaction of chloroformic esters and related compounds with various quinoline derivatives, including 6-methylquinoline, gave a series of addition products related to the Reissert compounds[679] (equation 43).

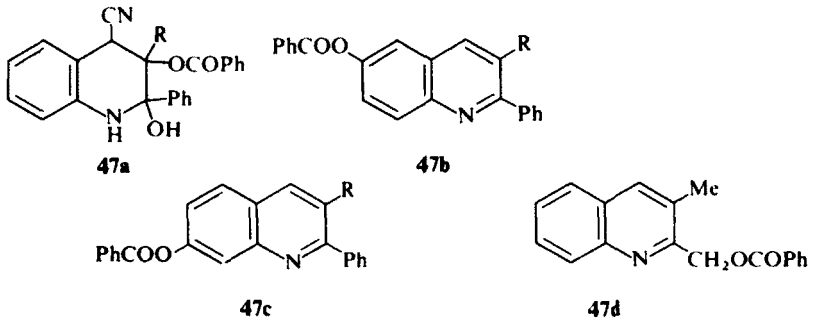
As shown in equation 43a, irradiation of a Reissert compound of quinoline, in ethanol, can lead to isomerization to cycloprop[*b*]indoles. With R = H in equation 43a, 46% of the *endo* product was formed and this was converted into the *exo* isomer when refluxed in decalin.[1657]



i, KCN aq., PhCOCl, 4 h; ii, HCl (conc.), heat, ½ h, room temp., 2 days

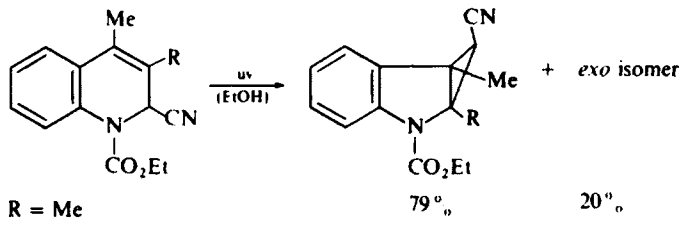
R	Mp. of (47) (°C)	Yield of (47) (%)	Yield of PhCHO Recovered as 2,4-dinitrophenylhydrazone (%)
6-Me	144	99	90
7-Me	164–165	64	84
4,6-Me_2	130–131	94	
5,6-Benzo	182	94	84

SCHEME 16 (ref. 678)



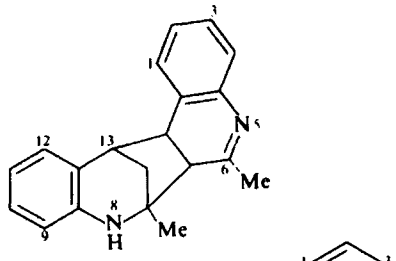
(43)

R^1 = 6–Me, 5-NH_2, 6-MeO, H, etc.
R^2 = OMe, OCH = CH_2, OPh, SEt, etc.
X = CN, OEt

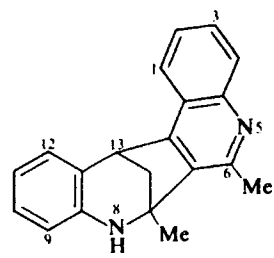


H. Syntheses of Condensed Ring Systems

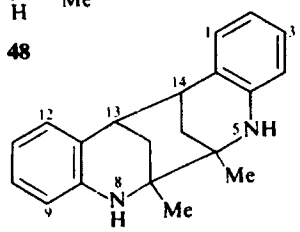
The reaction between 2-phenyllithium and 2-methylquinoline in tetrahydrofuran[680] gave 12.5% of 6a,7,13,13a-tetrahydro-6,7-dimethyl-7,13-methano-8*H*-quino[3,4-*c*]benzazepine (**48**) and 10.5% of the 7,13-dihydro derivative (**49**). Thermal decomposition of (**48**) gave 8% of (**49**) and 16% 5,6,7,8,13,14-hexahydro-6,7-dimethyl-6,14:7,13-dimethanodibenzo[*e*,*i*]-1,4-diazecin (**50**). See also Section I.5.C.a for the preparation of these and similar dimeric compounds by reduction of methylquinolines with zinc (or zinc amalgam) and acid, and electrolytically in both acidic and alkaline media.[501-508] Similarly, 2,6-dimethylquinoline gave the 2,6,7,11-tetramethyl analogue of (**48**), which decomposed slowly on standing at room temperature to the corresponding 2,6,7,11-tetramethyl analogue of (**49**).



48



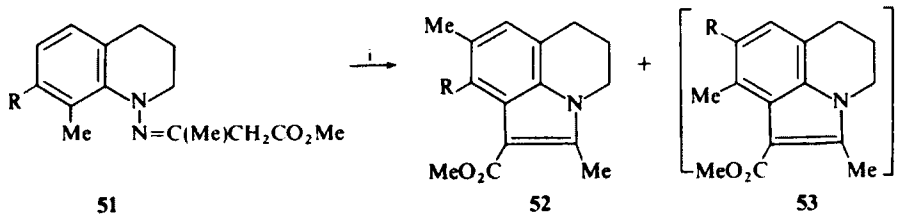
49



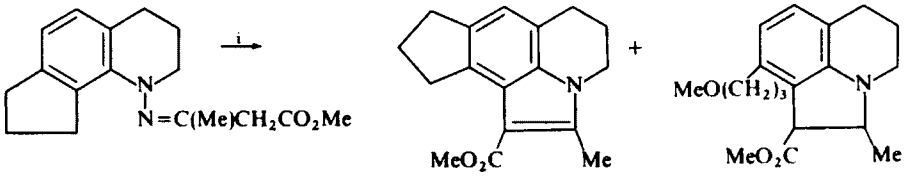
50

Fischer indole rearrangements of the hydrazones (**51**) and (**54**) resulted in ring closure to position 8 of the quinoline ring with consequent displacement of the 8-substituent[681] (see Scheme 17). Compound (**51**) (R = Me) gave (**52**) (R = Me), but (**51**) (R = CD_3) gave a mixture of (**52**) (R = CD_3) and (**53**) (R = CD_3, indicating that migration of the 8-substituent occurred by a double 1,2-shift. In general, 8-substituents with good migratory aptitudes (e.g. phenyl) underwent 1,2-shifts, but groups which formed stabilized cations (e.g. Et_2NCH_2) were eliminated.[681c]

The thermal reaction of sulphonyl azides with quinolines, pyridines and isoquinolines has been re-examined[682] and in most cases *N*-sulphonyliminopyridinium ylides are formed via an intermediate sulphonyl nitrene. 2-Methylquinoline, and also 1-methylisoquinoline and 6-methylphenanthridine, behave differently to give triazolo derivatives,



51 52 53

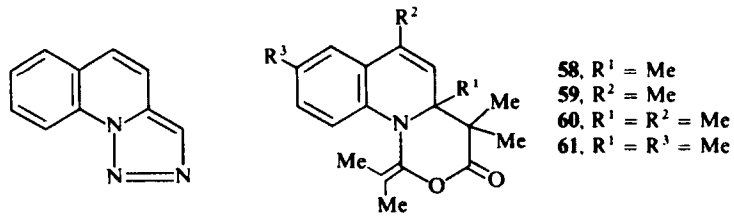


54 55 56

i, Fischer indole reaction

SCHEME 17

e.g. 1,2,3-triazolo[1,5-*a*]quinoline (**57**) from 2-methylquinoline. Adducts are formed from 2 mol of dimethylketen across the C=N bond of quinolines and isoquinolines to give derivatives of 3,4,5,6-tetrahydro-2-isopropylidene-5,5'-dimethyl-1,3-oxazin-6-one.[683] The products from 2-methyl-, 4-methyl-, 2,4-dimethyl- and 2,6-dimethylquinolines are indicated in (**58**)–(**61**), respectively.



58, R^1 = Me
59, R^2 = Me
60, $R^1 = R^2$ = Me
61, $R^1 = R^3$ = Me

57 $R^1 = R^2 = R^3$ = H, except as indicated

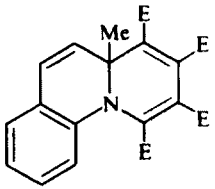
The structures of the adducts formed by acetylene dicarboxylic esters with pyridines, quinolines and isoquinolines to give derivatives of quinolizine and other condensed ring compounds have been the subject of extensive study since they were reported by Diels and Alder,[684] and there have been a number of reviews[685,686] (see also Part I, Section IV.1).

Quinolines with a 2-methyl substituent constitute a special case. They form a number of adducts including the angular substituted 11*a*-methylbenzo[*b*]quinolizines such as (**62**) from 2-methylquinoline. Other adducts with a 2 : 1 ester to quinoline ratio are usually known as types I, II and III and there are also some 'dark red' and 'blue' adducts with an ester to quinoline ratio of 3 : 1 or higher. Types I, II and III had been assigned structures including an azepine ring,[687,688] such as (**63**) for the type I product from 2-methylquinoline, but a recent X-ray crystallographic analysis of the type II compound

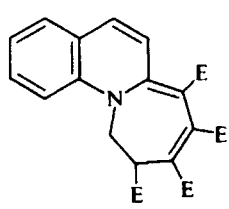
from 6-bromo-2-methylquinoline[689] originally thought to have structure (**64**) showed that the structure was in fact (**65**). From this it was deduced that the corresponding type I compound must be the geometrical isomer (**66**) rather than the bromo derivative of (**63**). The stereochemical assignments of the (9)-ester groups follow from the ^{1}H-nmr spectra. In (**65**) H-1 and the (9)-ester-methyl protons appear at high field owing to shielding of H-1 by the ester carbonyl group and of the (9)-ester-methyl protons by the benzenoid ring.

Adducts of types I and II have been isolated from the reactions of many quinolines[690] with 2-methyl groups or 2-α-hydrogens with dimethyl acetylenedicarboxylate, and their ^{13}C-nmr spectra show that they have structures analogous to those of the adducts from 6-bromo-2-methylquinoline. thus the type I adducts from 2-methyl-, 2,8-dimethyl-, 2,6-dimethyl-, 2,4-dimethyl-, 2,3-dimethyl- and 2-methyl-3-phenylquinolines have been allocated the structures (**67**)–(**72**).

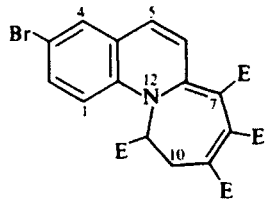
E = CO_2Me



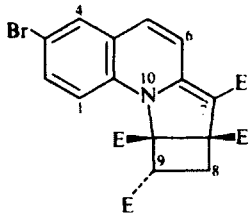
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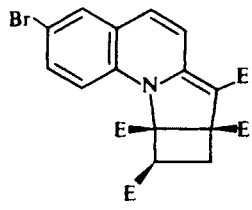
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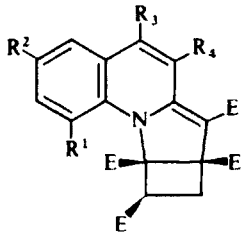
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65



66

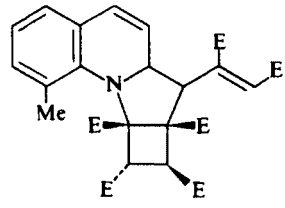


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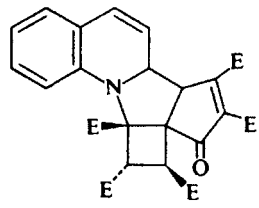
68, R^1 = Me
69, R^2 = Me
70, R^3 = Me
71, R^4 = Me
72, R^4 = Ph

$R^1 = R^2 = R^3 = R^4$ = H, except as indicated

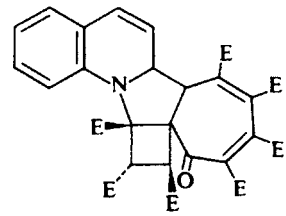
The 'red' 3 : 1 adduct from 2,8-dimethylquinoline has been shown by X-ray crystallographic analysis and by ^{13}C-nmr spectroscopy to have the structure (**73**).[691a] The 'blue' adduct from 2-methylquinoline was separated into a 'blue' and a 'purple' adduct. X-ray crystallographic analysis of the purple adduct[691b] has indicated structure (**74**) and the structure of the 'blue' compound, as shown by ^{13}C- and ^{1}H-nmr spectroscopy and its mass spectrum, was consistent with (**75**). Reference 690 includes a useful brief review of the situation up to that time.



73

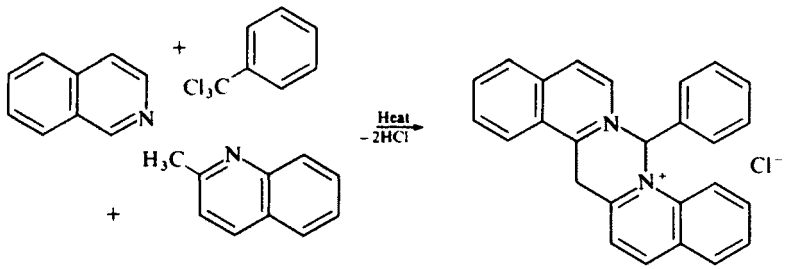


74



75

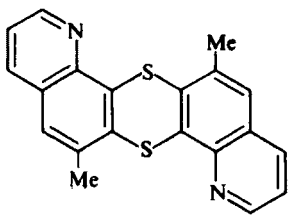
When 2-methylquinoline is heated with isoquinoline, benzotrichloride and zinc chloride at 120 °C, isoquinoline red is formed (equation 44).[809-811]



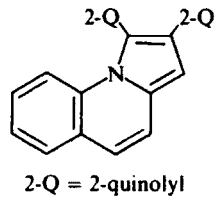
Isoquinoline Red (44)

6-Methylquinoline, when heated with sulphur chloride (S_2Cl_2) or sulphur dichloride (SCl_2) at 150 °C, gives *p*-toluthiaquinanthrene (**76**).[628]

When 2-methylquinoline was heated for 5 h with concentrated sulphuric acid, 1,2-di(2'-quinolyl)pyrrolo[1,2-*a*]quinoline (**76a**) was formed (1.7%),[1073] together with 1,2-di(2-quinolyl)ethane. The same products were also formed by boiling 2-methylquinoline with sulphur for 4 h. It is likely that the pyrroloquinolines are formed by cyclization of 1,2,3-triquinolylpropanes, which can be formed by addition of 2- or 4-methylquinolines across the ethylenic bond of 1,2-diquinolylethylenes.[1097]



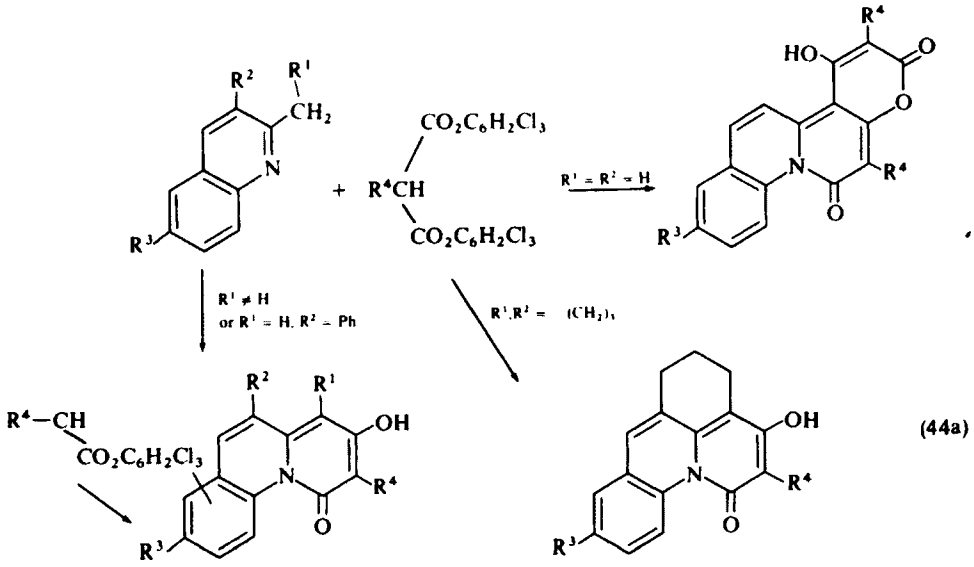
76



2-Q = 2-quinolyl

76a

2-Alkylquinolines other than 2-methylquinoline react with the trichlorophenyl esters of monosubstituted malonic acid at 250 °C to give derivatives of hydroxybenzo[*c*]-quinolizone. 2-Methylquinolines gave a pyranoquinolizone[1591] (equation 44a).



(44a)

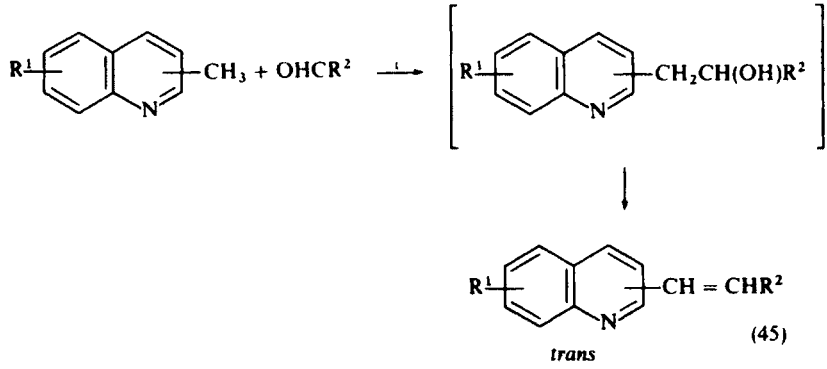
1. Condensation Reactions

a. CONDENSATION WITH ALDEHYDES AND KETONES 2- or 4-Alkylquinolines having a hydrogen atom at the activated α-position of the side-chain participate in aldol-type additions to aldehydes and some ketones. If there are two α-hydrogens, elimination of water from the intermediate carbinol usually occurs readily, or even spontaneously, to give vinylquinolines (alkenylquinolines), styrylquinolines (aralkenylquinolines) or heteroaralkenylquinolines. In many cases, particularly with formaldehyde or chloral, the intermediate carbinols (or di- or trimethylols from formaldehyde) can be isolated.[543,692–697,721,935]

Methyl groups at position 2 are the most reactive, but condensation occurs at position 4 if position 2 is blocked or has already reacted. Thus with benzaldehyde 2,4-dimethylquinoline condenses first at position 2 to give a monobenzal derivative, but with excess of aldehyde and more vigorous treatment the 2,4-dibenzal derivative is formed.[543,698–700] Methyl groups at other positions are unreactive,[701,702,719] although a 2,6-di(2′,4′-dinitrostyryl) derivative has been obtained from 2,6-dimethylquinoline and 2,4-dinitrobenzaldehyde.[703] The presence of an amino group at position 3 prevented all condensation reactions at a 2-methyl group even when the amine was acetylated.[830]

The relative reactivities of methyl groups in condensations with *m*-nitrobenzaldehyde in acetic anhydride formed a series: 9-methylacridine > 4-methylpyridine > 4-methylquinoline > 4-methylbenzo[*h*]quinoline > 4-methylbenzo[*f*]quinoline![704] A variety of condensing agents have been used, including acetic anhydride, zinc chloride, piperidine, sodium hydroxide, potassium methoxide in methanol, aluminium chloride,[705] concentrated hydrochloric acid, iodine[708] or nothing. Acetic anhydride, zinc chloride or no condensing agent are the most common choices. Acetic anhydride has been recommended as better than zinc chloride,[706] and zinc chloride has even been pronounced as harmful.[693]

The reaction has been studied kinetically with both acetic anhydride[707a] and zinc chloride[707b] as catalysts, and with a series of aryl aldehydes. It can be represented by the general equation 45.



(45)

$-CH_3$ = 2- or 4-; R^1 = substituent at any vacant position; R^2 = alkyl, aryl or heteroaryl
i, Heat alone, in solvent or with condensing agent (see text)

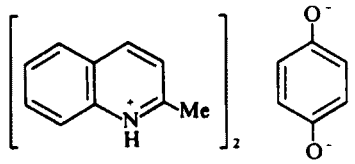
In acetic anhydride containing acetic acid at 130 °C with R^2 in equation 45 = *p*-MeO, *p*-Cl, *m*-NO_2 and *p*-NO_2, the reaction proceeded via addition, esterification (to acetate) and elimination. The intermediate quinolylethanols, and in one case also the acetate, were isolated. Addition was the rate-determining step and in the presence of acetic acid the elimination stage was the fastest. Acetic acid-catalysed addition was promoted by electron-withdrawing substituents on the aldehyde with a Hammett ρ value of +1.42.[707a]

With zinc chloride as condensing agent the mechanism proposed for the formation of 2-styrylquinoline involves the fast formation of a carbanion–$ZnCl_2$ complex from quinaldine, which then attacks the aldehyde in the rate-determining stage. The lack of reactivity of some methylquinolines was attributed to inadequacies of the carbanions formed rather than to difficulties in their formation. Rate constants for the various reaction steps were measured and an Arrhenius plot for the reaction of benzaldehyde with quinaldine at five temperatures gave the activation energy E_a = 22.2 kcal mol^{-1}, the enthalpy of activation ΔH^* = 21.4 kcal mol^{-1}, the free energy of activation ΔF^* = 27.7 kcal mol^{-1} and the entropy of activation ΔS^* = −16.7 e.u. mol^{-1} at 104 °C.[707b]

Details of the products formed and reaction conditions used can be found from the references given below and the tables of appropriate products (Tables 44, 46 and 47).
Vinylquinolines (2- and 4-quinolylalkenes): references 65, 139, 693, 709–718, 720.
2-Styrylquinolines: references 40, 87, 100, 104, 105, 139, 175, 543, 693, 698–708, 722–765, 929–933, 943, 954; [2-(2'-quinolyl)ethenyl]ferrocene, 1639
4-Styrylquinolines: references 61, 101, 431, 432, 543, 709, 717, 735, 744, 752, 766–775, 943, 951, 952.
1-(2'-Quinolyl)-2-heteroarylethenes: references 121, 776–794, 1525, 1543, 1546.
1-(4'-Quinolyl)-2-heteroarylethenes: references 779, 783, 784, 795–799, 946, 1525.
Quinolylbutadienes: references 103, 759, 800–803, 934, 955.
Quinolylhexatriene, -octatetrene and -dodecahexene: reference 803.

2-Methylquinoline also forms condensation products with a number of reactive ketones when they are heated together at 140 °C for suitable periods from 0.5 to 2.5 h.[834]

With $CO(CO_2Et)_2$, diethyl 2-quinaldyl tartronate was formed (47%); $CO(PhCO)_2$ gave quinaldylbenzoyl carbinol (24%); $PhCOCOCO_2Et$ gave ethyl quinaldylbenzoylglycolate (4%), but in dioxan the yield was increased to 54%; alloxan hydrate gave 5-hydroxy-5-(2-quinolyl)barbituric acid, and PhCOCOPh (benzil) in a steel bomb at 175 °C gave 38% of 1-(2′-quinolyl)-2-phenyl-2-benzoylethylene. The reaction of 2-methylquinoline with benzil has been confirmed and 2,3-dimethylquinoline gives the corresponding 3-methylquinolyl product.[835] Crystalline products were also formed with *p*-benzoquinone and phenanthraquinone[835] and the adduct with *p*-benzoquinone has been assigned the structure (**77**).[836] 2-Methylquinoline and 2,6-dimethylquinoline also react with Michler's hydrol (*p*-dimethylaminobenzyl alcohol) with loss of water to give 1-(2′-quinolyl)-2-*p*-dimethylaminophenylethane, or the 1-(6′-methyl-2′-quinolyl) derivative.[837]



77

TABLE 27. Products from Claisen Condensations with Alkylquinolines

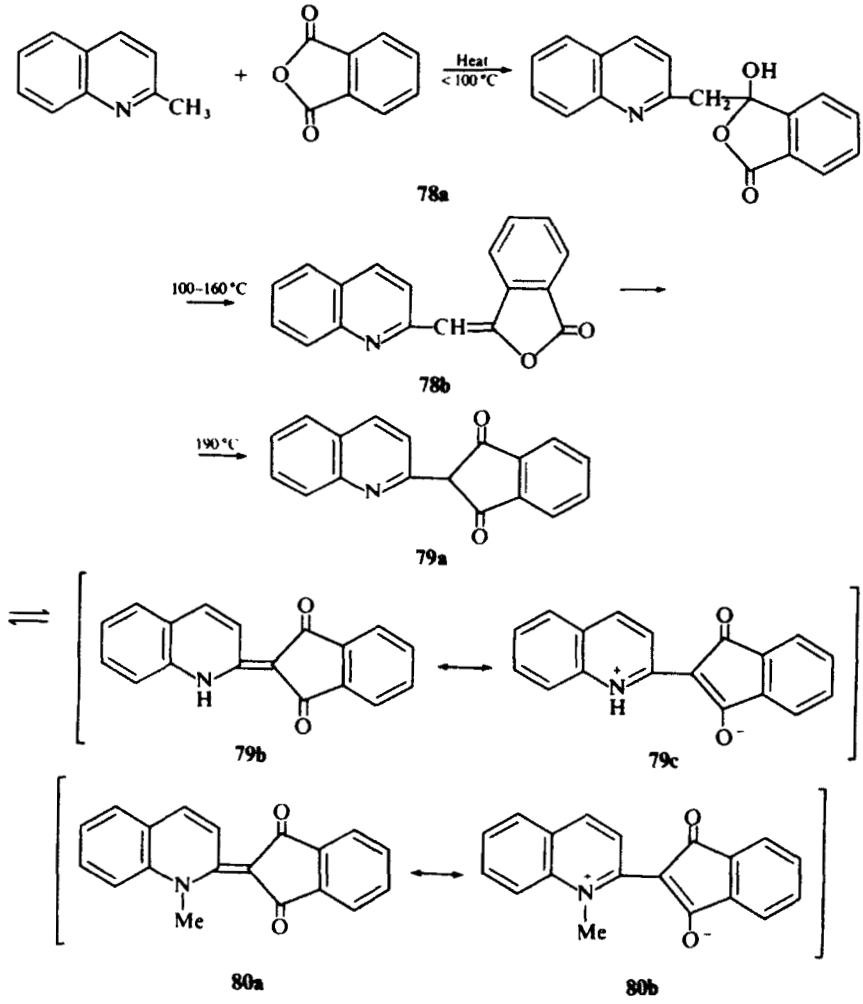
Alkyl-quinoline substituent	Ester	Reaction conditions	Product quinoline substituent (%)	Ref.
2-Me	$(CO_2Et)_2$	KOEt, Alc/Et_2O	2-CH_2COCO_2Et (90%)	804
4-Me	$(CO_2Et)_2$	KOEt, Alc/Et_2O	4-CH_2COCO_2Et (90%)	804
3-Me	$(CO_2Et)_2$	KOEt, Alc/Et_2O	No reaction	804
2-Me	$PhCO_2Et$	2–3 equiv. KNH_2	2-CH_2COPh (60–65%)	805
	p-$BrC_6H_4CO_2Et$	2–3 equiv. KNH_2	2-$CH_2COC_6H_4Br$-*p* (43%)	805
	o-$ClC_6H_4CO_2Et$	2–3 equiv. KNH_2	2-$CH_2COC_6H_4Cl$-*o* (35%)	805
	p-$MeOC_6H_4CO_2Et$	2–3 equiv. KNH_2	2-$CH_2COC_6H_4OMe$-*p* (72%)	805
	p-$MeC_6H_4CO_2Et$	2–3 equiv. KNH_2	2-$CH_2COC_6H_4Me$-*p*	805
2,3-$(CH_2)_3$	$(CO_2Et)_2$	KOEt, Alc/Et_2O	2,3-CH($COCO_2Et$)$(CH_2)_2$	806
2,3-$(CH_2)_4$	$(CO_2Et)_2$	KOEt, Alc/Et_2O	2,3-CH($COCO_2Et$)$(CH_2)_3$ (50%)	806
2-Me	$PhCO_2Et$	KNH_2 (liq. NH_3)	2-CH_2COPh (62%)	807
	CH_3CO_2Ph	KNH_2 (ether)	2-CH_2COCH_3 (35%)	807
	$(CH_3CO)_2O$	$NaNH_2$ (ether)	2-CH_2COCH_3 (36%)	807
4-Me	$PhCO_2Et$	KNH_2 (ether)	4-CH_2COPh (44%)	807
	$PhCO_2Et$	$NaNH_2$ (liq. NH_3)	4-CH_2COPh (56%)	807
2-Me	$(CO_2Et)_2$	(i) KNH_2 (liq. NH_3, Et_2O)	2Q—CH=C(CO$_2$H)—CH_2—2Q[a]	808
		(ii) 6-N AcOH	(No Claisen product)	

[a] 2Q = 2-quinolyl.

2-Methylquinoline can also participate in Mannich reactions; thus with equimolar amounts of diethylammonium chloride and formaldehyde in aqueous solution a good yield of 2-(2′-diethylaminoethyl)quinoline was obtained, although diethylamine does not react with methylolquinaldine.[838]

b. CONDENSATIONS WITH ESTERS The α-hydrogen atoms of 2- and 4-alkylquinolines are sufficiently acidic to enable them to participate in reactions, such as the Claisen condensation, which involve attack by the carbanion at a positive carbon centre. Table 27 gives the results of condensations with a selection of esters.

c. CONDENSATIONS WITH PHTHALIC ANHYDRIDE AND RELATED DERIVATIVES OF DI- AND POLYCARBOXYLIC ACIDS When 2-methylquinoline is heated cautiously with phthalic anhydride, compound (**78a**) is formed, followed at 100–160 °C by (**78b**) (iso-



SCHEME 18

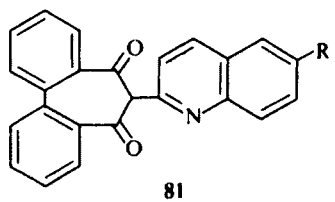
quinophthalone), and finally at about 190 °C quinophthalone (quinoline yellow) (**79a, b, c**) is formed[100,791,810c,d,812–815] (Scheme 18).

Spectroscopic similarities between *N*-methylquinophthalone (**80**) and quinophthalone indicate that the hybrid tautomer (**79b** ↔ **79c**) is the more important. The extended conjugation of the dipolar contributions (**79c** and **80b**) can account for the colour.[816]

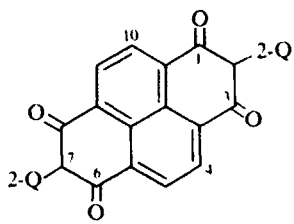
Other alkylquinolines having a methyl group at position 2 can form related quinophthalones, e.g. 2,4-dimethylquinoline,[429,818,825] 2,6-dimethylquinoline,[812a,c,814b] 2-methyl-4-ethylquinoline,[825] 2,8-dimethyl-5-isopropylquinoline,[820] 2,6,8-trimethylquinoline,[812c,821,822] 2-methyl-4-phenylquinoline,[817,819] 2-methyl-4-benzylquinoline,[730] 2-methyl-8-chloroquinoline, 2-methyl-8-bromoquinoline and 2-methyl-8-hydroxyquinoline.[1662]

4-Methylquinoline has been reported to condense with phthalic anhydride to give a phthalone,[812e] but normally only methyl groups at position 2 react leaving other groups originally present as substituents on the phthalone. As with 2-methylquinoline itself, 2,6-dimethyl- and 2,6,8-trimethylquinolines all give 'isoquinophthalones' corresponding to (**78b**) when heated to 100–160 °C. Although zinc chloride is usually recommended as a condensing agent to give the phthalone, this can be formed by heating the reactants on their own and at least one report[815] states that the use of zinc chloride reduces the yield owing to the formation of a double salt with the original quinoline base. *o*-Dichlorobenzene has been suggested as a solvent or diluent for the reaction.[823] The quinophthalone can be sulphonated with fuming sulphuric acid (23% SO_3, 150 °C, 2 h) and the sodium sulphonate salt had a fastness to light equal to that of the original quinoline yellow.[820]

Similar condensations have been reported with other anhydrides of di- and polycarboxylic acids. 2-Methylquinoline and diphenic anydride gives with zinc chloride ($ZnCl_2$) 49% of (**81**, R = H). Without $ZnCl_2$ the yield was 33% and with excess of $ZnCl_2$ 11%;[824] with 2,6-dimethylquinoline the 6-methyl group did not participate and (**81**, R = Me) was formed. 2-Methylquinoline condenses with the anhydrides of naphthalene-1,4,5,8-tetracarboxylic acid and perylene-3,4,9,10-tetracarboxylic acid[826] to give 2,7-di-(2'-quinolyl)-1,3,6,8-tetraoxo-1,2,3,6,7,8-hexahydropyrene (**82**) and 2,9-di(2'-quinolyl)-1,3,8,10-tetraoxo-1,2,3,8,9,10-hexahydrodibenzo[*cd,ij*]perylene (**83**), respectively.

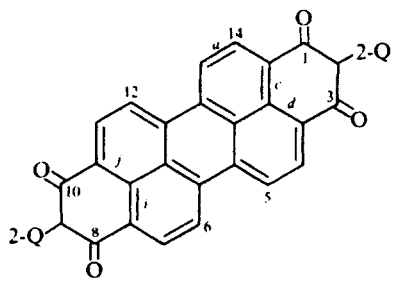


81



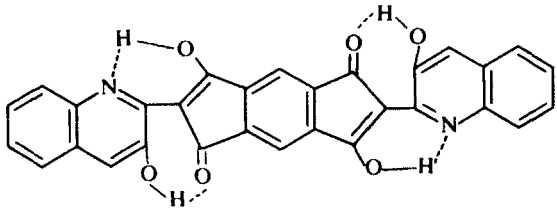
2-Q = 2-quinolyl

82



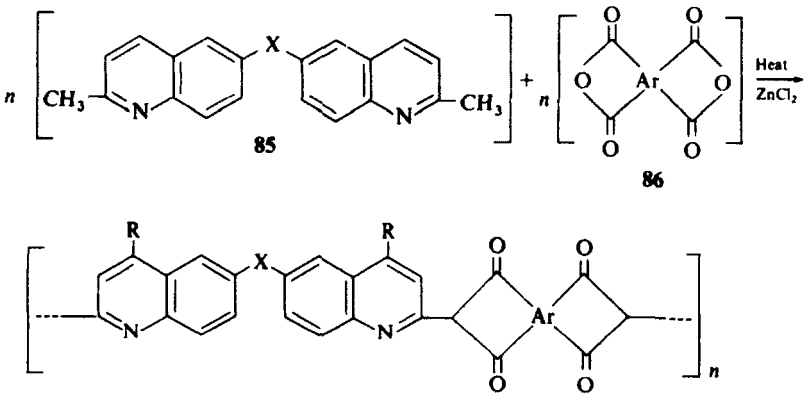
83

The dianhydride of pyromellitic acid (benzene-1,2,4,5-tetracarboxylic acid) gave diquinophthalone pigments with 2-methylquinoline, 2,3- and 2,4-dimethylquinolines, and also with 3-hydroxy-2-methylquinoline (**84**). The presence of intramolecular hydrogen bonds was indicated by ir and nmr studies of (**84**), which also showed good light and migration fastness in plasticized PVC.[827]



84

Polyquinophthalones (**87**) have been prepared by condensations of bis-2-methylquinolines (**85**) and aromatic tetracarboxylic acid anhydrides (**86**) in the presence of zinc chloride[828,1431,1492] equation 46).



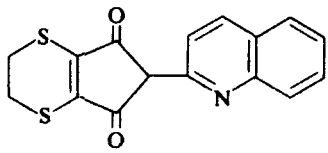
85 **86**

(46)

87

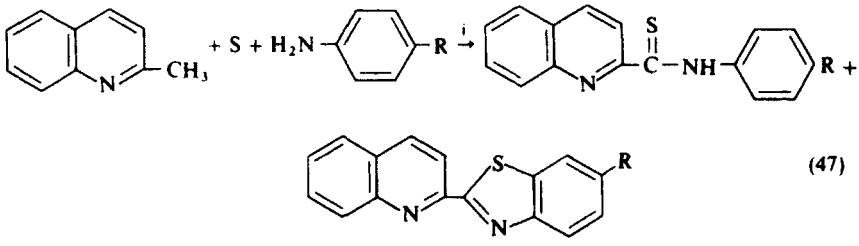
R = H, Me; X = O, SO_2, CH_2 or direct bond

When condensed with 3,6-dithia-3,4,5,6-tetrahydrophthalic anhydride, 2-methylquinoline (and a variety of 2-methylpyridine derivatives) gave the appropriate dithiaphthalones, such as (**88**) from 2-methylquinoline.[829]



88

d. CONDENSATIONS WITH AMINES AND SULPHUR; WILLGERODT–KINDLER REACTION 2-methylquinoline condenses with some *para*-substituted anilines and sulphur to give thioamides and the benzothiazolylquinolines (**89**)[831] (equation 47). With β-

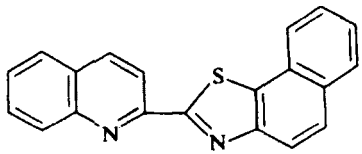


(47)

89

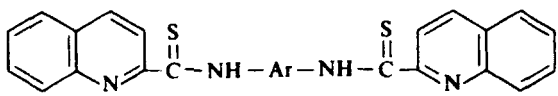
i, Reflux, 160–165 °C, 20 h, ($-H_2S$)
R = H, Me, OMe, OEt*, OPr, OPr^i*, OBu
* With R = OEt or OPr^i (**90**) was obtained only by a modified procedure

naphthylamine, 2-(2′-quinolyl)naphtho[2,1-*d*]thiazole (**90**) was formed.[1227] In the same way with R = Cl, Br, CO_2H, SO_2NH_2 or NMe_2 in equation 47 or using 2-aminoquinoline in place of the aniline derivative the appropriate thioamides were obtained.[832a] With R = NO_2 in equation 47 the product was 1,4-bis(2′-thioquinaldinamido)benzene

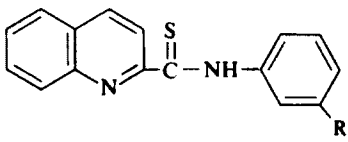


90

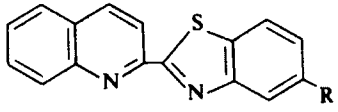
(**91**) and with benzidine as the amine function the biphenyl derivative 4,4′-bis-(2″-thioquinaldinamido)biphenyl (**92**) was obtained. Similar products were also obtained with *o*-toluidine, 4,4′-diaminodiphenylsulphide, di(*p*-aminophenyl)methane, 3,6-diaminocarbazole, 2,7-diaminofluorene, urea and guanidine carbonate. With hydrazine, 1,2-di(2′-quinolyl)ethane (3.6%) was isolated,[832b] which can also be formed when 2-methylquinoline alone is heated with sulphur. With *o*-phenylenediamine, 2-methylquinoline and sulphur at 150–210 °C, 2-(2′-benzimidazolyl)quinoline was formed.[1526] In order to clarify the mechanism of the cyclization of thioanilides to benzothiazoles, 2-methylquinoline was heated with a series of *m*-(Me, Cl or H)-substituted anilines or nitrobenzenes and sulphur by the Willgerodt–Kindler method (I) and by a modified Jacobsen reaction (II). Method (I) gave a thioanilide (**93**) and one of the possible benzothiazoles (**94a** or **b**), but method II gave both possible benzothiazoles.[833]



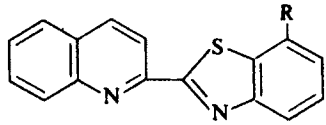
91, Ar = *p*-phenylene
92, Ar = 4,4′-biphenylene



93



94a



94b

J. Photochemical Reactions

Photodebromination of bromoquinolines and bromoalkylquinolines (e.g. 4-bromo-2-methylquinoline) results from ultraviolet irradiation of an aqueous–alcoholic solution of the base containing sodium hydroxide or potassium cyanide or an aliphatic amine.[841] The reaction is reported to involve electron donation by the nucleophile to the excited bromoquinoline to give a radical anion which loses Br^-. The heterocyclic radical can then abstract hydrogen from the alcohol.

2-Alkylquinolines with three or more carbons in the side-chain, capable of splitting off an alkene, undergo the McLafferty rearrangement when irradiated.[842a,214] 2-Butylquinoline after 58 h gave 45% of 2-methylquinoline and propylene, whereas 2-ethylquinoline was stable after irradiation for 60 h. If the γ-hydrogen on the side-chain is attached to an oxygen atom, e.g. 2-(2′-quinolyl)ethanol, then an aldehyde is formed in place of the olefin.[842b]

Mass spectrometric examination of deuterium-labelled 2-propylquinoline showed that it underwent the McLafferty rearrangement as a result of electron-impact fragmentation. 2-(2′-Hydroxyethyl)quinoline gave 73% of 2-methylquinoline and formaldehyde after irradiation for 18 h. The formation of 2-deuteriomethylquinoline and formaldehyde from 2-(2′-deuterioxyethyl)quinoline indicated that abstraction of hydrogen from the hydroxyl group must occur. On irradiation 2-(2′-methoxyethyl)quinoline was stable and in the mass spectrometer the base peak was due to the 2-vinylquinoline cation.

4-Methylquinoline was among the compounds studied by irradiation in methanol, ether or methanol acidified with hydrochloric acid.[843] Semiquinone radicals were detected by esr spectroscopy. In the neutral solvents hydrogen abstractin occurred by a monophotonic process from an (n–π^*) excited state, whereas in the acidic medium a biphotonic process occurred which involved electron transfer from methanol to a protonated upper excited triplet state of the heterocycle.

Photorearrangements of methylquinoline *N*-oxides by irradiation for 24 h in solution, or in potassium bromide discs, resulted in the formation of good yields (~90%) of the corresponding 2-(1*H*)-quinolones,[844] with the exception of 2-methylquinoline-*N*-oxide, which gave a poor yield of 3-methyl-2-(1*H*)-quinolone and an unidentified compound when irradiated in a potassium bromide disc.

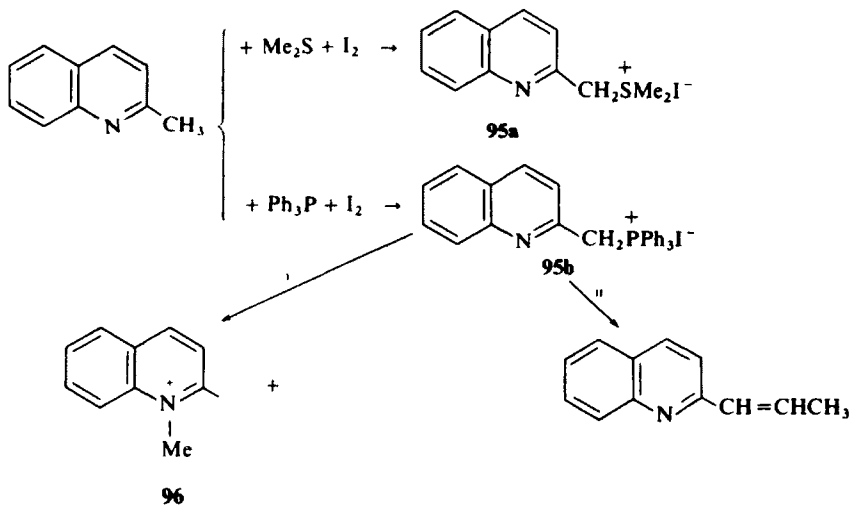
When exposed to sunlight for 1 week as a fine powder or in solution in benzene, benzylidenequinaldine [1-(2′-quinolyl)-2-(phenyl)ethylene] dimerized to what was believed to be one of the isomeric di(2-quinolyl)diphenylcyclobutanes.[1547]

K. Salt Formation and Complexes

Alkylquinolines form salts as a result of protonation by acids and quaternization by alkyl or acyl halides or other potential electrophilic species such as dimethyl sulphate or cyanogen iodide.[845] In these respects they resemble quinoline itself. The general effects of the alkyl substitutents are to increase the basic properties as a result of their electron-donating character but substituents at position 2 or 8 may interfere with quaternization or complex formation as a result of steric effects.

a. Quaternary Salts The steric effect of a substituent at position 2 is shown by a comparison of the reactions of 2- and 4-methylquinolines with α,ω-dibromoalkanes.[846,847] 4-Methylquinoline gives bis-quaternary salts with only small amounts of elimination products with all the halides except for dibromoethane. 2-Methylquinoline, and other 2-substituted quinolines, give only elimination products in all cases.

Sulphonium and phosphonium salts with 2-quinaldyl substituents (**95a** and **b**) have been prepared by treating 2-methylquinoline with dimethyl sulphide or triphenylphosphine and iodine.[848,849] Methylation of the nitrogen with dimethyl sulphate followed by addition of sodium perchlorate gave the diquaternary salt (**96**). When treated with alcoholic sodium ethoxide and then acetaldehyde, (**95**) gave 2-propenylquinoline (Scheme 19); 2,4- and 2,6-dimethylquinolines behave similarly.



i, Me_2SO_4, heat $NaClO_4$; ii, EtONa, CH_3CHO

SCHEME 19

b. Charge-transfer Complexes Alkylquinolines form numerous complexes of the donor–acceptor type, particularly with halogens and organic compounds. Most of the complexes with aromatic polynitro compounds are useful for purification and identification purposes. The following are examples: bromine,[850] iodine,[851,852] catechol, resorcinol and quinol,[1640] benzoic acid,[1642] 2′-hydroxy-2,4,4,4′,7-pentamethylflavan,[853]

phloroglucinol,[854] 1,3,5-trinitrobenzene,[855,856,1641] picric acid,[856] 2,4,7-trinitrofluorenone,[857] styphnic acid,[858] 3,5-dinitro-*p*-toluic acid,[859] 2-nitro-1,3-indandione,[860,1643] tetracyanoquinodimethane[1503] and 2-hydroxy-3,5-dinitropyridine.[1644]

c. COMPLEXES WITH BORON AND METALS Alkylquinolines form amine boranes with sodium borohydride,[861] coordination compounds with triphenylboron[862] and highly coloured insoluble complexes with decaborane.[863] Examples of the many complexes with metal ions or organometallic compounds will be found in the following papers: aluminium,[864] beryllium,[865] cadmium,[866-868,924] copper (Cu^+),[869,870] copper (Cu^{2+}),[871-878,1646] chromium,[879,1533] cobalt,[880-882,1645] dysprosium,[1647] gold,[1389] iron,[883-886,1646] manganese,[887-889,1646] mercury,[890-894] molybdenum,[895] nickel (Ni^{2+}),[878,896-900,1646,1648] niobium,[901] osmium,[902,903] palladium,[904,905,1649] rhenium,[906-909] rhodium,[910] silver (Ag^+),[911,912] tin (Sn^{4+}),[913] titanium (Ti^{3+}),[914] (Ti^{4+}),[915] tungsten,[916] vanadium,[914,917,1646] zinc,[918-921] and zirconium.[922] The recovery of copper from leaching solutions using 6-dodecyl-3-methylquinaldinic acid has been described.[874] The copper chelate was partitioned into kerosene. Tungsten can be recovered from effluent waste from the preparation of W–Ni sulphide catalysts by addition of water-soluble alkylquinolines.[916] An optically active complex is described[904] in which the chirality of a carbon involves a carbon to palladium bond.

II. Alkenylquinolines and Aralkenylquinolines

1. Preparation

Many alkenylquinolines can be prepared by methods already described for the direct synthesis of quinolines (see Section I.1) or for the preparation of alkylquinolines from quinoline compounds (see Section I.3). Examples include 2-propenylquinoline, 2-(2'-methylpropenyl)quinoline[925,926] and cyclopentenylquinoline[927] by the Friedländer synthesis, 2,3-cycloheptadecadienoquinoline[928] by the Pfitzinger synthesis, 2-vinylquinoline and 2-methyl-4-(2'-propenyl)quinoline,[125,126,923,925] cyclopentenylquinoline[127] and 2-(3'-butenyl)quinoline[124] by the action of organometallic reagents on quinoline. The following sections describe methods which are more specfic for alkenyl- or aralkenylquinolines but which have their parallel for the synthesis of the corresponding pyridine derivatives.

A. Dehydration of Carbinols

Elimination of water from a quinolylcarbinol is one of the commonest methods for the preparation of vinyl and styrylquinolines and related compounds. The elimination may be acid or base catalysed and occurs readily when the new double bond is conjugated with the quinoline ring system. The carbinols themselves are most frequently obtained by an aldol type of addition between a 2- or 4-alkylquinoline and an aldehyde or ketone. To obtain alkenyl substituents at other positions of the quinoline ring the appropriate quinoline aldehyde must be used and condensed with a suitable compound having an active hydrogen. The elimination of water frequently occurs without isolation of the intermediate carbinol[936] and such cases are considered in the next section (Section II. 1b); see also (Section I.5,I.a). Examples of dehydration of carbinols are given in Table 28. Elimination of water from the isomeric 1- or 3-hydroxycyclopenteno[*b*]quinolines (**97a** and **b**) gave a mixture of the tautomeric (1*H*)-, (3*H*)- and (4*H*)-cyclopentadieno-[*b*]quinolines (**98**), (**99**) and (**100**), respectively[940] (see equation 48).

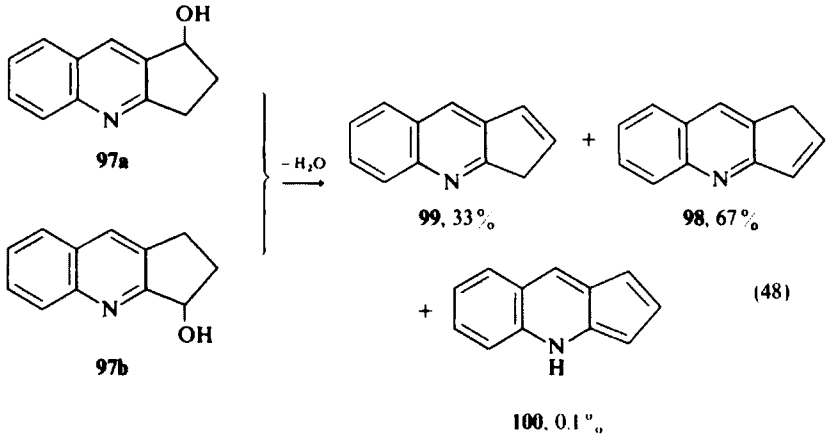


TABLE 28. Alkenylquinolines Formed by Dehydration of Quinolylcarbinols

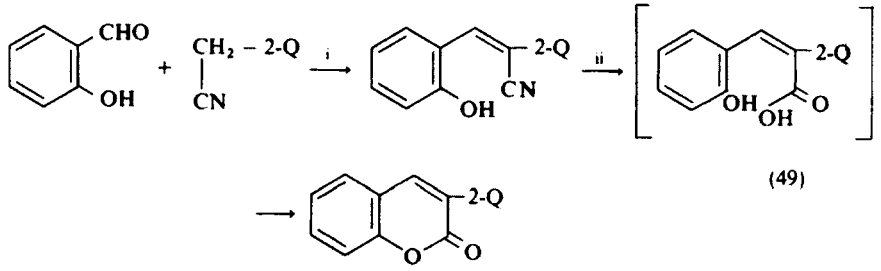
Position	Quinolyl carbinol substituent	Dehydration conditions	Ref.
2	CH_2CH_2OH	AcOH, HCl, 150–160 °C	964
2	CH_2CH_2OH	NaOH, polyglycol, 180 °C, or 1% $KHSO_4$, 1% $NH_4H_2PO_4$, 1% H_3PO_4 or 1% H_2SO_4	1053
2	$CH_2CH(OH)CCl_3$	PCl_5, $CHCl_3$	965
2	$CH_2CH(OH)$ Ph	Ac_2O	966
2	$CH_2C(OH)MeCMe{=}CHCH{=}CHPh$	Et_2O, dry HCl	963
2	$CH_2CHOHCH{=}CHPh$	Et_2O, dry HCl	963
2	$CH_2C(OH)Ph_2$	—	635
2	$CH_2COH(Ph)(o\text{-}NH_2C_6H_4)$	H_2SO_4 (Conc.) 45 min 90 °C	937
2	$CH_2COH(p\text{-}MeOC_6H_4)(o\text{-}NH_2C_6H_4)$	H_2SO_4(conc.) 1 h, 95 °C	937
2	Cyclopentan-2-ol	KOH, hydroquinone 0.05 mmHg	938
2	Cyclohexan-2-ol	Ac_2O, heat	939
2	Cyclohexan-2-ol	$KHSO_4$	1319
2	$CH_2CH(OH)C_6H_4NO_2\text{-}p$	Ac_2O, heat	953

B. Condensations with Carbonyl Compounds

Probably the most important method for the preparation of 2- and 4-vinyl, styryl and 2-heteroarylvinylquinolines is the direct condensation of a quinoline derivative having a methyl group at position 2 or 4 with an aldehyde or ketone by heating the compounds together without a condensing agent or with acetic anhydride or zinc chloride. This reaction has been discussed in Section I.5.Ia and the references given there, in conjunction with Tables 44, 46 and 47, should enable details of individual preparations

to be found. The reaction normally proceeds by dehydration of the intermediate carbinol, formed as described in Section II.1.A, which is not actually isolated.

The following are variations of this method, the most important of which uses a quinoline aldehyde together with a suitable potential carbanion. This reversal of the functional groups enables condensations to be made at positions other than 2 and 4 of the quinoline ring. Quinoline 6- and 8-carbaldehydes have been condensed with *p*-nitrophenylacetic acid,[948] 2- and 4-methylpyridines, 9-methylacridine[944b] and various thiazoles and selenazoles[944a,946] to give the appropriate 1-(6′-quinolyl)-2-aryl(or heteroaryl)ethenes, with loss of carbon dioxide from the nitrophenylacetic acid condensations. The nitrostyrenes were also subsequently reduced with tin and hydrochloric acid to the aminostyrenes.[948] 3-*p*-Nitrostyrylquinoline and 8-*p*-nitrostyrylquinoline[947,948] were prepared similarly by heating the aldehydes with *p*-nitrophenylacetic acid and a trace of piperidine at 130–140 °C, (yield 60%).[947] 3-(2′-Quinolyl)coumarin (**101**) was prepared from salicylaldehyde and 2-quinolylacetonitrile[950] (equation 49).

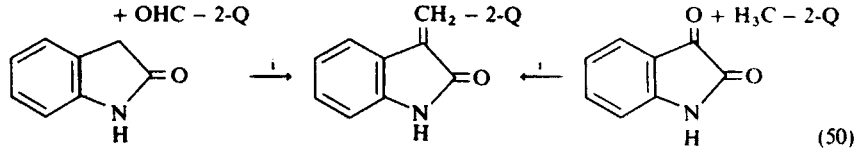


(49)

101

2-Q = 2-quinolyl
i, Piperidine; ii, hydrolysis and ring closure

3-Quinaldinylideneoxindole (**102**) was formed both by condensation of quinoline-2-carbaldehyde and oxindole (**103**) or from isatin (**104**) and quinaldine[945] (equation 50). Quinoline 2-, 4-and 6-carbaldehydes have been condensed with 1,2,3,4-tetraphenylcyclo-



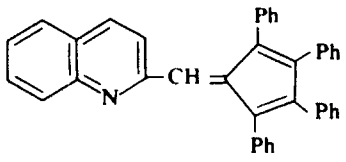
(50)

103 **102** **104**

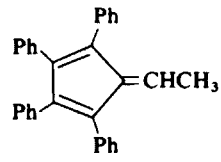
2-Q = 2-quinolyl
i, Fusion with $ZnCl_2$

pentadiene and sodium methoxide to give the 6-substituted fulvenes, e.g. (**105**) and 6-methyl-1,2,3,4-tetraphenylfulvene (**106**) with quinoline-4-carbaldehyde gave 1-(4′quinolyl)-2-(1″,2″,3″,4″-tetraphenylfulven-6″-yl)ethylene (**107**).[961]

A series of aromatic aldehydes including benzaldehyde, pyridine-2- and -4-carbaldehydes and quinoline-2- and -4-carbaldehydes (RCHO) condense with

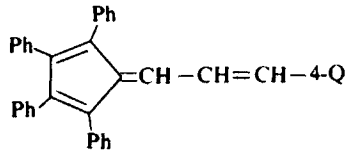


105



106

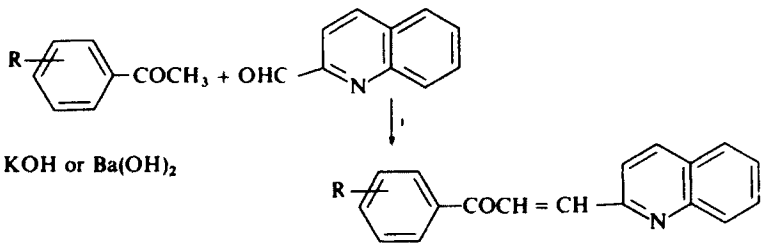
4-Q = 4-quinolyl



107

$Ph_2P(O)CHPhP(O)(OPh)_2$ to give 12–73.5% yields of the phosphinylstilbenes $Ph_2P(O)CPh = CHR$.[1524] Mixtures of *cis* and *trans* products were obtained and the larger quinoline aldehydes gave predominantly *cis*-isomers and the smaller phenyl or pyridyl aldehydes formed the *trans*-isomers preferentially.

Various 1-benzoyl-2-(2′-quinolyl)ethenes (**108**, R = H, 4-Cl, 4-OH, 3-CO_2H and 3-NO_2) were prepared by condensation of quinoline-2-carbaldehyde with the appropriately substituted acetophenone in the presence of potassium hydroxide or barium hydroxide[461] (equation 51).



i, KOH or $Ba(OH)_2$

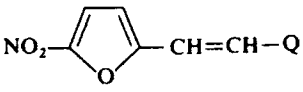
(51)

108

Wittig reagents or phosphoranes can be used to convert quinoline aldehydes into quinolylalkenes, styrylquinolines or heteroarylvinylquinolines,[128,129,848,956,1527] e.g. 3-styrylquinoline was prepared by the Wittig synthesis from quinoline-3-carbaldehyde and benzyltriphenylphosphonium bromide. The product was a mixture of *cis*- and *trans*-isomers, which were separated by column chromatography on alumina. Elution with light petroleum gave the *cis*-isomer, followed by benzene, which gave the *trans*-isomer.[1527] Compounds (**109**) were prepared from quinoline-2- or -4-carbaldehydes and the Wittig reagent from 5-nitro-2-furylmethyl chloride[949] and (**110a**) was prepared from quinoline-2-carbaldehyde and the Wittig reagent from *p*-bischloromethylbenzene.[941]

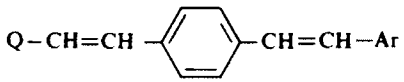
The reaction has also been used to synthesize unsymmetrical divinylbenzenes, e.g. (**110b**) using *p*-Q—CH=CH—C_6H_4—$CH_2P^+Ph_3Br^-$ as the Wittig reagent and ArCHO as the aldehyde. Yields of 50–95% were obtained.[1530]

2-Diethyl quinolylmethyl phosphonate and benzaldehyde condense in dioxan with potassium metal to give 2-styrylquinoline.[942]



109

Q = 2- or 4-quinolyl



110

(a) Q = Ar = 2-quinolyl
(b) Q = 2-quinolyl, Ar = 2-furyl, *p*-tolyl, *p*-$Me_2NC_6H_4$, *p*-$Ph_3P{=}NC_6H_4$

C. Miscellaneous Methods of Preparation

When 5-nitroquinoline and α-methylstyrene are passed through a Vycor tube at 600 °C under nitrogen with a contact time of 11.4 s, 1-phenyl-1-methyl-2-(5′-quinolyl)ethylene (18%) and 5-(1′-phenyl-2′-propenyl)quinoline (14%) were formed.[957]

A ring expansion of skatole when treated with 3-chloro-3-methyl-1-butyne in acetone and anhydrous potassium carbonate gave a 30% yield of the yellow compound 4-methyl-3-(2′-methylpropenyl)quinoline.[958] Flash thermolysis of 1-(2′-quinolyl)-1-acetoxy-3-butene through a quartz tube at 500–900 °C gave 1-(2′-quinolyl)butadiene and 1,2-dihydroacridine as the main products, together with benzo[*f*]quinoline (10%).[959] 2-Methylquinoline has been vinylated to give 2-allylquinoline by addition across the triple bond of acetylene in an autoclave at 200 °C and 35–40 atm in the presence of powdered potassium hydroxide.[591] Benzylation of 2-and 4-methylquinoline and 2,4-dimethylquinoline was achieved by treatment of the bases with benzyl alcohol and potassium hydroxide followed by dehydrogenation either spontaneously[960] or by means of added benzaldehyde.[224] Diazotization of 5-aminoquinaldine in dilute hydrochloric acid and coupling with cinnamic acid in acetone in the presence of sodium acetate and copper(II) chloride gave 5-styrylquinaldine (13%). 6-Styrylquinaldine was obtained by the same method, and also 5- and 6-(4′-phenylbutadien-1′-yl)quinaldine. 2-Methyl-8-aminoquinoline, however, gave only 2-methyl-8-chloroquinoline.[617]

The direct alkylation of quinoline with olefins and SiO_2–Al_2O_3 catalysts and dehydrogenation of the alkylquinoline to an alkenylquinoline has been described,[117] and also a process for improving the yield of the unsaturated product by depolymerization at low pressures (10–19 mmHg).[962]

Two Claisen-type rearrangements result in the formation of alkenylquinolines in high yields. When a suspension of the salt of 1-crotyl-2-methylquinolinium bromide in benzene is treated with 1N sodium hydroxide solution, 3-methyl-4-(2′-quinolyl)but-1-ene is formed[212] (see equation 22, Section I.3.H.a). Also an allyl group from a 4-quinolyl allyl ether can migrate to the α-carbon of an alkyl side-chain at position 2 to give an alkenyl quinoline[1054] (see Schemes 20 and 21, Section II.3.E).

When the hydrobromide of 3-bromo-3-(2′-quinolyl)propanoic acid was heated with potassium carbonate, decarboxylation and elimination of hydrogen bromide gave a poor yield of 2-vinylquinoline.[965] Similarly, β-iodoethylquinoline, when boiled with sodium hydroxide in acetone solution, gave 4-vinylquinoline.[967]

2. Physical Properties and Uses

A. General Physical Properties

A summary of the physical properties of alkenylquinolines and aralkenylquinolines is given in Tables 44–47. The vinylquinolines, in common with many other similar compounds (e.g. styrene and vinylpyridines), readily polymerize. 2-Vinylquinoline could not be distilled at 10 mmHg;[761] 4-vinylquinoline solidified slowly when kept under vacuum and most of the compound polymerized when distilled under high vacuum.[967]

The dipole moments calculated from dielectric data in benzene at 25 °C were found to be 2.0 D for vinylquinoline and 2.16 D for 2-isopropenylquinoline. The direction of the dipole of the vinyl group is towards the ring with the more negative carbon next to the ring.[968]

The polarographic behaviour of some pyridylvinylquinolines has been investigated.[969] All the compounds were polarographically active and were reduced to ethane derivatives in the first phase of the irreversible electrode processes, followed by reduction of the quinoline ring.

The partition of a series of organic bases, including 8-methylquinoline, 2-phenylquinoline and 5,6- and 7,8-benzoquinolines, between aqueous phosphoric acid and a series of organic solvents has been studied by paper chromatography using the moist paper technique. The order of increasing extraction ability was cyclohexane < pentanol < benzene ≈ trichloroethane < chloroform, except at high phosphoric acid concentrations when pentanol was the strongest solvent.[396]

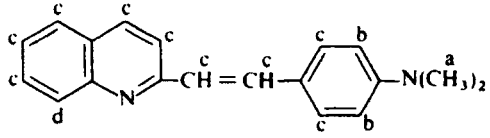
B. Spectroscopic Properties

The absorption spectra of styrylquinolines[970] and substituted styrylquinolines[971,972] in the ultraviolet and visible regions show bands at λ_{max} 285 nm (log ε = 4.486), 324 nm (log ε = 4.449) and 339 nm for 2-styrylquinoline.[970] The absorption spectra of a series of 2-(3′,4′-hydroxy- and -methoxystyryl)quinolinium iodides has been studied in the 200–1000 nm region in dimethylformamide, methanol, aqueous alkali and water. Four bands were observed in the regions 485–590, 375–450, 292–330 and 210–230 nm.[973]

The influence of the nitro group in 2-(*o*,*m*- and *p*-nitrostyryl)quinoline on selected vibration bands in the infrared specta has been investigated.[1523]

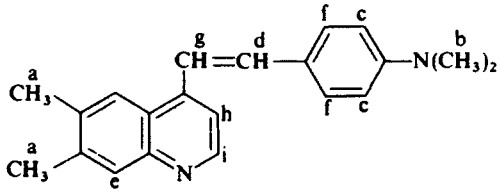
The photochemistry of azastilbenes showed that the nitrogen atom strongly affects the properties of the excited state. The effect of azulene on the direct and sensitized *cis–trans* photoisomerization of 3-styrylquinoline showed that both processes occurred via a triplet mechanism. The ultraviolet spectra of both *cis*- and *trans*-3-styrylquinolines were given.[1527]

The following assignments have been made of the observed ^{1}H-nmr resonances of substituted styrylquinolines (δ p.p.m. downfield from TMS): (i) 2-[4′-(dimethylamino)styryl]quinoline:



(a) = 2.91; (b) = 6.69; (c) = 7.20–7.80; (d) = 8.01 (solvent = $CDCl_3$); Ref. 1571k

(ii) 6,7-dimethyl-4-[4'-(dimethylamino)styryl]quinoline:



(a) = 2.50; (b) = 3.06; (c) = 6.76; (d) or (g) = 7.20; (e) = 7.40; (f) = 7.50; (g) or (d) = 7.64; (h) = 7.91; (i) = 8.75 (solvent = $CDCl_3$); ref. 1571

The fragmentation pattern of 4-styrylquinoline by electron impact is reported to involve loss of hydrogen from the molecular ion during ring rearrangement to give the 3-styrylbenzocyclopentadienonimine cation, which then loses nitrogen. The formation of the 1-phenylbenzodibutylene cation was also recorded.[974] In a study of substituted 4-styrylquinolines, the influence of the substituents on the fragmentation patterns was discussed.[1051]

C. Uses

a. PHOTOGRAPHIC USES 2- and 4-(*p*-dimethylaminostyryl)quinolines are used extensively as components of photographic emulsions for direct printout processes,[974-980] heat developable processes[981] and dry copy printing.[982] Carbon tetrabromide or the less volatile tribromoacetophenone can be used as activators in the free radical photo system.[976] A photosensitive resin has also been described in which the active component consists of a mixture of vinylferrocene and a nitrogen-containing heterocycle such as 2-vinylquinoline.[983] Silver halide-type photographic emulsions have also been supersensitized by the use of dicarbocyanines and styryl bases, including 2-styrylquinoline, 2-(*o*-aminostyryl)quinoline, 2-(*p*-hydroxystyryl)quinoline, 2-(*p*-dimethylaminostyryl)quinoline[984] and 1-alkyl-2-(*p*-diethylaminostyryl)quinolinium iodides.[954] Patents covering the formulation of a liquid developer for electrostatic latent images use 2- and 4-vinylquinolines and 2- and 4-allylquinolines as starting materials.[1528]

b. BIOLOGICAL AND MEDICAL USES In a study of the antibacterial properties of heterocyclic bases including acridines, benzoquinolines and styrylquinolines, Albert and co-workers[985] have shown that two factors are important—the degree of ionization of the base as measured by its pK_a value and the degree of 'flatness' of the molecule. The introduction of a 2-*trans*-styryl substituent on to a quinoline molecule increases the area of 'flatness' and greatly enhances the antibacterial properties of the strongly ionized 4-aminoquinoline, but has little effect on the weakly ionized 6-aminoquinoline. Earlier reports on the antibacterial action of styrylquinolines are also available.[986,987] A series of furyl- and nitrofurylvinylquinolines[988-994] and butadienylquinolines[1008,797] have

been shown to exhibit antibacterial activity, particularly 2- and 4-[2′-(5″-nitro-2″-furyl)vinyl]quinoline. 2-[2′-(5″-Nitro-1″,3″,4″-thiadiazol-2″-yl)vinyl]quinoline[788,995] and 2-[2′-(5″-methylsulphonyl-2″-furyl)vinyl]quinoline[996] have also been reported to have antibacterial or antifungal activity and a series of thirteen styrylquinolines were tested for antiviral properties.[997] Antitumour and antileukaemic activity of 4-(4′-dimethylaminostyryl)quinoline and closely related compounds has been studied extensively,[768b,784,998–1004] and this compound was also listed as having definite carcinogenic properties when administered under controlled conditions at several dose levels to male and female rats.[1005] In a comparative study to assess the use of microorganisms for the screening of potential antitumour agents it was found that 95% of compounds found to be tumour-active in animal studies can be detected by virtue of inhibitory effects on microorganisms; these included 2- and 4-(4′-dimethylaminostyryl)-quinoline, eleven methyl homologues of the 4-isomer, one phenyl derivative and 2-(*m*-nitrostyryl)quinoline.[1006] In view of the activity of 4-(4′-dimethylaminostyryl)quinoline against Walker 256 tumours in rats and against KB tumour cells in cultures, 4-(3′-4′-methylenedioxystyryl)quinoline and 4-(3′-4′-diethoxystyryl)quinoline were similarly tested. They did not show clear activity against the Walker tumour but produced a 50% reduction in growth rate of KB cells in the tissue culture.[1007]

A series of nitrofuran derivatives including 2-[1′-methyl-2′-(5″-nitro-2″-furyl)vinyl]-quinoline were effective as food preservatives for fish products at the 2 p.p.m. level.[1009] Compounds having a —CH=CH—R group (where R has 6–9 carbon atoms) attached to the 2- or 4-position of quinoline (or pyridine) have marked insecticidal properties, e.g. against green cabbage aphid and greenhouse red spiders; examples tested were 2-heptylidene-, 2-butylidene- and 2-furfurylidenequinaldine.[1010]

c. Uses of Polymers Polymers or copolymers of vinylquinolines have been used for coating paper, steel,[1011] and food cans[1012] for preparing plastic films,[1011] as an acid-soluble rust-resistant coating,[1013a,b] as a constituent of thermosetting resins,[1014] as anion-exchange resins,[1015–1017] as a demulsifier for oil-in-water emulsions,[1018] in fibre manufacture,[1019] as a constituent of synthetic rubbers,[1020,1021] as a water-soluble polyelectrolyte,[1022] in adhesive formulations,[1023] as a plastic cathode for a primary battery[1024] and in the quaternized form as a bonding agent for laminated metals, wood, ceramics, plastics or fabrics.[1544] 2- or 4-styryl- or vinylquinolines are recommended as additives in nickel plating baths to improve the ductility, brightness and levelling of the deposit.[1025]

A regenerable insoluble coupling reagent for use in peptide synthesis has been prepared by polymerization of a mixture of 6-isopropenylquinoline, styrene and divinylbenzene (200:300:8) and activation with ethyl chloroformate, ethanol and triethylamine in methylene chloride.[1516] The utility of the product (an *N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline polymer) for use in automated processes has been investigated.[1515]

A vinylquinoline copolymer has also been used as a liquid developer for electrostatic latent images.[1661]

d. Miscellaneous Uses A series of 1-(2′ and 4′-quinolyl)-2-benzofuranyl(and naphthofuranyl)ethenes have found uses as dyes or fluorescent whiteners for polyester fibres or as colour formers in copying processes.[789] The compound (**110**, Q = 4-quinolyl), prepared by condensation of 4-methylquinoline with benzene-1,4-dicarbaldehyde, has been used to dye acrylic fibres in greenish yellow shades.[772] The dyeing properties of 2-styrylquinoline and of 2-(*o*-, *m*- and *p*-nitrostyryl)-, 2-(*p*-dimethylaminostyryl)-, 2-(*p*-aminostyryl)- and 2-(3′,4′-methylenedioxystyryl)quinoline have been investigated.[761]

3. Chemical Properties and Reactions

A. Oxidation

Oxidation of 2- or 4-styrylquinolines or 4-methyl-2-styrylquinoline with chromic acid and sulphuric acid results in the fission of the alkene double bond to give benzoic acid and the appropriate quinoline 2- or 4-carboxylic acid.[100,428,693,814b,1027] Oxidation of 4-vinylquinoline with potassium permanganate and sulphuric acid gave formic acid and quinoline-4-carboxylic acid.[967] Oxidation of 2-styrylquinoline with hydrogen peroxide and acetic acid gave the *N*-oxide of quinoline-2-carboxylic acid.[1028]

Ozonolysis of 2-styrylquinoline gave a low yield of quinoline-2-carboxylic acid, which was increased to 92% yield on further treatment with hydrogen peroxide (3%). 4-Styrylquinoline and 3'-nitro-4-styrylquinoline gave high yields of quinoline 4-carboxylic acid, and 2-styryl-4-methylquinoline gave 4-methylquinoline-2-carboxylic acid. Attempts to isolate the expected aldehyde intermediates were unsuccessful.[698]

B. Reduction

Reduction of styrylquinolines with sodium and ethanol results in saturation of the alkenyl double bond and hydrogenation of the heterocyclic ring of the quinoline nucleus. 2-Styrylquinoline gave 2-(2'-phenethyl)-1,2,3,4-tetrahydroquinolone.[104] Corresponding products were obtained from the following derivatives of 2-styrylquinoline: 6-methyl-,[105] 4'-methyl-[104] 6-methyl-4'-methyl-,[105] 4'-isopropyl-,[104] 2'-hydroxy-, 4'-hydroxy- and 4'-hydroxy-3'-methoxy-.[760]

With hydrogen iodide and red phosphorus as reducing agent in acetic acid at 0 °C, 2- and 4-styrylquinolines gave the corresponding phenylethylquinolines with only the alkenyl bond reduced.[101] Similar results were obtained by the reduction of 4-(2'-hydroxystyryl)- and 2-(4'-methoxystyryl)quinolines.[757]

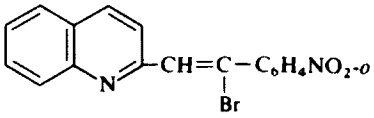
Styrylquinolines with nitro groups on the phenyl ring can be reduced to the amines by tin and hydrochloric acid or by iron and acetic acid without affecting the remainder of the molecule, but with the nitro substituent on the quinoline nucleus reduction with tin and hydrochloric acid gives the aminophenylethylquinoline. Examples of the former are 2-(4'-nitrostyryl)quinoline,[726,1030] 6-methyl-2-(2',3'- and 4'-nitrostyryl)quinolines[754] and also 2-[4'-(2''-nitrophenyl)-1',3'-butadienyl]quinoline,[801] and of the latter 5-nitro-2-styrylquinoline[929] and the 6-nitro-, 8-nitro- and 4'-methyl-5-nitro analogues.[929]

The products from catalytic hydrogenation depend upon the catalyst and conditions used. 2-Pentenylquinoline, when hydrogenated with a Pd/C catalyst at 50 °C in ethanol, gave 2-pentylquinoline,[65] and 2-(3',4'-dimethoxystyryl)quinoline with Pd/C in acetic acid gave the phenylethylquinoline.[762] A series of 2-styrylquinolines substituted in the phenyl ring, when hydrogenated with a Pd/C catalyst, gave the 2-phenylethyl-1,2,3,4-tetrahydroquinolines, but with a Raney nickel catalyst under pressure the completely hydrogenated 2-(2'-cyclohexylethyl)decahydroquinolines were formed.[1031]

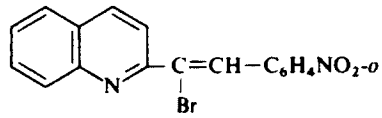
In an investigation of the selectivity of catalysts in the hydrogenation of styrylquinolines it was found that with a Pd/C catalyst with 1 mol of hydrogen absorbed, 2- and 4-styrylquinoline-1-oxides gave the phenylethyl-1-oxides, but with a Raney nickel catalyst the oxygen of the *N*-oxide of the 4-styrylquinoline-*N*-oxide (but not of the 2-styrylquinoline-*N*-oxide) was removed before reduction of the side-chain.[1032] Hydrogenation of 8-allyl-7-hydroxyquinoline with a Pd/C catalyst gave 8-propyl-7-hydroxyquinoline[1026] and 3,3-dichloro-1-(2'-quinolyl)propane was reduced to the propane derivative.[694] 2- and 4-styrylquinolines were reduced quantitatively to the phenylethylquinolines with 2 mol of toluene-4-thiol;[202,1029] the thiol was oxidized to the disulphide $(p\text{-}MeC_6H_4S—)_2$.[202] 4-Dimethylaminostyrylquinoline was similarly reduced with *p*-thiocresol.[1052]

C. Addition reactions

a. ADDITION OF HALOGENS Halogens react with styrylquinolines by direct addition across the alkenyl double bond.[104,105,693,753,760,1033,1034] The addition products are useful for the preparation of alkynylquinolines by elimination of 2 mol of hydrogen halide.[1034] The elimination of 1 mol of hydrogen halide is also possible to regenerate the side-chain unsaturation, which probably accounts for the reported formation of a mixture of two monobromo substitution products, e.g. (**111**) and (**112**) when 2- or 4-(2'-nitrostyryl)quinolines are treated with bromine in carbon disulphide.



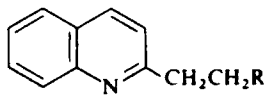
111



112

2-Styrylquinoline for example in acetic acid or carbon disulphide with 1 mol of bromine gave 2-(1',2'-dibromo-2'-phenylethyl)quinoline (94% yield). With 2 mol of bromine 1-bromo-2-(1',2'-dibromo-2'-phenylethyl)quinolinium bromide was formed (75% yield).[1559] In contrast, 2-phenylethylquinoline with bromine gave 2-phenylethylquinolinium perbromide $(C_9H_6\overset{+}{N}HCH_2CH_2Ph)Br_3^-$. The 1-bromoquinolinium salt acted as a brominating agent for acetone and similar compounds.

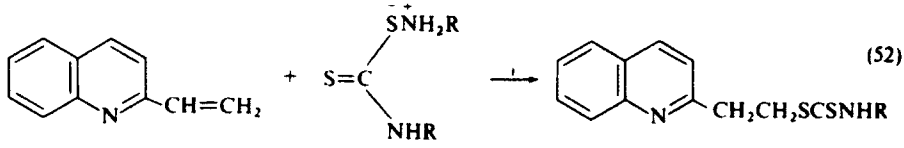
b. ADDITION OF ORGANIC MOLECULES When boiled with absolute alcohol the picrate of 4-vinylquinoline gives the picrate of 2-(4'-quinolyl)ethoxyethane.[967] Potential carbanions such as acetophenone, phenyl ethyl ketone or diethyl malonate participate in a Michael addition with 2-vinylquinoline when refluxed or heated to 160–170 °C with metallic sodium or sodium ethoxide in ethanol to give (**113a**, **b** or **c**), respectively.[1035]



113

(a) R = CH_2COPh; (b) R = CHMeCOPh; (c) R = $CH(CO_2Et)_2$

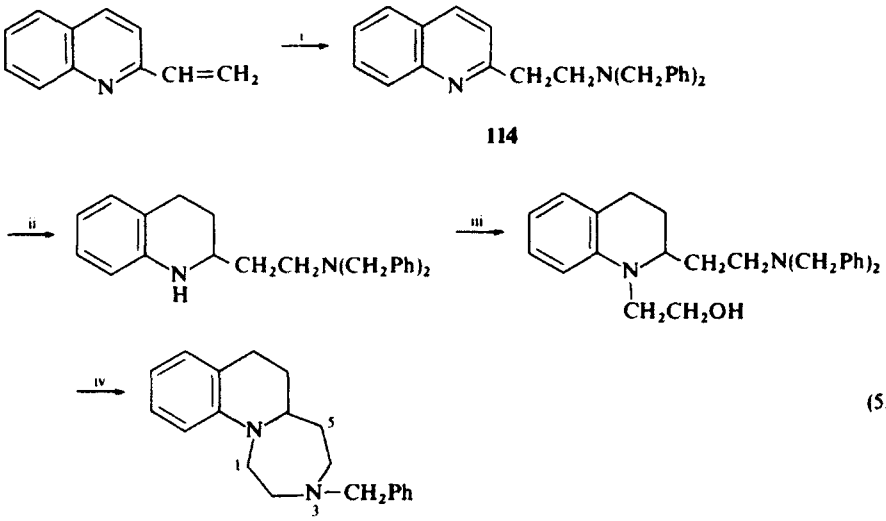
Phenyllithium with 2-styrylquinoline in anhydrous ether, after hydrolysis of the initial product with water, gives 2-benzhydrylmethylquinoline by a Michael-type addition.[764] The quinolyl esters of *N*-substituted dithiocarbamic acids were prepared by the Michael addition of amine salts of *N*-substituted dithiocarbamic acid to 2-vinylquinoline[1036] (equation 52).



(52)

i, ACOH, H_2O/Et_2O, 0 °C (yield 68.5%)

Dibenzylamine with 2-vinylquinoline forms 2-(2′-dibenzylaminoethyl)quinoline (**114**) as the first stage of the synthesis of 3-benzyl-1,2,3,4,5,5a,6,7-octahydro-1,4-diazepino[1,7-*a*]quinoline (**115**),[1037] (equation 53).



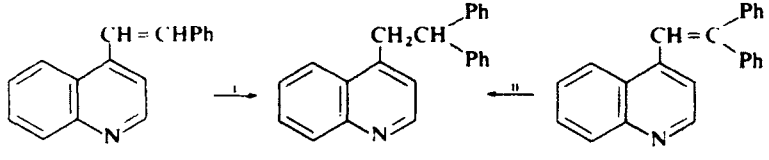
114

115

(53)

(i) $(PhCH_2)_2NH$; (ii) Bouveault–Blanc reduction (Na/ether); (iii) ethylene oxide; (iv) $ClCO_2Et$; HBr

The addition of benzene to 2- or 4-styrylquinoline in the presence of aluminium chloride and dry hydrogen chloride gives the benzhydryl derivative (**116**),[766a] e.g. equation 54. Owing to the reversibility of the process, the *p*-chloro-, *m*-bromo- and *p*-bromostyrylquinolines also give the benzhydryl derivative.[766b]

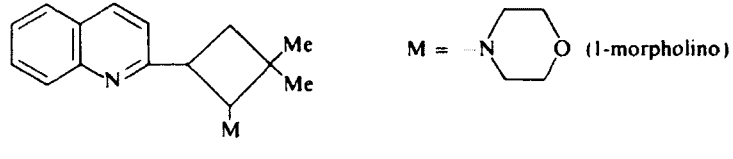


(54)

116

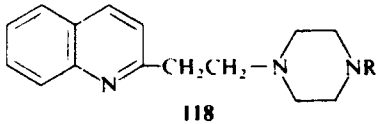
i. C_6H_6, $AlCl_3$, HCl; ii. H_2, Pd C

2-Vinylquinoline, when allowed to stand under nitrogen for 3 days in acetonitrile solution with 1-morpholinoisobutene, gives 3-(2′-quinolyl)-2-(1″-morpholino)-1,1-dimethylcyclobutane (**117**).[1038]



117

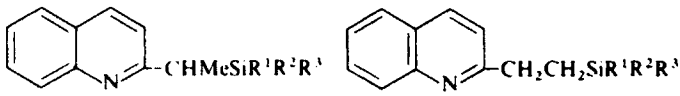
1-Substituted-4-[2′-(2″-quinolylethyl)]piperazines (**118**) were prepared by addition of the appropriate piperazine across the vinyl group of 2-vinylquinoline.[1039,1540]



118

R = Ph, substituted Ph, Me, Ch_2Ph, CH_2CH_2Ph

Maleic anhydride did not react with 2-styrylquinoline except to form the maleate salt.[1040] Hydrosilylation of 2-vinylquinoline with $HSiR^1R^2R^3$ (where R^1 = Me, Et, OEt; R^2 = Me, Et, Pr, Bu, OEt; R^3 = Pr, Bu, $OSime_3$, Et, OMe) in the presence of a 0.1 M solution of $H_2PtCl_6.6H_2O$ in 2-propanol at 120–160 °C for 10 h gave 27–56% yields of mixtures of **118a** and **118b** (90–50 : 10–50).[1531]



118a **118b**

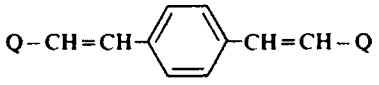
D. Polymerization

Owing to the tendency for vinylquinolines to polymerize when distilled[761] or under the influence of heat or light, or even when stored under vacuum,[967] various polymerization inhibitors have been recommended to enable the monomer to be handled more easily. These include inorganic polysulphides (0.15%),[1041a] ammonium thiocyanate (0.5–1.0%), 2,4-dinitrophenyl thiocyanate[1041b] and sulphone phthalein compounds (0.001–3.0%).[1042] The synthesis of pure 2-vinylquinoline and its copolymerization with styrene, isoprene, chloroprene and acrylonitrile has been described.[714,1043] In a study of the influence of pH on the viscosity of polymers of methyl-substituted *N*-oxides of 2-vinylquinoline details have been published of the synthesis and polymerization of a series of methyl-2-vinylquinolines, namely the 4-, 6-, 7- and 8-methyl derivatives and the 4,6-, 4,7- and 4,8-dimethyl derivatives,[1044] and the nmr spectra of the monomers and polymers were given. The *N*-oxides were prepared from the vinyl polymers by oxidation with hydrogen peroxide in acetic acid. The vinyl polymers were prepared by passing formaldehyde gas into ethereal solutions of the 2-lithiomethyl derivatives and subsequent distillation of the alcohol so formed with sodium hydroxide. The polymers were also prepared by heating the monomers at 120 °C for 24 h under nitrogen. Polymers of the *N*-oxides having a methyl group at position 4 of the quinoline ring were soluble in aqueous acetone at pH values below 4 and viscosity increased rapidly with decreasing pH. Polymers with no substituent at position 4 were soluble at pH greater than 6 and the viscosity varied only slightly with pH.

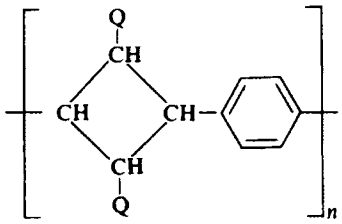
Copolymerization of 2-styrylquinoline with 2-vinylpyridine gave products compatible at high temperatures with polymers such as isotactic polypropylene and formed fibres and films [1045] The use of 2-vinylquinolines in copolymers is recommended for improving the dyeing properties of fibres from polyolefins to acid dyes[1046,1049] and polyacrylonitriles.[1047] Quaternary interpolymers of a vinylquinoline methylmethacrylate, an acylamide and styrene produce resins which mordant acid dyes, and give clear flexible films

compatible with hydrophilic colloids such as gelatin and useful for photographic applications.[1048] The preparation of 17 photoconductive polymers including copolymers of 2-vinylquinoline have been reported;[715] these are used in conjunction with an activating substance and a dye sensitizer on electrical conducting supports in photographic reproductions.

The photopolymerization, by sunlight or ultraviolet irradiation, of the *trans–trans*-isomer of the diolefin (**119**) gave a polymer with high crystallinity and melting point, soluble only in strong acids. Spectroscopic examination by infrared and nmr techniques indicated a linear structure with recurring cyclobutane rings in the chain (**120**).[747a]



119



120

Q = 2-quinolyl

A dimer of 4-vinylquinoline, non-volatile in steam, was obtained by evaporation with concentrated hydrochloric acid and liberation by a base. The dimer decomposed on distillation under reduced pressure.[967] Attempts to polymerize 2-isopropenylquinoline and to form copolymers with butadiene, styrene or methyl methacrylate, with dibenzoyl peroxide as catalyst were unsuccessful.[712] The Q and e values of about 100 vinyl monomers have been determined by a linear least-squares technique.[1050]

E. Miscellaneous Reactions

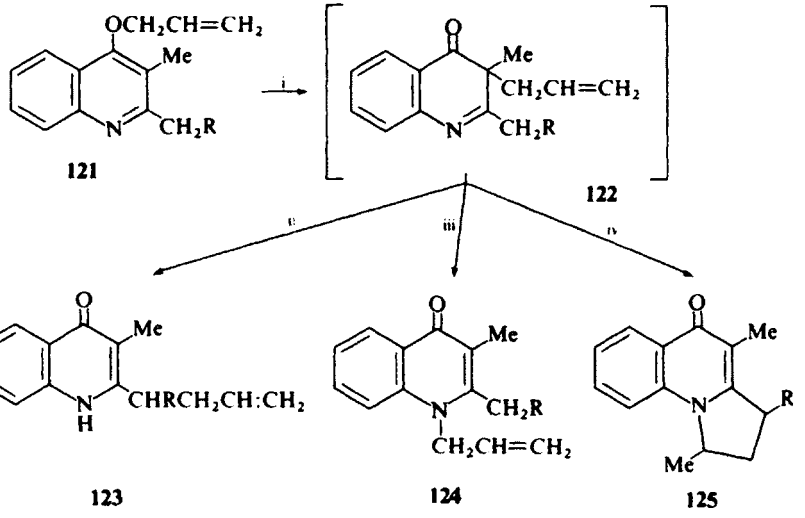
An interesting high-yield 'out-of-ring' migration of an allyl group by a Claisen-type rearrangement from position 4 to the α-carbon of an alkyl side-chain at position 2 of the quinoline ring has been reported. Some concurrent migration to the nitrogen (position 1) also occurs[1054] (see Schemes 20 and 21).

In Scheme 20 the 4-allyl ethers (**121**) rearrange via the common intermediate (**122**) to give (**123**), (**124**) and (**125**). In Scheme 21 the two starting compounds (**126**) and (**127**) give the common intermediate (**128**), which again rearranges by competing reactions each with 6-membered ring transition states to give compounds (**129**), (**130**) and (**131**) in the proportions stated. The close agreement of the experimentally determined product distributions is consistent with the proposed Claisen-type mechanism.

When boiled with ethanol for 6 h, the picrate of 4-vinylquinoline was converted into the picrate of 4-quinolyl ethyl ether.[967] When treated with chlorine, bromine or iodine in acetic acid or with bromine and hydrogen bromide or carbon disulphide the *NN*-dihalogeno-2-styrylquinoline is reported to be formed, presumably (**132**).

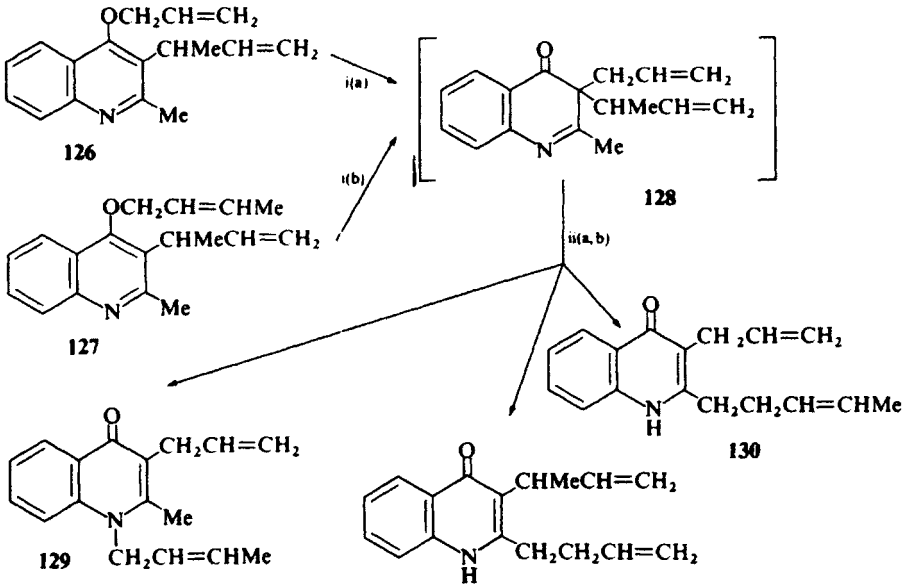
The *trans* form of (**132**) was converted to the *cis* form (21.9%) by treatment with hydrogen peroxide in acetic acid.[1028]

Diazotization of 2-aminostyrylquinoline derivatives (**133**, Ar = Ph, *p*-C_6H_4OMe) in acid of concentration of 0.2–8.0 N gave the 3-2′-quinolylcinnolines (**134**) in yields dependent on the acid concentration and nature of the aryl substituent[1055] (equation 55). With Ar = *p*-C_6H_4OMe maximum yields were 85% at 5.0–8.0 N acid concentrations. With Ar = phenyl yields were 35% in 0.2 N acid but lower at higher acid concentrations.



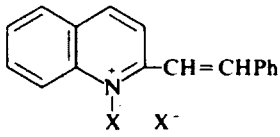
i, 200 °C, ½ h; ii, R = H, 92 %; R = ($CH_2CH{=}CH_2$), 90 %; iii, R = H or ($CH_2CH{=}CH_2$), 2 %; iv, R = H, 2.1 %; R = ($CH_2CH{=}CH_2$), 0.6 %

SCHEME 20

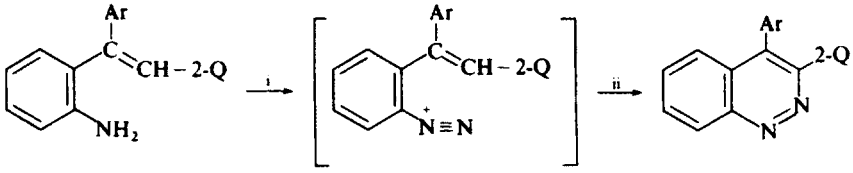


i(a and b), 200 °C, ½ h; ii(a), (**129**) 84 %, (**130**) + (**131**) (1:4.5), 13 %; ii(b), (**129**) 83.5 %, (**130**) + (**131**) (1:4.3), 14 %.

SCHEME 21



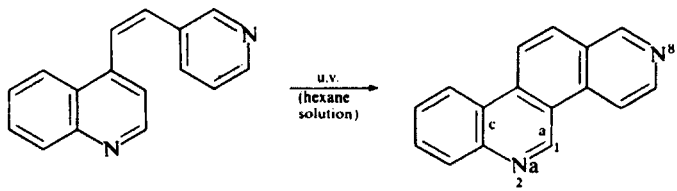
132



133 134 (55)

2-Q = 2-quinolyl i, Diazotization; ii, $-H^+$

Irradiation of dilute solutions of 1-(3′-pyridyl)-2-(4″-quinolyl)ethene (**135**) in hexane or cyclohexane with ultraviolet light gave benzo[*c*]-2,8-phenanthroline (**136**) as the major product (equation 56). Attempted photocyclization of the 2-styryl analogue failed to give any cyclized product.[1056] Electrostatic repulsion of non-bonded nitrogen electrons is considered to be the factor responsible for the diminished photocyclization reactivity of those initial conformations of 1,2-bis(azaaryl)ethylenes, including 1-(7′-quinolyl)-2-(3″-pyridyl)ethylene, having short N—N distances.[1529]



135 136 (56)

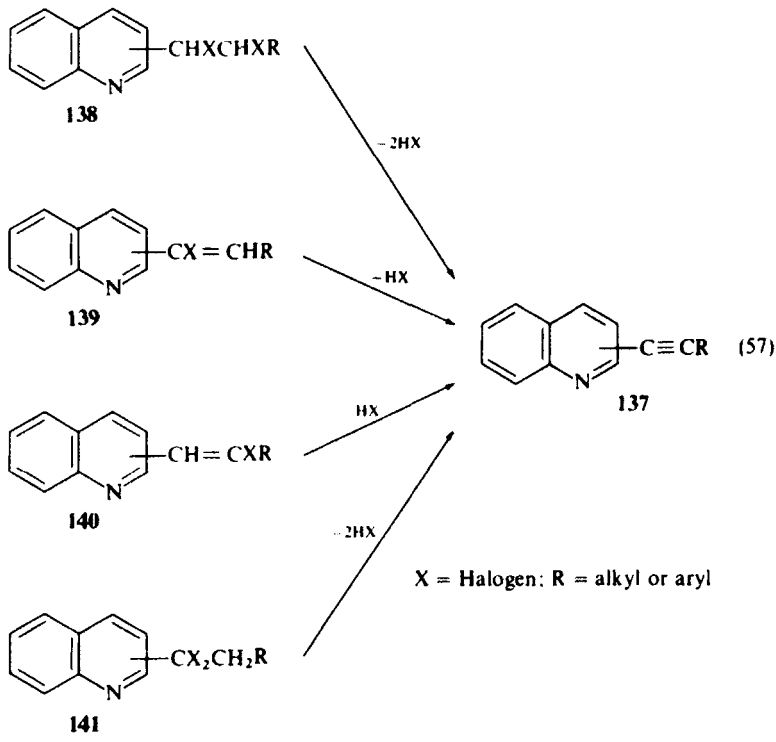
The mechanistic similarity between hydrogen–deuterium exchange reactions in styrylquinolines and aliphatic compounds has been shown by means of Hammett-type correlations and solvent effects[1057] (see also refs. 248–252).

Treatment of 2-vinylquinoline with dimethylsulphonium methylide or dimethylsulphoxonium methylide gave 2-cyclopropylquinoline.[1658]

III. Alkynylquinolines and Aralkynylquinolines

1. Preparation

An important method for the preparation of alkynylquinolines and aralkynylquinolines (**137**) is by the base-catalysed elimination of hydrogen halide from a side-chain, particularly when the new alkynyl bond is conjugated with the quinoline or aryl rings or both (see equation 57).

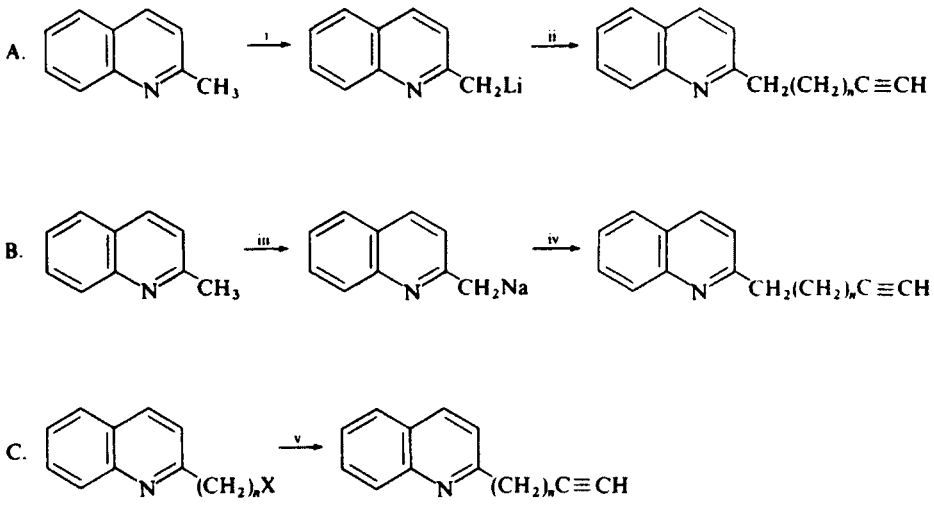


The 1,2-dihaloquinolylalkanes (**138**) can be readily obtained by direct addition of halogen to the quinolylalkenes.[734,1034,1058,1059] The monohalogenated quinolylalkenes (**139**) and (**140**) are formed by the elimination of 1 mol of hydrogen halide from the compounds (**138**), and the *gem*-dihalides (**141**) are formed by the action of phosphorus halide on appropriate quinolyl ketones.[1060] Examples of these methods are the preparations of 2-(phenylethynyl)quinoline,[1034,1061-1063] 4-(phenylethynyl)-quinoline,[1058,1059] 3-, 4-, 5-, 6-, 7- and 8-ethynylquinolines,[1060] 2-[(*p*-chlorophenyl)-ethynyl]quinoline[734,1064] and 2-methyl-6-(phenylethynyl)quinoline.[1065]

Gautier *et al.*[1071] described three methods for the preparation of ω-quinolylalkynes in which the acetylenic bond is unconjugated with the quinoline ring system. Scheme 22 illustrates the principles involved, and highest yields were obtained by method B. The products obtained are shown in Table 29.

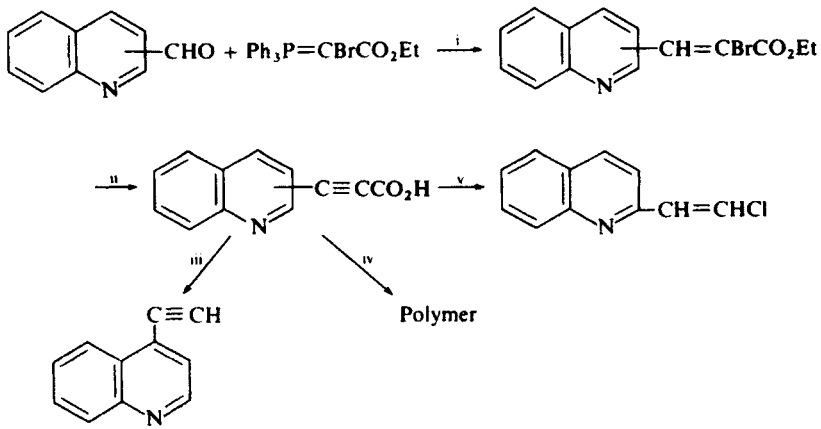
The use of the Wittig reaction for the preparation of quinolyl-substituted α-bromoacrylic esters is shown in Scheme 23. The 4-quinolyl isomer, after saponification and elimination of hydrogen bromide, was decarboxylated to give 4-quinolyl-acetylene.[1522] The 2-quinolyl ester under the same conditions polymerized; the hydrochloride of the 2-quinolylacetylenic acid in the presence of copper sulphate gave 2-(2′-chlorovinyl)quinoline by addition of hydrogen chloride.

Alkali metal acetylides can be used to alkynate quinoline *N*-oxides by direct action in dimethyl sulphoxide as solvent.[1066] 4-(2′-Quinolyl)butyne is among the monoaminoalkynes prepared for screening for fungicidal activity.[1067] Bis-1,4-(2′-



i, PhLi; ii, $Br(CH_2)_nC{\equiv}CH$; iii, Na, Liq. NH_3; iv, $I(CH_2)_nC{\equiv}CH$; v, $NaC{\equiv}CH$, liq. NH_3

SCHEME 22 (ref. 1071)



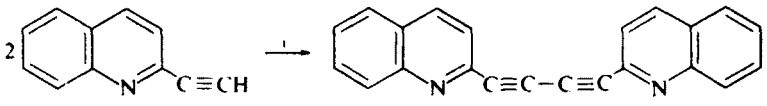
i, Wittig reaction, C_6H_6, $PhCO_2H$ (95–96% yield); ii, OH^- (2- and 4-quinolyl substituents); iii, 4-quinolyl isomer, decarboxylation, (75% yield); iv, 2-quinolyl isomer, attempted decarboxylation; v, 2-quinolyl isomer, HCl, $CuSO_4$ (32% yield)

SCHEME 23

quinolyl)buta-1,3-diyne was prepared by the addition of a solution of 2-ethynylquinoline in ethylene glycol dimethyl ether to copper(I) chloride and *NN'*-tetramethylethylenediamine at 30–35 °C followed by refluxing for 20–60 min[1068] (equation 58).

TABLE 29. Preparation of Alkynylquinolines[1071]

Method (see Scheme 22)	Quinoline moiety (substituent)	Acetylene moiety	Product (quinoline substituent at position 2)	Yield (%)
A	2-Methyl	$BrCH_2C{\equiv}CH$	$-CH_2CH_2C{\equiv}CH$	50
			$+ -CH(CH_2C{\equiv}CH)_2$	10
A	2-Methyl	$Cl(CH_2)_3C{\equiv}CH$	$-(CH_2)_4C{\equiv}CH$	45
A	2-Methyl	$I(CH_2)_3C{\equiv}CH$	$-(CH_2)_4C{\equiv}CH$	70
B	2-Methyl	$I(CH_2)_3C{\equiv}CH$	$-(CH_2)_4C{\equiv}CH$	80
A and B	2-Methyl	$I(CH_2)_4C{\equiv}CH$	$-(CH_2)_5C{\equiv}CH$	—
A and B	2-Methyl	$I(CH_2)_9C{\equiv}CH$	$-(CH_2)_{10}C{\equiv}CH$	—
C	$-(CH_2)_3Br$	$NaC{\equiv}CH$	$-(CH_2)_3C{\equiv}CH$	75–80



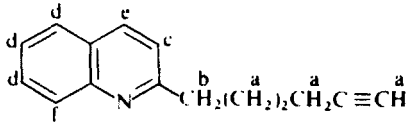
(58)

i, CuCl, $MeO(CH_2)_2OMe$, $Me_2N(CH_2)_2NMe_2$ (50–98%)

2. Physical Properties and Uses

The general physical properties of alkynyl- and aralkynylquinolines are listed in Table 48. The electronic spectra of 2-(phenylethynyl)quinoline[1063] and of 2-methyl-6-(phenylethynyl)quinoline[1065] have been studied.

The following assignments have been made for the observed ^{1}H-nmr spectrum of 2-(6′-hexynyl)quinoline (δ p.p.m. downfield from TMS; solvent = CCl_4):



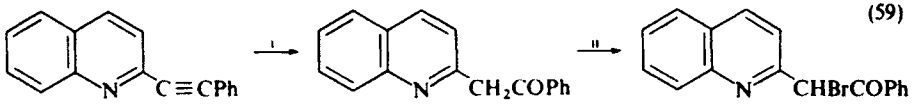
(a) = 1.20–2.35; (b) = 2.89; (c) = 7.06; (d) = 7.25–7.87; (e) = 7.84; (f) = 8.04; $^3J_{3,4}$ = 8.2 Hz (ref. 1571m)

Various alkynylquinolines have been considered for use as bactericides,[1069] insecticides,[734b] pesticides,[1066] fungicides,[1067] analgesics,[734b,1064] intermediates for the preparation of vinyl compounds and in the pharmaceutical and cosmetic industries,[1066,1069] and as stabilizers for chlorinated hydrocarbon solvents.[1066]

3. Chemical Properties and Reactions

When heated with sulphuric acid (e.g. 65% solution), addition of water converts phenylethynylquinolines into phenacylquinolines. In this way 2-phenacyl-,[1034] 4-phenacyl,[1058,1059,1061] 2-(*p*-chlorophenacyl)-[734,1064] and 4-(*p*-chlorophenacyl)-

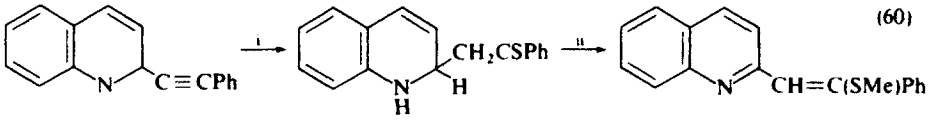
quinolines have been prepared.[1064] Treatment of the phenacylquinolines with bromine in acetic acid results in bromination of the side-chain methylene group. Equation 59 illustrates these reactions for 2-phenylethynylquinoline.



(59)

i, H_2SO_4 (65%) (+ H_2O); ii, Br_2, HOAc

The oxidative coupling of 2-ethynylquinoline to give 1,4-bis-2'-quinolylbuta-1,3-diyne (equation 58) has been described above. When treated with iodine in liquid ammonia, ethynylquinolines gave (iodoethynyl)quinolines, which are used in the pharmaceutical industry as bactericides and fungicides.[1069] 2-Phenylethynylquinoline was converted by hydrogen sulphide in ethanol at 70 °C to 2-thiobenzoylmethylene-1,2-dihydroquinoline, which on methylation with dimethyl sulphate and sodium hydroxide gave 1-(2'-quinolyl)-2-phenyl-2-(methylmercapto)ethene (**142**)[1063] (equation 60).



(60)

142

i, H_2S, EtOH, 70 °C (88%); ii, Me_2SO_4, NaOH

The reactions of the 2-ω-alkynylquinolines, prepared by the methods of Scheme 22 and listed in Table 29, were studied, and the following reactions of the ethynyl groups were reported.[1071] On hydrogenation with Raney nickel catalyst the side-chain was saturated to give Q-$(CH_2)_n$Et (where Q = 2-quinolyl). Hydration with Deniges reagent ($HgO/H_2SO_4/H_2O$) gave the acetyl derivative Q-$(CH_2)_n COCH_3$. Ethynylation of the acetyl derivative with sodium acetylide in liquid ammonia gave Q-$(CH_2)_n$C(OH)MeC≡CH. Aminomethylation with dimethylamine, trioxan and copper(II) acetate gave Q-$(CH_2)_n$C≡CCH_2NMe_2. Hydrogenation of the alkynylamine with Raney nickel catalyst in ethanol gave Q-$(CH_2)_{n+3}NMe_2$. Alkylation of the sodium derivative with butyl bromide in liquid ammonia gave Q-$(CH_2)_n$C≡CBu and condensation of the lithium derivative with acetone gave Q-$(CH_2)_n$C≡CC(OH)Me_2. The alkylations and condensations with acetone were subject to competition with the corresponding reaction at the α-position of the side-chain.

IV. Di- and Polyquinolylalkanes, -Quinolylalkenes and -Quinolylalkynes

This section is limited to the free bases of the title compounds and does not include more than passing references to their quaternary salts, which will be covered in a separate chapter and which include the important family of cyanine dyes.[1074]

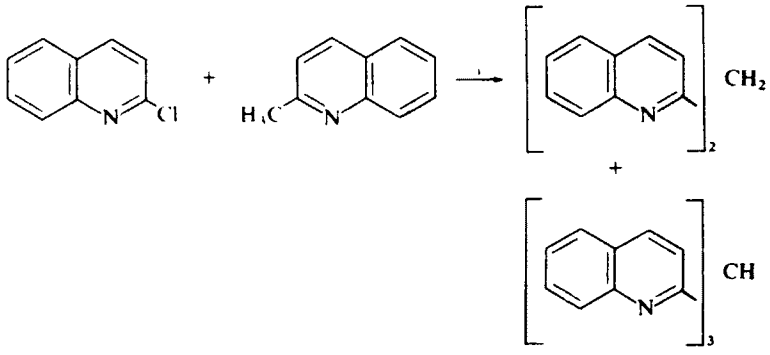
1. Preparation

A. Preparation of Di- and Polyquinolylalkanes

There are many examples of the preparation of diquinolylalkanes by the use of standard quinoline syntheses to complete both quinoline rings. Thus, a Skraup synthesis starting from bis(*p*-aminophenyl)methane gave bis(6-quinolyl)methane,[1080] and from the same starting material a synthesis gave bis[6-(2'-hydroxyquinolyl)]methane.[1081] Bis[6-(2'-methylquinolyl)]methane and bis[6-(2'-phenylquinolyl)]methane were prepared by the Pfitzinger synthesis from 5,5'-diisatylmethane and acetone or acetophenone, respectively.[1082] Methods of synthesis from intermediates already containing the quinoline rings usually start with a substituent such as methyl, bromomethyl, polybromomethyl or halogen in the 2- or 4-positions. Hydrogenation or other chemical reduction of the quinolylalkenes or quinolylalkynes is also possible.

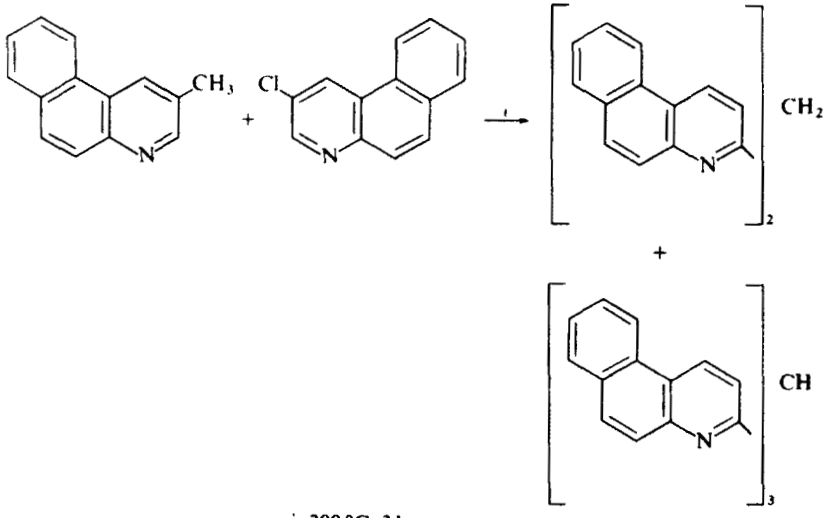
When 2-chloroquinoline was heated with an equimolar amount of 2-methylquinoline with or without some 2-methylquinolinium chloride, bis(2-quinolyl)methane was formed together with some tris(2-quinolyl)methane (equation 61). With 2 mol of 2-chloroquinoline tris(2-quinolyl)methane was the main product (70%).[1075] Separation was effected with alcoholic picric acid when the dipicrate of the more basic bis(2-quinolyl)methane separated first.[1075b] Similarly, (2-quinolyl)(4-quinolyl)methane and bis- and tris(3-benzo[*f*]quinolyl)methanes were formed from 2-methylquinoline and 4-chloroquinoline and from 3-methylbenzo[*f*]quinoline and 3-chlorobenzo[*f*]quinoline, respectively[1076] (equation 62). In the place of the 2-chloroquinoline, 2-(1*H*)-quinolone with phosphorus pentachloride has also been used.[1083] The preparation of bis(2-quinolyl)methane from 2-chloroquinoline or 2-bromoquinoline and 2-methylquinoline was shown to produce also 2-β-naphthylquinoline.[1077] Bis(2-quinolyl)methane was also formed from the lithium derivative of 2-methylquinoline and quinoline (equation 63), and by hydrolysis and decarboxylation of bis(2-quinolyl)acetonitrile, which is itself formed by the condensation of 2-chloroquinoline and acetonitrile[1075c] (equation 64). 1,2-Bis-(2'-quinolyl)ethane has also been prepared from the lithium derivative of quinaldine.[1078a] Two moles of 4-chlorinated quinolines have been shown to condense with compounds containing a reactive methyl group, in the presence of sodium in liquid ammonia, to give quinolylmethanes. For example, 2-methylbenzothiazole with 4-chloroquinoline gave bis(4-quinolyl)benzothiazolylmethane.[207]

When heated with sulphur or sulphuric acid, 2-methylquinoline formed 1,2-bis(2'-quinolyl)ethane[1073] (4.6%), which with selenium dioxide in dioxan gave 1,2-bis(2'-quinolyl)ethylene. The latter, when heated with a further 1 mol of 2-methylquinoline

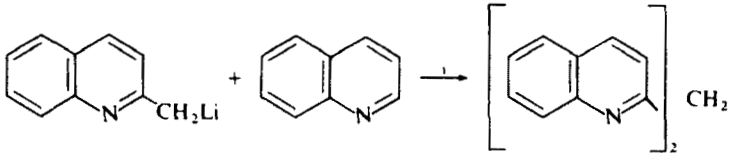


(61)

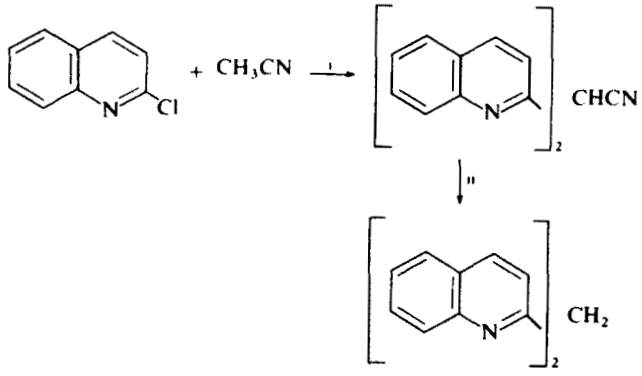
i. Heat, sealed tube, 1 h, 180–210 °C



i, 300 °C, 3 h



i, 110 °C, THF, 8 h, $ZnCl_2$, yield 12 %

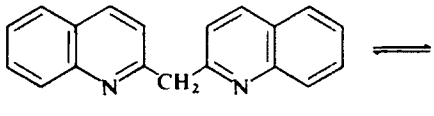


i, $NaNH_2$, PhMe; ii, 70 %, H_2SO_4, 4 h

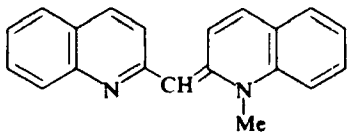
containing some of its hydrochloride, gave a 17% yield of 1,2,3-tris(2'-quinolyl)-propane[1073] by addition of 2-methylquinoline across the ethylenic double bond. A similar addition of 2-methylquinoline across the ethylenic double bond of 2-*p*-hydroxy-

styrylquinoline by heating the two compounds for 5 h at 135 °C gave 1,3-bis(2'-quinolyl)-2-(*p*-hydroxyphenyl)propane.[1096] A further series of substituted triquinolylpropanes have also been prepared by this method.[1097] Quinaldine has also been converted to 1,2-bis(2'-quinolyl)ethane in higher yield by heating with sulphur and copper bronze under nitrogen at 165–170 °C (20% yield).[1078a]

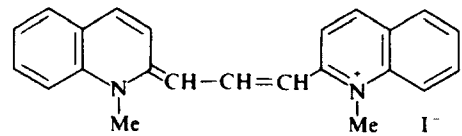
The action of degassed rhodium-on-carbon on 2-methylquinoline resulted in the formation of some bis(2-quinolyl)methane, tris(2-quinolyl)methane and 1,2-bis(2'-quinolyl)ethane, in addition to the main product of biquinolyls.[1072] By heating 2-methylquinoline methiodide with 2-chloroquinoline at 210 °C followed by treatment with sodium hydroxide, compound (**144**) was formed, which can be regarded as the *N*-methyl derivative of the tautomeric form (**143b**) of bis(2-quinolyl)methane.[1083,1084] Compound (**144**) is also formed from bis(2-quinolyl)methane by methylation with dimethyl sulphate.[1075b] Reduction of bis-2-(1'-methylquinolyl)trimethincyanine iodide (**145**) with hydrogen iodide gave the dimethiodide of bis-1,3-(2'-quinolyl)propane.[1085]



143a ⇌ **143b**

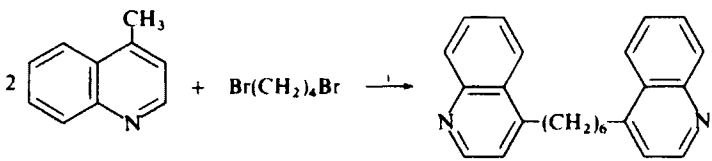


144



145

The quaternary bis[1-(4'-methylquinolyl)]alkanes have been prepared from 4-methylquinoline and the polymethylene dibromides, $Br(CH_2)_nBr$ (n = 3–6, 8 and 10) (see Section I.5.K.a); with sodamide in liquid ammonia, however, bis(4-quinolyl)alkanes are formed[1086] (equation 65).



i, $NaNH_2$, liq. NH_3 (65)

In Wurtz-type reactions, 2- or 4-bromomethylquinolines, when refluxed with sodium in xylene for 6 h, gave 1,2-bis(2'- or 4'-quinolyl)ethanes in 46% and 42% yields, respectively,[1070] but the reaction of quinaldine with sulphur and copper bronze described above[1078a] is considered to be a better preparative method. Preparation of 1,2-bis(2'-quinolylethane) by condensation of 2 mol of 2-chloromethylquinoline with copper bronze in pyridine, was not possible owing to the formation of a quaternary pyridinium

salt.[1078a] Condensation of quinoline-1-oxide with diethyl malonate in acetic anhydride gave 34% of the bis(2-quinolyl)malonic ester which, on hydrolysis and decarboxylation by boiling with 20% hydrochloric acid for 2 h, gave bis(2-quinolyl)methane.[938, 1087]

When 2 mol of quinaldine were heated with benzaldehyde and zinc chloride at 150–160 °C, 1,3-bis(2'-quinolyl)-2-phenylpropane was formed.[775] With quinoline and benzaldehyde and concentrated hydrochloric acid as condensing agent the product was bis(6-quinolyl)phenylmethane.[1088] In the latter case a variety of substituted benzaldehydes were effective (*p*-OMe, *p*-OH, *p*-NO_2, *p*-Me_2N and 2,4-di-OH), but the *m*-CO_2H compound was deactivating and aliphatic aldehydes did not condense. 1,2,3,4-Tetrahydroquinoline and its *N*-methyl derivative were more reactive than quinoline, and *N*-methyl-1,2,3,4-tetrahydroquinoline condensed with formaldehyde in acidic solution to give the bis(1-methyl-1,2,3,4-tetrahydroquinolyl)methane.[1089] Formaldehyde also condensed with 2 mol of 1,2-dimethylquinolinium iodide in the presence of a trace of piperidine to give 1,3-bis(2'-quinolyl)propane and 2,6-dimethylquinoline gave the corresponding 1,3-bis[2'-(6'-methylquinolyl)]propane.[1085]

1,2-Diquinolylethanes can be obtained by reduction of the corresponding ethenes; thus, 1-(2'-quinolyl)-2-(6''-quinolyl)ethene was reduced with hydrogen iodide and red phosphorus at 150 °C to the diquinolylalkane[1033] and the di-*N*-oxide of 1,2-bis(2'-quinolyl)ethylene was reduced by iron and acetic acid at 100 °C to 1,2-bis(2'-quinolyl)ethane.[1090] The quaternary diquinolylmethane 1-(2'-quinolylmethyl)-quinolinium bromide is formed by the reaction of quinoline with 2-bromomethylquinoline.[1078a] 1,2-Di(2'-quinolyl)ethane was one of the products formed when 2-methylquinoline reacted with sulphuric acid.[1628]

B. Preparation of Di- and Polyquinolylalkenes

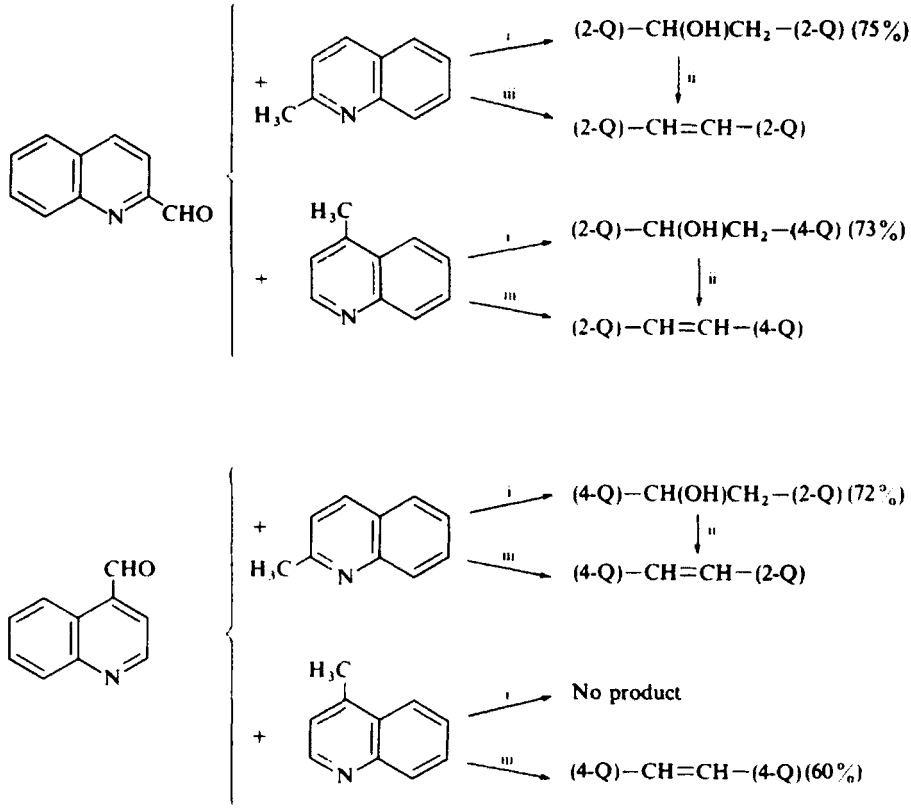
As in the preparation of vinylquinolines, styrylquinolines and heteroarylvinylquinolines, of which they are a special case, the diquinolylalkenes can be obtained by dehydration of the intermediate alcohols formed by the condensation of 2- or 4-methylquinolines with quinoline carbaldehydes,[1079, 1091, 1092] (see Scheme 24). 1,2-Bis-(4'-quinolyl)ethene was also obtained by the oxidation of 4-methylquinoline with selenium dioxide.[1091] Hammick and co-workers,[1078a] however, were unable to prepare the compound (m.p. 325 °C) described by Kaplan and Lindwall[1091] as a diquinolylethylene, but obtained the *trans*-diquinolylethylene, m.p. 190 °C.

When 2-dibromomethylquinoline (**151**)[1114] was heated with copper bronze in pyridine, *trans*-1,2-bis(2'-quinolyl)ethylene (*β*-**150**) was formed, which on irradiation with ultraviolet light rearranged to the higher melting *cis*-isomer (*α*-**150**)[1078] (see Scheme 25, in which the *α*- and *β*-prefixes refer to the higher and lower melting geometrical isomers, respectively; the assignments of configuration are explained in Section IV.2.C). The *trans*-isomer (m.p. 190–193 °C) was also formed by decarboxylation of *α*,*β*-bis(2-quinolyl)acrylic acid by copper chromite in quinoline at 130 °C.[1093]

Condensation of quinoline with epichlorhydrin in the presence of sodium hydroxide gave a product believed to be 1,3-bis(2'quinolyl) propane.[924, 1094] The Wittig synthesis in a two-phase system has been used to prepare 1,4-bis(2'-quinolyl)- and 1,4-bis(4'-quinolyl)buta-1,3-dienes by the treatment of RCH=PPh_3 with glyoxal or with RCH=CHCHO, where R = 2- or 4-quinolyl.[1095]

C. Preparation of Di- and Polyquinolylalkynes

1,2-Bis(2'-quinolyl)acetylene has been prepared by heating 2-tribromomethylquinoline in pyridine with a suspension of copper bronze[1078] (see Scheme 25). The diquinolylacetylene has also been prepared from 1,2-dibromo-1,2-bis(2'-quinolyl)ethane either by



2-Q = 2-quinolyl; 4-Q = 4-quinolyl
i, Reflux, 6 h, in EtOH (80%); ii, reflux, 3 h, with Ac_2O or heat with $ZnCl_2$;
iii, Ac_2O + AcOH, sealed tube, 110–120 °C overnight

SCHEME 24

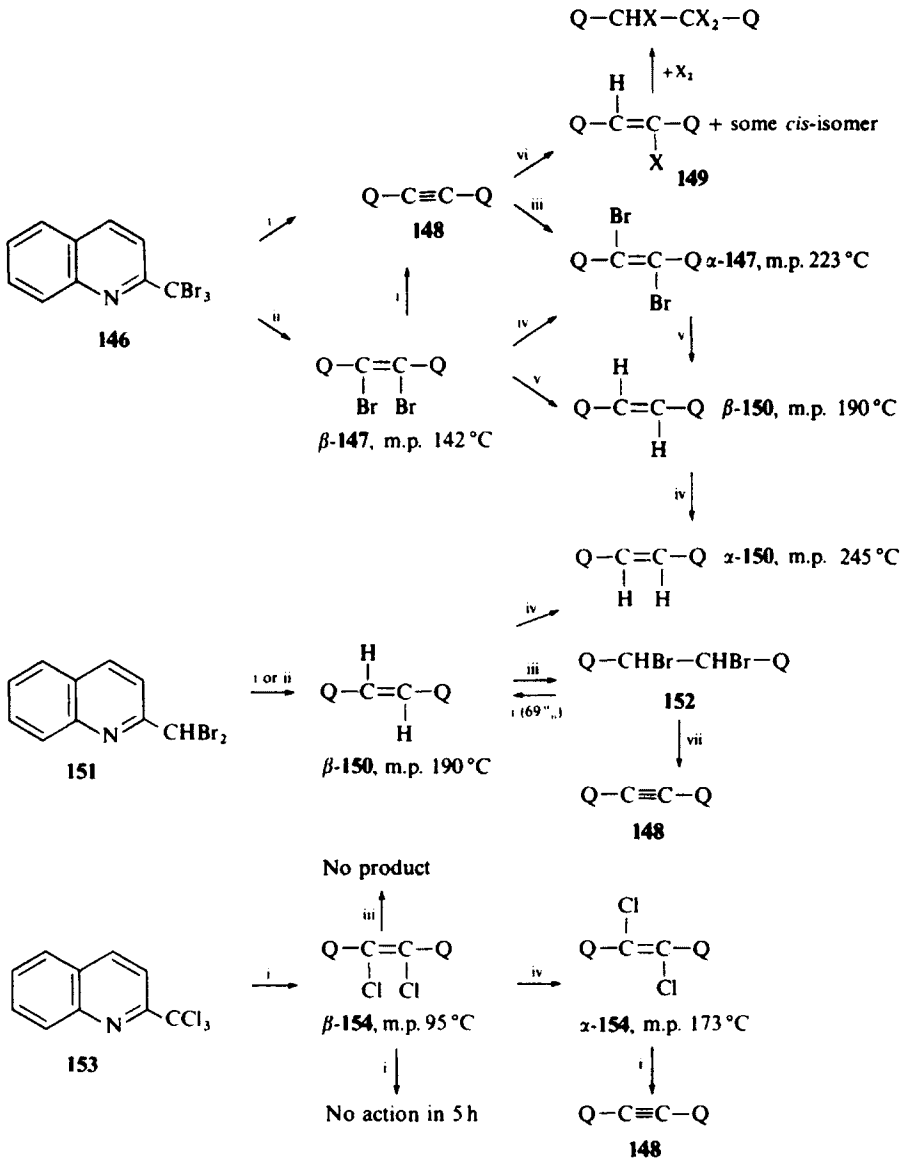
treatment with copper bronze in pyridine[1078b] or by refluxing with ethanolic potassium hydroxide[1079] or potassium hydroxide in dioxan.[1073] The dibromoquinolylethane was prepared from *trans*-1,2-bis(2′-quinolyl)ethylene by addition of bromine.[1079]

2. Physical Properties and Uses

A. General Physical Properties

Some physical properties of known examples of the di- and polyquinolylalkanes, quinolylalkenes and quinolylalkynes are given in Tables 43, 47 and 48, respectively.

The dipole moments of *trans*-1,2-bis(2′-quinolyl)ethylene and some of its *cis*- and *trans*-halogen derivatives have been reported[1078b] (see Table 30). The configurational assignments are based on the arguments given in Section IV.2.C, for which they provide confirmatory evidence.



Q = 2-quinolyl; X = Cl or Br; α = higher melting, β = lower melting geometrical isomer
i, Reflux with suspension of Cu bronze in pyridine;
ii, solution in pyridine added slowly to Cu bronze in pyridine at room temp.;
iii, addition of bromine (1 mol) (or chlorine as appropriate);
iv, irradiation (uv); v, Pd on $SrCO_3$, KOH;
vi, addition of HX;
vii, ethanolic KOH[1079]

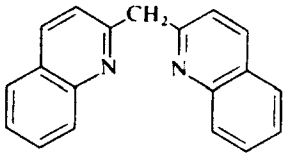
SCHEME 25 (ref. 1078)

TABLE 30. Dipole Moments of Some 1,2-Bis(2'-quinolyl)ethylenes

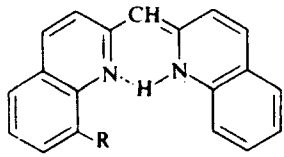
Formula No. (Scheme 25)	Compounds (Q = 2-quinolyl)	Dipole moment (D)
β-**150**	*Trans*-QCH=CHQ	1.60
α-**154**	*Trans*-QCCl=CClQ	1.54
β-**154**	*Cis*-QCCl=CClQ	4.87
α-**147**	*Trans*-QCBr=CBrQ	1.36
β-**147**	*Cis*-QCBr=CBrQ	4.68

B. Tautomerism of Diquinolylmethanes

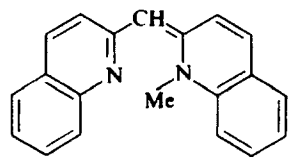
The tautomerism of the quinolylmethanes has been a subject of investigation over an extended period.[1075, 1098-1102] Bis(2-quinolyl)methane, for example, exists in solution as an equilibrium mixture of two prototropic forms, a colourless form (**155**) and a red isomer (**156**, R = H).[1075, 1098, 1011]



155



156



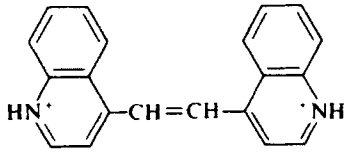
157

The structure of the red form has been confirmed by an X-ray crystallographic analysis of its 8-bromo derivative[1101] (**156**, R = Br). Two equivalent formulations of the red isomer (**156**, R = H) are clearly possible with the bridged hydrogen H-bonded to either of the two nitrogen atoms—a situation described as 'electromesomerism'.[1099] The colourless isomer (**155**) formed colourless diacid salts and the red isomer (**156**, R = H) formed red monoacid salts.[1075b] The formation of an *N*-methyl derivative (**157**) of the red isomer was found to inhibit tautomerism and only red monoacid salts were formed.[1075b]

The equilibrium (**156**, R = H)⇌(**155**) has been studied spectroscopically at 477 nm in various solvents[1098, 1100] and the ratios of concentrations, K_T = [**155**]/[**156**, R = H], at 20 °C were found to be as follows: benzene, 20; methanol, 2.9; ethanol, 1.9; propanol, 1.45; 3-methylbutanol, 0.84; carbon disulphide, 0.21; pyridine, ~1.7; and quinoline, ~1.5.[1098] A later study[1100] showed no simple relationship between K_T and solvent properties except in a homologous series of solvents, such as the alcohols. Similar studies have been carried out on other quinolylmethanes such as 9-phenanthridyl-2-quinolylmethane[1103] and on 1,3-bis(2'-quinolyl)-2-phenylpropane.[1109]

The phototropic behaviour of the 1,2-bis(4'-quinolyl)ethylene dication, (**158**)⇌violene [the radical cation of (**158**)], has been examined by esr (flash) and absorption spectrometry of solutions of the dioxalate of (**158**) in ethanol at 77–356 K.[1113] The rate constant of the reverse reaction was

$$K_1 = 10^{11}\exp-\left[\frac{14{,}300(\text{cal mol}^{-1})}{RT}\right]\text{s}^{-1}$$



158

C. Geometrical Isomerism of the 1,2-diquinolylethylenes

The assignment of the conformations of the geometrical isomers of 1,2-bis(2'-quinolyl)ethylene and some of their halogen substitution products has been investigated by Hammick *et al.*[1078] (see Scheme 25). The higher melting isomers were distinguished by the prefix α and the lower melting isomers by β. The ultraviolet absorption spectra of the diquinolylethylenes (see Table 31) indicated that in the lower melting β-isomer (**β-150**) the quinolyl groups were conjugated, as the compound absorbed at a higher wavelength than quinoline, with an enhanced molar absorptivity. The spectrum resembled that of 2,2'-binaphthyl, which is able to achieve coplanarity of the two aromatic ring systems. The spectrum of the α-isomer, however, (**α-150**) resembled the non-planar 1,1'-binaphthyl and had a λ_{max} similar to that of quinoline but with twice the molar absorptivity, indicating two unconjugated quinoline rings. Models showed that only the *trans*-1,2-diquinolylethylene could achieve a conjugated (planar) configuration. The higher melting α-isomer was therefore assigned the *cis*-configuration and the β-isomer the *trans*-configuration.

Owing to the sizes of the halogen atoms, none of the halogenated quinolylethylenes was able to assume a completely conjugated conformation, so that spectral evidence was less useful for these assignments (see Table 31). In the *cis*-isomers one quinolyl ring can

TABLE 31. Ultraviolet Absorption Spectra of Some Quinolylethylenes (ref. 1078a)

Formula No. (Scheme 25)	Compound		λ_{max} (nm) and (ε)[a]		
	1,1-Binaphthyl		230 (39,000)		290[b] (12,600)
	2,2'-Binaphthyl		255 (89,000)		310 (18,000)
	Quinoline			275 (4,500)	311[b] (6,300)
(**α-150**)	α-1,2-Bis(2'-quinolyl) ethylene	*cis*	235 (30,000)	270 (10,000)	313[b] (12,500)
(**β-150**)	β-1,2-Bis(2'-quinolyl)-ethylene	*trans*		272 (49,500)	350 (36,000)
(**α-154**)	α-1,2-dichloro-1,2-bis(2'-quinolyl)-ethylene	*trans*	235 (31,500)		315[b] (8,000)
(**β-154**)	β-1,2-Dichloro-1,2-bis(2'-quinolyl)-ethylene	*cis*	230 (49,000)		320[b] (12,800)
(**α-147**)	α-1,2-Dibromo-1,2-bis(2'-quinolyl)-ethylene	*trans*	240 (35,000)		315[b] (8,000)
(**β-147**)	β-1,2-Dibromo-1,2-bis(2'-quinolyl)-ethylene	*cis*	240 (46,000)		320[b] (13,300)

[a] Molar absorptivities (ε) are given in parentheses.
[b] Approximate centre of fine structure bands.

conjugate with the double bond, which explains the higher molar absorptivities for these compounds.

Of the dibromoquinolylethylenes, the higher melting α-isomer (α-**147**) was assigned the *trans*-configuration as it was formed by the stereospecific *trans*-addition of bromine to the diquinolyl acetylene (**148**). It could also be readily debrominated to the acetylene.[1078b] The β-isomer (β-**147**), formed by condensation of 2 mol of 2-tribromomethylquinoline, was therefore the *cis*-isomer. These assignments were consistent with dipole moment measurements (see Section IV.2.A) and their infrared spectra.[1078a] Similar considerations applied to the dichloroquinolylethylenes (α- and β-**154**). In contrast to the unsubstituted quinolylethylenes, the size of the halogen substituents of the dihalogenated derivatives results in the *trans*-isomers having the higher energy. The monohalogen derivatives, formed by addition of hydrochloric acid or hydrobromic acid to the diquinolyl acetylene, are in an intermediate position in which the *trans*-isomers are only slightly more stable than the *cis*-isomers. Thus ultraviolet irradiation results in the conversion of the 1,2-bis-(2'-quinolyl)ethylenes into the *cis*-isomers and the 1,2-dihalo-1,2-bis(2'-quinolyl)ethylenes into the *trans*-isomers[1078] (see Scheme 25).

It was also noted[1078a] that the ultraviolet absorption spectrum of 1,2-bis(6'-methyl-2'-quinolyl)ethylene-1,2-diol was not consistent with the *trans*-conformation proposed by Buehler and Edwards.[1115]

D. Uses

The di- and triquinolylmethanes have been studied extensively on account of their relationships to the triphenylmethane dyes,[1075, 1088, 1104] the cyanine dyes[1094, 1105, 1106, 1109] and quinoline red.[1075, 1107] As might be expected, these investigations included studies of their electronic[1075, 1107] and infrared spectra.[1106]

Triheterocyclic-substituted methanes have been used as sensitizers for photographic film in the blue-green region[207] and 1,2-bis(2'quinolyl)ethylene for electrophotographic reproduction processes.[1092] The di-*N*-oxide of 1,6-bis(4'-quinolyl)hexane was prepared for pharmacological screening[1086] and a series of 1,3-bis(substituted quinolyl)propanes have been studied as potential amoebicides.[1096] Tris(2-quinolyl)methane was included in a list of 73 new laser dyes.[1108]

3. Chemical Properties and Reactions

A. Chemical Properties of Di- and Triquinolylalkanes

a. Oxidation and Substitution Reactions of Residual Alkane Hydrogens Bis(2-quinolyl)methane was oxidized to bis(2-quinolyl) ketone in 60% yield by treatment with potassium permanganate in acetone at room temperature for 48 h.[1087] Similar oxidations giving appropriate derivatives of the ketone were achieved with 4-nitrosodimethylaniline, sodium nitrite and benzenediazonium chloride.[1075d] Tris(2-quinolyl)methane was oxidized to the carbinol with chromic acid in acetic acid[1117] and with hydrogen peroxide.[1075a] The remaining methane hydrogen of tris(2-quinolyl)-methane can be replaced by bromine with bromine in chloroform[1075e] by the nitro group with sodium nitrite in acetic acid or with nitric acid in ethanol[1075a] and by a benzyl group with benzyl iodide.[1107]

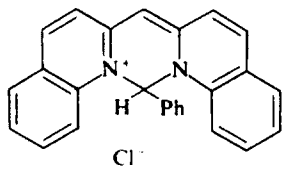
1,2-Bis(2'-quinolyl)ethane, on oxidation with selenium dioxide for 2 h under reflux in dioxan, gave 1,2-bis(2'-quinolyl)ethylene,[1073] but with chromic acid in sulphuric acid 1,1-2,2-tetrakis(2'-quinolyl)ethane was formed.[1076]

b. Reduction Reduction of tris(6-quinolyl)methane with tin and hydrochloric acid gave tris[6-(1,2,3,4-tetrahydroquinolyl)]methane as a result of hydrogenation of the

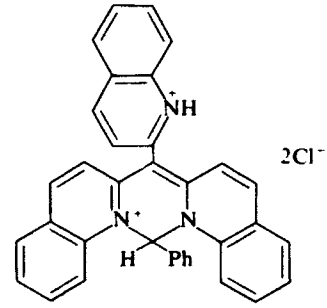
heterocyclic rings.[1104] This compound was oxidized by lead dioxide in acetic acid or by chloranil in ether to a violet–blue dye, with a coppery lustre in the solid state. When heated cautiously above its melting point the leuco base passed through a green stage with the loss of four atoms of hydrogen, suggesting the formation of a dye related to malachite green.

c. Formation of Chelate Compounds Bis(2-quinolyl)methane reacts with some bivalent metal halides to give tetrahedral dihalobis(2-quinolyl)methane chelates. The radius of the metal ion must be greater than 0.70 Å and the ion must be capable of forming tetrahedral complexes.[1110,1111] Chelates were prepared from Co^{2+}, Zn^{2+}, Be^{2+} [1100,1101] and Cd^{2+} ions[924] but not from Mn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+} or Pt^{2+}. The colourless complexes were acidic and formed red anions. A proton on a hydrogen bridge between two nitrogen atoms can also form chelate complexes with Li^+, Na^+, K^+ or Cs^+. These alkali metal compounds were very sensitive to hydrolysis and were deep red in colour.[1112] The relationships between the ionic radii, rates of dissociation and absorption maxima were studied.

d. Formation of Quinoline Red and Related Compounds The synthesis of quinoline red from bis(2-quinolyl)methane and benzyl chloride indicated that its structure was as shown in (**159**).[1107] This was supported by the formation of a compound $C_{35}H_{26}N_3Cl_3$, presumably (**160**), from tris(2-quinolyl)methane and benzyl chloride.



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B. Chemical Properties of Diquinolylalkenes

The addition of bromine to *trans*-1,2-bis(2′-quinolyl)ethylene (*β*-**150**) gives the dibromide (**152**) by saturation of the ethylenic bond. Treatment with ethanolic potassium hydroxide then results in elimination of 2 mol of hydrogen bromide to give 1,2-bis(2′-quinolyl)-acetylene (74%)[1079] (see Scheme 25). Reduction of the quinolylethene with iron powder and acetic acid results in addition of two hydrogen atoms to give 1,2-bis(2′-quinolyl)-ethane.[1090] *cis*-1,2-Dibromo-1,2-bis(2′-quinolyl)ethylene is very unreactive and resists attack by alcoholic silver nitrate, silver acetate in acetic acid, potassium permanganate in acetone, dilute or concentrated sulphuric acid, aqueous sodium hydroxide and even fused potassium hydroxide.[1078a] It is debrominated to the acetylene by refluxing with copper bronze and pyridine although the corresponding *cis*-dichloro derivative was not dechlorinated under these conditions. The *trans*-dihalogenodiquinolylethylenes give the diquinolylacetylene more easily. The 1-chloro- and 1-bromo-1,2-bis(2′-quinolyl)

ethylenes (**149**) (presumably *trans*-) formed by addition of hydrogen chloride or hydrogen bromide to the diquinolylacetylene, add chlorine or bromine to give 1,1,2-trihalogeno-1,2-bis(2'-quinolyl)ethanes[1078b] (see Scheme 25).

Electrostatic repulsion of non-bonded nitrogen electrons is considered to be the factor responsible for the diminished photocyclization reactivity of those initial conformations of 1,2-bis(azaaryl)ethylenes [including 1,2-bis-(6'-quinolyl)ethylene and 1,2-bis-(7'-quinolyl)ethylene] having short N–N distances.[1529]

C. Chemical Properties of Diquinolylalkynes

Addition of chlorine or bromine to the 1,2-bis-(2'-quinolyl)acetylenes gave the higher melting *trans*-isomers of the symmetrical dihalogenodiquinolylethylenes.[1078,1079] Addition of hydrogen chloride gave mainly the *trans*-1-chloro-1,2-bis(2'-quinolyl)-ethylene, hydrogen bromide added less readily and gave slightly more *cis*-isomer, as shown by their ultraviolet spectra. Attempted addition of hydrogen iodide gave the *trans*-1,2-bis-(2'-quinolyl)ethylene together with a compound that readily lost iodine.[1078b] On reduction 1,2-bis(2'-quinolyl)acetylene gave the corresponding *trans*-ethylene.[1116]

V. Arylquinolines and Heteroarylquinolines

1. Isolation and Synthesis

The title compounds are frequently obtained by methods which involve the synthesis of the quinoline ring. These methods are discussed in Part I, Chapter 2, and many examples are included in Tables 1–3 at the end of that chapter. The following account is limited to examples of the isolation of aryl and heteroaryl quinolines from plant products or their synthesis from intermediates which already contain the quinoline moiety.

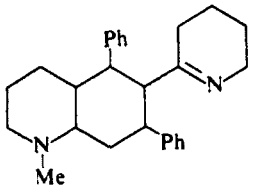
A. Isolation from Plants

The alkaloid lobinaline (**161**) has been isolated from *Lobelia cardinalis* and its structure was determined and confirmed by chemical and spectroscopic analysis and by the synthesis of its demethylated and aromatized derivative 5,7-diphenyl-6-(2'-pyridyl)-quinoline (**162**).[1118,1119] The related alkaloids syphilobine (A) (**163a**) and syphilobine (F) (**164**) were isolated from *Lobelia syphilitica*,[1120] and dehydrogenation of (**164**) with palladium–charcoal at 200–210 C gave the fully aromatic derivative (**163b**). The structures were confirmed by spectroscopic analysis.

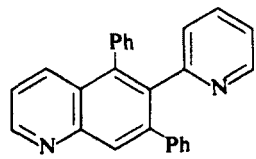
Four imidazolylquinoline alkaloids, macrorine (**165a**), isomacrorine (**165b**), macrorungina (**165c**) and normacrorine (**165d**), have been isolated from *Macrorungia longistrobus*.[1121,1122] Their structures were established by degradation experiments,[1121] synthesis from 2-acetylquinoline[1122] and spectroscopic and mass spectrometric examination.[1123] Isomacrorine was also synthesized from the methyl ester of 1-methylimidazole-5-carboxylic acid.[1157] The alkaloid dubamine (**166**) was among a series isolated from the seeds of *Haplophyllum latifolium*[1541] and *Haplophyllum dubium*[1542] by chromatography on alumina. Others include robustine (**167a**) ψ-fagarine (**167b**) and dictamnine (**167c**).[1264]

B. Arylations with Organometallic Compounds

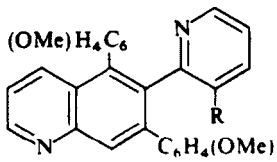
Arylation of quinoline or quinoline-1-oxides with lithium aryls and Grignard reagents has been reviewed in Part I, Chapter 1, Sections IV.1 and IV.2, and the corresponding



161

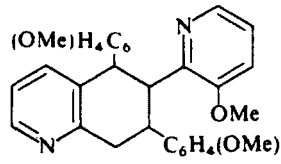


162



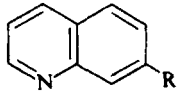
163

(a) R = H;
(b) R = OMe

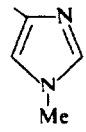


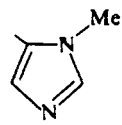
164

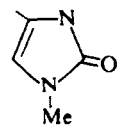
alkylations have also been discussed in Section I.3.C.a above. The lithium reagents are frequently prepared by the action of butyllithium on a bromo derivative of benzene[1124-1127] or directly on a reactive aromatic compound such as thiophene[1128] or 1-methylindole.[1129]

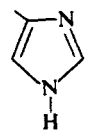


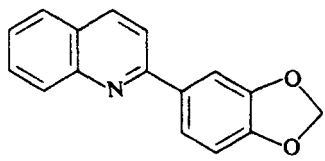
165

(a) R = 

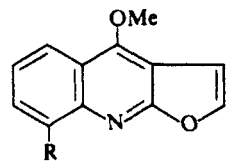
(b) R = 

(c) R = 

(d) R = 



166



167

(a) R = OH; (b) R = OMe; (c) R = H

Arylation occurs at position 2 of the quinoline ring as a result of oxidation of the 1,2-dihydro dervative first formed by addition. The addition product can sometimes, but not always, be isolated as an intermediate.[1130,1136,1137] Nitrobenzene is frequently used as a mild oxidizing agent to facilitate this stage of the reaction. If position 2 of the quinoline ring is already substituted the product is either a 2,2-derivative of a 1,2-dihydroquinoline as in the reactions of phenyllithium and *p*-tolyllithium with 2-phenylquinoline,[1138] or the 2-substituent may be displaced as in the formation of 2-phenylquinoline by the reaction of phenylmagnesium bromide on the *N*-oxide of 2-methoxyquinoline[1153] or 2-chloroquinoline.[1156] The *N*-oxide of 4-methoxyquinoline with phenylmagnesium bromide gave 2-phenyl-4-methoxyquinoline.[1153] Aryl- and heteroarylquinolines prepared by these methods are listed in Table 32.

TABLE 32. 2-Aryl- and 2-Heteroarylquinolines Prepared with Organolithium Compounds or Grignard Reagents

Substituents on quinoline derivative prepared	Yield (%)	Ref.
Arylquinolines from Lithium Reagents		
2-Methyl-2-phenyl-1,2-dihydro-	47	1130
2-Phenyl-		1131
2-Phenyl- (+ a little 4-phenyl-)		124
4-Methyl-2-phenyl	64.6	1132
2,2-Diphenyl-4-methyl-1,2-dihydro-	12.5	1132
4-Methyl-2-phenyl	54	497
5-Methyl-2-phenyl	57	450
2-(*o*-Methoxyphenyl)-1,2-dihydro-	68	1133
2-(*o*-Hydroxyphenyl)-	—	1133
2-(*o*-Methoxyphenyl)-	41	1134
2-(*p*-Bromophenyl)-	42	1135
2-(*m*-Bromophenyl)-	65	1135
2-(*m*-Chlorophenyl)-6-methyl-	57	1124
2-(*p*-Chlorophenyl)-6-methyl-	30	1124
2-(*p*-Chlorophenyl)-7-methyl-	25	1124
2-(*f*-Chlorophenyl)-8-methyl-	—	1124
2-(*p*-Dimethylaminophenyl)-	50–65	1125
2-(*p*-Dimethylaminophenyl)-6-methyl-	50–65	1125
2-(*p*-Dimethylaminophenyl)-7-methyl-	50–65	1125
2-(*p*-Dimethylaminophenyl)-8-methyl-	50–65	1125
2-(*p*-Methoxyphenyl)-6-methyl-	46.2	1125
2-(*p*-Methoxyphenyl)-7-methyl-	61	1125
2-(*p*-Methoxyphenyl)-8-methyl-	—	1125
2-[(*p*-Trimethylsilyl)phenyl]-	33.7	1136
2-(*p*-Terphenyl-4-yl)-	33.4	1136
6-chloro-1,2-dihydro-2-(*p*-dimethylaminophenyl)-	44	1137
6-Chloro-2-(*p*-dimethylaminophenyl)-	30.4	1137
2-(*p*-Diethylaminophenyl)-	27	1137
6-Chloro-2-(*p*-diethylaminophenyl)-	30	1137
2-(*p*-Diethylaminophenyl)-8-methyl-	26	1137
2-(*p*-Diethylaminophenyl)-6-methoxy-	22	1137
2-(*o*-Diethylaminophenyl)-	34	1137
2-(*o*-Diethylaminophenyl)-8-methyl-	35	1137
2-(*m*-Dimethylaminophenyl)-	7	1137
2-(*m*-Dimethylaminophenyl)-8-methyl-	26	1137
2-(*o*-Dimethylamino-5-methylphenyl)-	26	1137
2-(*o*-Dimethylamino-5-methylphenyl)-8-methyl-	28	1137

TABLE 32 (*cont.*)

Substituents on quinoline derivative prepared	Yield (%)	Ref.
3,4-Dihydro-3-(*p*-dimethylaminophenyl)benzo[*f*]-	62	1137
3-(*p*-Dimethylaminophenyl)benzo[*f*]-	56	1137
2,2-Diphenyl-1,2-dihydro-	23	1138
2-Phenyl-2-*p*-tolyl-1,2-dihydro-	—	1138
2-*o*-Biphenylyl-	50	1138
2-*m*-Biphenylyl-	—	1138
2-*p*-Biphenylyl	—	1138
2-[(*m*-Trifluoromethyl)phenyl]-	68	1139
2-[(*m*-Trifluoromethyl)phenyl]-8-methyl-	—	1139
2-[(*p*-Dipropylarsino)phenyl]-	60	1127
2-[(*p*-Dipropylarsino)phenyl]-8-methyl-	79	1127
2-(Cyclopentadienyl)- (Fe derivative)	~2.4	1140, 1141
1,1'-Bis(2-quinolyl)ferrocene	~0.9	1140, 1141
Heteroalkylquinolines from Lithium Reagents		
2-(2'-Pyridyl)-	—	1126
2-(2'-Thienyl)-	38	1128, 1260
2-(1'-methyl-2'-indolyl)-	54	1129
2-(3'-{6"-[5'"-(2""-Pyridyl)-2'"-thienyl]}-4"-pyrimidinyl)phenyl-	48	1142
2,2'-(2",5"-Thiophendiyl)bis-(4,4'-nonyl)-	—	1143
2-(5"-Hexadecyl-2'-thienyl)-4-nonyl-	—	1143
4-Methyl-2(2'-thienyl)-	—	1143
4-Nonyl-2-(2'-thienyl)-	—	1143
2,2'-(2",5"-thiophenediyl)bis-	—	1144, 1260
2,2'-(2,2'-bithiophen)-5,5'-diylbis-	—	1144
2-(2,2'-Bithiophen)-5-yl-	—	1144, 1260
2,2'-(1,2-Ethanediyldi-5,2-thiophendiyl)bis-	—	1144
2-{5-[2-(2-Thienyl)ethyl]-2-thienyl}-	—	1144
2-(1-Benzylimidazol-2-yl)-	—	1145
2-(2-Thianaphthenyl)-	49	1146
2-[5-(Triphenylsilyl)-2-thienyl]-	40	1147
2-[5-(Triphenylsilyl)-2-thienyl]-4,7-dichloro-	—	1147
2-[5-(Triphenylsilyl)-2-thienyl]-6-methoxy-	—	1147
2-[*p*-(2,5-dimethyl-1-pyrryl)-phenyl]-	23	1148
2-[*p*-(2,5-Dimethyl-1-pyrryl)phenyl]-8-methyl-	5	1148
2-[5'-(2"-Thienyl)-2'-thienyl]-	—	1260
2-[5'-(2"-Benzothiazolyl)-2'-thienyl]-	—	1260
Arylquinolines from Grignard Reagents		
2-Phenyl-	90.95	1149
2-Phenyl-	66	1150
2-Phenyl-	—	1151
2-Phenyl-	32.8	1152
6-Methyl-2-phenyl-	—	1152
6-Methyoxy-2-phenyl-	35.0	1152
4-Methoxy-2-phenyl-	—	1153
2-Pentadeuteriophenyl-	—	1265

Although the organometallic reagents most frequently used for the arylation of quinoline are the aryllithium compounds and Grignard reagents, others have been used, such as phenylsodium which with quinoline gave a 67% yield of 2-phenylquinoline,[138]

and pyrrylpotassium, which, when heated at 60 °C with 2-bromoquinoline and benzene in a sealed tube, gave a 40% yield of 2-(2'-pyrryl)quinoline. The sodium derivative of malonic ester, however, did not react under these conditions.[1154] The 1-oxides of quinoline and substituted quinolines with phenylmagnesium bromide in tetrahydrofuran gave 2-phenylquinoline-1-oxides as the main products together with some of the 2-phenylquinolines. At lower temperatures, 1-hydroxy-2-phenyl-1,2-dihydroquinolines were obtained.[1155] 2-Phenylquinoline was also prepared by displacement of a 2-methylsulphonyl group from quinoline by phenylmagnesium bromide or phenyllithium.[1554]

C. Homolytic Arylation

a. Homolytic Arylation with Diaroyl Peroxides Phenyl radicals, from the thermal decomposition of dibenzoyl peroxide at temperatures from 80 to 118 °C, attack quinoline to give a mixture containing all the monophenylquinolines.[1189,1190] Benzoic acid, quinoline-1-oxide and biquinolyls are also formed.[1190] The proportions of the phenylquinoline isomers were found to be 2-phenyl- 6%, 3-phenyl- 14%, 4-phenyl- 20%, 5-phenyl- 12%, 6-phenyl- 8%, 7-phenyl- 8% and 8-phenyl 30%.[1190] 2-Phenyl-4-nitroquinoline-1-oxide was similarly prepared from 4-nitroquinoline-1-oxide.[1191] In a comparison of the homolytic phenylations of various heterocyclic bases in acetic acid and in a non-acidic medium (excess of the heterocycle), the change from quinoline to its conjugate acid resulted in an increased reactivity approximately 2-fold, as shown by competitive substitutions with nitrobenzene as the reference compound.[1192,1193] In contrast to similar experiments with pyridine, reactivity in the acidic medium was not localized at a particular position, but reactivities at positions 2 and 4 were enhanced.[1194]

b. Homolytic Arylations with Diazo Compounds When 3-aminoquinoline is diazotized and the product is allowed to decompose at pH 8 in the presence of benzene, 3-phenylquinoline is formed (Gomberg–Hey reaction).[1195] The reaction fails with 2-aminoquinoline (and probably also with 4-aminoquinoline), which does not form a stable diazonium salt, but 8-aminoquinoline (and, one would expect, the remaining aminoquinolines which can be diazotized) can be used as the source of heteroaryl radicals. Other aromatic compounds can replace benzene. Thus, with pyridine as substrate 3-aminoquinoline gives 3-(2'-pyridyl)- and 3-(4'-pyridyl)quinolines[1196] but not 3-(3'-pyridyl)quinoline as was originally suggested.[1197] Similarly, 3-amino-4-phenylquinoline and 3-amino-4-*p*-tolylquinoline gave the corresponding 4-phenyl- and 4-*p*-tolyl(pyridyl)quinolines.[1315]

This reaction has now been improved by the use of pentyl or isoamyl nitrite as the diazotizing agent to give a 35% yield of 3-phenylquinoline[1198] and 20–50% yields of 3- and 8-(2'-thienyl)quinolines together with some 3'-thienyl isomer.[1199a] The product ratio of 3-(2'-thienyl)quinoline to 3-(3'-thienyl)quinoline was 85 : 15. The relative reactivities of thiophene towards the quinolyl radicals (benzene = 1) was 3-quinolyl = 1.35 and 8-quinolyl = 1.70. The relative reactivities of thiophene towards other radicals (generated photolytically) was cyclohexyl = 3.0, benzyl = 9.0 and phenyl = 1.4.

The reactions of 3- and 8-quinolyl radicals (generated from the amines with isoamyl nitrite) on various aromatic compounds have been studied in detail.[1199b] The total yields of monosubstitution products, isomer ratios, relative reactivities of the radicals with the various aromatic compounds compared to their reactivity with benzene, and the reactivities of the quinolyl radicals compared to phenyl radicals have been measured (see Table 33). The quinolyl radicals can be seen to be electrophilic in character, but were less electrophilic than pyridyl radicals. The reaction constitutes a useful method for the preparation of 3- and 8-arylquinolines.

TABLE 33. Reactions of Quinolyl Radicals with Aromatic Compounds[1199b]

Aromatic compound (substrate)	3-Quinolyl radicals: Product ratio[a] o- (%)	m- (%)	p- (%)	Total Yield (%)	Reactivity (C_6H_6 = 1)	8-Quinolyl radicals: Product ratio[a] o- (%)	m- (%)	p- (%)	Total Yield (%)	Reactivity (C_6H_6 = 1)	Phenyl radicals: reactivity C_6H_6 = 1)
Toluene	62	21	17	35	1.65	62	20	19	25	1.5	1.65
Bu^t-benzene	20	53	27	38	—	25	51	23	25	—	—
Chloro-benzene	56	25	19	35	1.15	46	28	26	27	1.0	1.65
Benzo-nitrile	53	14	23	33	2.8	45	14	41	24	2.7	3.5
Anisole	71	14	15	36	3	70	10	20	29	2.9	1.85

[a] The products are 3(or 8)-(*o*-, *m* or *p*-substituted aryl)quinolines.

c. THERMAL DECOMPOSITION OF ARALKYL PHENYL ETHERS When benzyl phenyl ether[140] and α-naphthylmethyl phenyl ether[1200] were each heated in sealed tubes with quinoline at 260–270 °C for up to 14 days, 2-(*o*- and *p*-hydroxyphenyl)quinolines were among the products formed as a result of the thermal decomposition of the ethers into aralkyl radicals and phenoxy radicals. Although 2- and 4-benzylquinolines were also isolated from the reaction with benzyl phenyl ether, the corresponding α-naphthylmethylquinolines were not formed.

d. HOMOLYTIC ARYLATION BY DECOMPOSITION OF TRIAZENES The decomposition of 1-(5′-quinolyl)-3,3-dimethyltriazene in benzene gave a 13% yield of 5-phenylquinoline[1201] and similarly, when hydrogen chloride was passed into 1-(3′-quinolyl)-3,3-dimethyltriazene in boiling benzene, 3-phenylquinoline was formed.[1195]

e. HOMOLYTIC ARYLATION BY HETEROARYL RADICAL ANIONS Heterocyclic radical anions have been detected by esr when quinoline (and other heterocycles) are heated with aromatic compounds such as phenol, thiophen, indole, 1-methylindole, aniline, dimethylaniline or diethylaniline in the presence of aluminium powder and mercury(II) chloride for about 8 h at 100–200 °C, and the appropriate arylquinolines are formed.[1202–1204] For example, 1-methylindole gave a product consisting of 10% of 1-methyl-3-(2′-quinolyl)indole, 30% of 1-methyl-3-(4′-quinolyl)indole and 14% of 1-methyl-2-(2′-quinolyl)indole. Also prepared were 2-(*p*-hydroxyphenyl)quinoline, 2- and 4-(*p*-diethylaminophenyl)quinoline, 2-[3′(1*H*)(indolyl]quinoline and 2-(*p*-aminophenyl)-quinoline. Similar results were achieved by heating quinoline for 8 h with the aromatic compound and activated sodium powder.[1205] Lithium, calcium, magnesium, zinc, aluminium, titanium, tin, antimony, chromium, manganese, iron, nickel, cerium and cadmium were also used in place of sodium as heteroarylation catalysts.

f. HOMOLYTIC ARYLATION BY THERMAL DECOMPOSITION OF NITRO COMPOUNDS A series of aromatic compounds including quinoline were arylated by heating with aryl nitro compounds such as nitrobenzene, *m*-dinitrobenzene, 1,3,5-trinitrobenzene, 1-nitronaphthalene, *p*-nitrotoluene, *p*-nitromethyl benzoate, 6-nitrobenzimidazole, *m*-

nitrotrifluoromethylbenzene and dimethyl 5-nitroisophthalate.[1206] The reaction conditions specified varied widely with temperatures from 400–1000 °C, pressures of 0.01–1000 atm and reaction times of 0.1 s to 10 h.

D. Other Synthetic Methods also Applicable to Alkylquinolines

Many of the other synthetic methods discussed in Section I.3 for the preparation of alkylquinolines are also suitable for the preparation of aryl- and heteroarylquinolines.

a. Reduction of Chloro Derivatives (see Section I.3.Aa) The chloro derivatives of arylquinolines which may frequently be obtained from the hydroxy compounds or quinolones by the action of phosphoryl chloride may be reduced to the arylquinolines. For example, 4-phenyl-2-(1*H*) quinolone and 3-methyl-4-phenyl-2-(1*H*)-quinolone were converted to the chloro derivatives with phosphoryl chloride and then reduced with PdO–$CaCO_3$ in ethanol to 4-phenylquinoline and 3-methyl-4-phenylquinoline, respectively.[1158]

b. Reduction of Hydroxy Compounds or Quinolones (see Section I.3.A.b) 2-Phenylquinoline has been prepared by the reduction of the following compounds by distillation with zinc dust: 2-phenyl-4-(1*H*)-quinolone,[1159–1161] 2-(3′-hydroxyphenyl)-quinoline[1162] and 6-hydroxy-2-(4′-hydroxyphenyl)quinoline.[1163] 4-Phenylquinoline was similarly formed from 4-phenyl-2-(1*H*)-quinolone[1164] and 7-hydroxy-2-methyl-4-phenylquinoline gave 2-methyl-4-phenylquinoline.[1165]

c. Decarboxylation of Aryl- and Heteroarylquinolinecarboxylic Acids (see Section I.3.E) Aryl- and heteroarylquinolines are formed by decarboxylation of the quinolinecarboxylic acids. The general principles and experimental methods discussed for alkylquinolines (*loc. cit.*) are applicable. Hydroxycarbonyl groups at positions 2 and 4 are the most readily eliminated,[168,817,930,931,1166–1186] but decarboxylations at other positions have also been reported.[1170,1187] The most frequent use of this method constitutes the final stage of the Pfitzinger synthesis of quinolines via the cinchoninic acids (see Part I, Chapter 2, Section IIID, and Table 3 at the end of that chapter).

d. Ring Enlargement of Indoles (see also Section I.3.H.e) In a study of the pyrolysis of *N*-methyl-, 2-methyl- and 3-methylindoles and *N*-benzyl- and 3-benzylindoles it was shown that in addition to migrations of the substituents, a competing reaction was the ring enlargement to quinoline and substituted quinolines. *N*-Benzylindole gave 2-phenylquinoline as the major ring expansion product and 3-benzylindole gave 3- and 4-phenylquinolines.[1188]

e. Condensation of Methylquinolines with Amines and Sulphur (Willgerodt–Kindler Reaction) As described in Section I.5.I.d, the 2-(2′-benzothiazolyl)quinolines (**89**) and (**94a** and **b**) were prepared by the Willgerodt–Kindler reaction and the Jacobson reaction,[833] and also 2-(2′-quinolyl)[2,1-*d*]naphthothiazole (**90**).[1241]

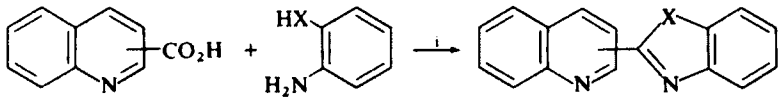
f. Friedel–Crafts Substitutions Quinolines with halogen substituents at positions 2 and 4 will participate in Friedel–Crafts substitutions with a reactive aromatic compound as substrate. Thus 2-chloroquinoline with resorcinol and aluminium chloride gave 2-(2′,4′-dihydroxyphenyl)quinoline and 4,7-dichloroquinoline gave 4-(2′,4′-dihydroxyphenyl)-7-chloroquinoline. With 4-chlororesorcinol 2-chloroquinoline gave 2-(5′-chloro-2′,4′-dihydroxyphenyl)quinoline.[1219] A further example involving ring closure

following a Friedel–Crafts reaction on a substituent phenyl group is given in the following section (V.1.E.a).

E. Methods Involving the Ring Closure of the Substituent Aryl or Heteroaryl Moiety

a. ARYLQUINOLINES A typical example of the ring closure of a carbocyclic ring to form an arylquinoline is the condensation of phthalic anhydride with the phenyl substituent of 6-phenylquinoline in the presence of aluminium chloride and sodium chloride to give 6-(2'-anthraquinonyl)quinoline.[1218]

b. BENZOXAZOLYL-, BENZOTHIAZOLYL- AND BENZIMIDAZOLYLQUINOLINES When treated with the appropriate *o*-substituted aromatic amine, quinolinecarboxylic acids are converted into benzoxazol-2-yl-, benzothiazol-2-yl- or (1*H*)-benzimidazol-2-ylquinolines as a result of the normal syntheses of the heterocyclic rings[1207,1211] (equation 66).

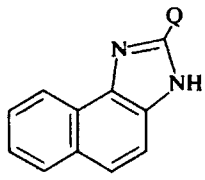


(66)

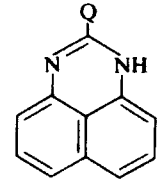
X = O, S or NH

i, Equimolar proportions of reagents heated at 180–250 °C for 1–1.5 h ($-2H_2O$) ref. 1207, or polyphosphoric acid, ref. 1211

Quinoline nitriles or carbaldehydes have also been used in place of the acid and in the latter case an oxidation is necessary in order to give the final product. 2- or 4-methylquinolines and sulphur have also been used in conjunction with appropriate *o*-substituted anilines.[1548] all possible (i.e. 2- to 8-) (1*H*)-benzimidazol-2'-ylquinolines have been prepared from the appropriate quinoline carboxylic acids and *o*-phenylenediamine.[1207] Similar condensations of quinoline-2-carboxylic acid with *o*-aminophenol, *o*-aminothiophenol, *o*-phenylenediamine and 1,2- and 1,8-diaminonaphthalenes gave respectively 2-(benzoxazol-2'-yl)-, 2-(benzothiazol-2'-yl)-, 2[(1*H*)-benzimidazol-2'-yl]quinolines, 2-(2'-quinolyl)-(1'H)-naphtho[1",2"-*d*]imidazole (**168**) and 2-(2'-quinolyl)-(1*H*) naphtho[1", 8a", 8"-*de*]pyrimidine (**169**).[1209]



168



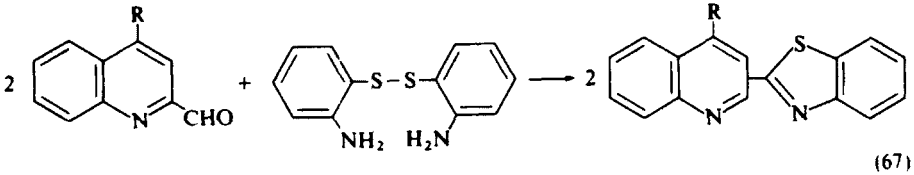
169

Q = 2-quinolyl

Using appropriate methylquinolinecarboxylic acids with *o*-aminophenol, *o*-aminothiophenol or *o*-phenylenediamine, the twelve possible heteroarylquinolines were prepared with a methyl substituent at positions 2 or 4 and a heteroaryl substituent at positions 4 (or 2) or 6 of the quinoline ring.[1210] For eventual diazotization and coupling

to β-naphthol (to produce dyes for polyamide fibres), the 2-(*o*-, *m*- and *p*-aminophenyl)-4-[(1′*H*)benzimidazol-2′-yl]quinolines were prepared from the substituted quinoline-4-carboxylic acids and *o*-phenylenediamine.[1211]

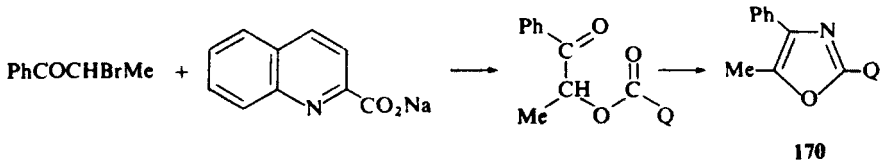
2-Cyanoquinoline has been used to prepare 2-[(1′*H*)-benzimidazol-2′-yl]-quinoline.[1208,1212] Quinoline-2-carbaldehyde and 4-phenylquinoline-2-carbaldehyde have been condensed with *o*-aminophenol and the product after oxidation with lead tetraacetate gave 2-(benzoxazol-2′-yl)quinoline or its 4-phenyl derivative.[1213] The corresponding 2-(benzothiazol-2′-yl) and 4-phenyl(benzothiazol-2′-yl)quinolines were prepared from quinoline-2-carbaldehyde or 4-phenylquinoline-2-carbaldehyde and bis(2-aminophenyl) disulphide[1213a,c] (equation 67). 2-[(1′*H*)Benzimidazol-2′-yl]-quinoline was prepared from the 2-carbaldehyde and *o*-phenylenediamine.[1214]



(67)

R = H or Ph

c. Oxazolyl-, Pyrazolyl-, Triazolyl-, Tetrazolyl- and Oxadiazolylquinolines The cyclization with ammonia of aroylalkyl esters of quinoline-2-carboxylic acid results in the formation of oxazolylquinolines[1223] such as 2-(2′-quinolyl)-4-phenyl-5-methyloxazole (**170**) (equation 68).



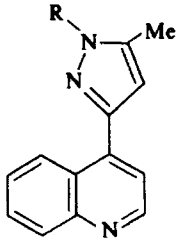
170

(68)

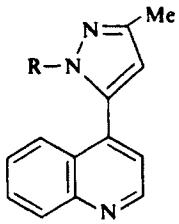
Q = 2-quinolyl

Hydrazine or phenylhydrazine converts acetoacetylquinolines to pyrazolylquinolines. Thus 4-acetoacetylquinoline with phenylhydrazine[1234] gave a mixture of the isomeric 4-(1′-phenyl-5′-methylpyrazol-3′-yl)quinoline (**171a**, R = Ph) and 4-(2′-phenyl-5′-methyl-pyrazol-3′-yl)quinoline (**171b**, R = Ph,) and hydrazine[1224] gave 4-(5′-methyl-pyrazol-3′-yl)quinoline, (**171a** ⇌ **171b**, R = H). The quaternary methiodide of the latter compound failed to exhibit the hypoglycaemic activity characteristic of the corresponding pyridinium salt. The action of hydrazine hydrate on the derivatives of 2-methylenequinoline (**172a**, R = CN or CO_2Et) gave the 2-(3′-amino-5′-hydroxylaminopyrazol-4′-yl)-quinoline (**172b**).[1537] The treatment of 5(2′-amino-5′-nitroanilino)quinoline with sodium nitrite and dilute hydrochloric acid gave 5-(5′-nitrobenzotriazol-1′-yl)quinoline (**173**).[1235]

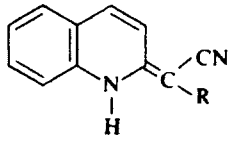
3-Cyanoquinoline was converted into 3-(5′-tetrazolyl)quinoline (**174**) by the action of sodium azide in dimethylformamide.[1225] When quinoline-6-carboxylic acid amidoxime was warmed with excess of ethyl chloroformate, 3-(6′-quinolyl)-1,2,4-oxadiazol-5-one



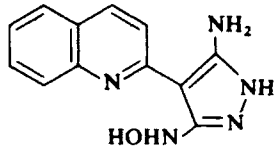
171a



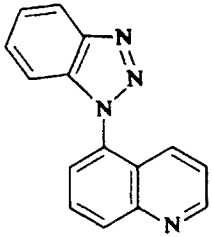
171b



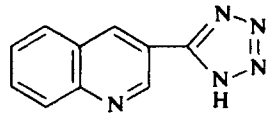
172a



172b

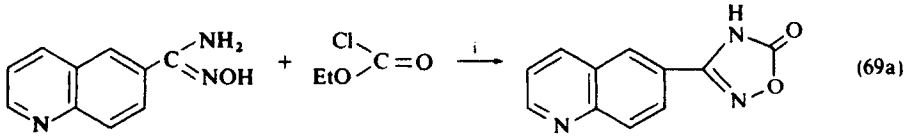


173



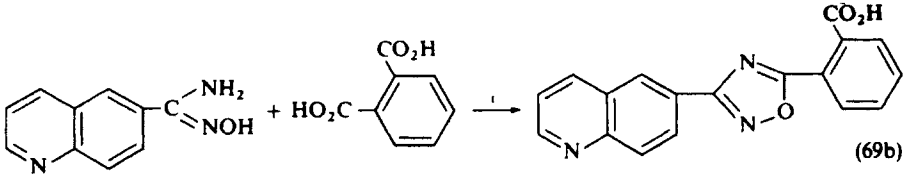
174

was formed[1236] (equation 69a), and fusion with phthalic anhydride have 5-(2′-hydroxycarbonylphenyl)-3-(6″-quinolyl)1,2,4-oxadiazole (equation 69b). The 5′-substituted 2-(1′,3′,4′-oxadiazol-2′-yl)quinolines were prepared by ring closure of the appropriate 2-quinolyl hydrazides[1510] (equation 69c).



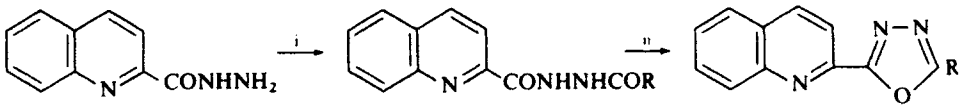
(69a)

i, Excess of $ClCO_2Et$, warm



(69b)

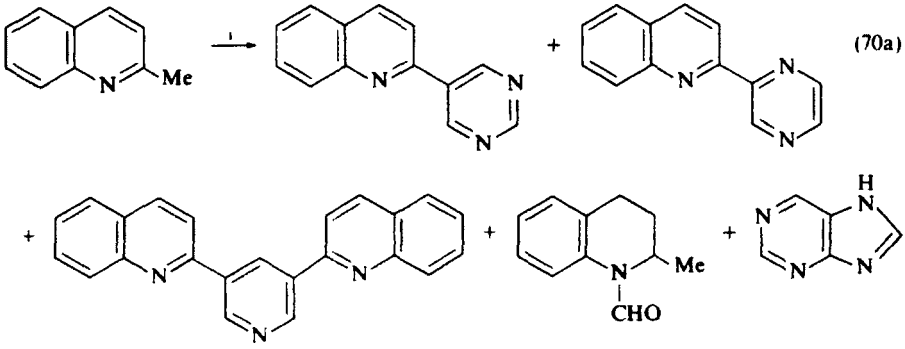
i, Fuse



R = Ph, *m*-$NO_2C_6H_4$, *o*-$MeOC_6H_4$ (69c)

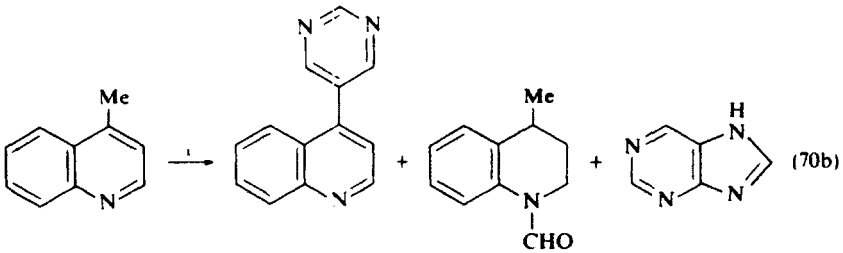
i, RCOCl, pyridine (60–91%); ii, $POCl_3$ (26–38%)

d. PYRAZINYL-, PYRIMIDINYL-, QUINOXALINYL- AND QUINAZOLONYL-QUINOLINES The reaction of formamide with 2- or 4-methylquinolines results in the synthesis of new heterocyclic substituents and *N*-formylation.[1532] 2-Methylquinoline gave 2-(5′-pyrimidinyl)quinoline, 2-(2′-pyrazinyl)quinoline, 3,5-bis(2′-quinolyl)pyridine, 1-formyl-2-methyl-1,2,3,4-tetrahydroquinoline and purine (equation 70a). 4-Methylquinoline gave 4-(5′-pyrimidinyl)quinoline, 1-formyl-4-methyl-1,2,3,4-tetrahydroquinoline and purine (equation 70b).



(70a)

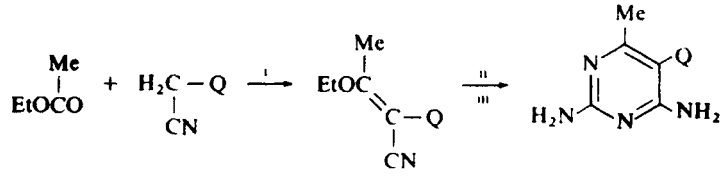
i, $HCONH_2$



(70b)

i, $HCONH_2$

The synthesis of pyrimidinylquinolines by condensation of 3-alkoxy-2-(2′-quinolyl)acrylonitriles has been described.[1220] The starting compound was 2-quinolylacetonitrile, as shown in equation 71, and the product was 2,4-diamino-6-methyl-5-(2′-quinolyl)pyrimidine (**175**), isolated as its hydrochloride salt.

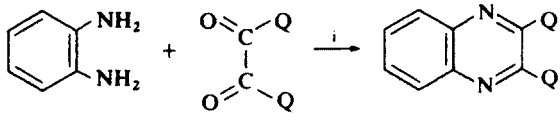


(71)

Q = 2-quinolyl **175**

i, Na, Et_2O, 5 days, room temp.; ii, CH_2N_2 [from $Me(NO)NCONH_2$], heat, stand overnight; iii, guanidine [$HN{=}C(NH_2)_2$], reflux with conc. NaOH. Acidify (HCl); ref. 1220

Condensation of quinaldil with *o*-phenylenediamine by boiling for 1 h in acetic acid gave 2,3-bis(2′-quinolyl)quinoxaline (**176**)[1215] (equation 72).

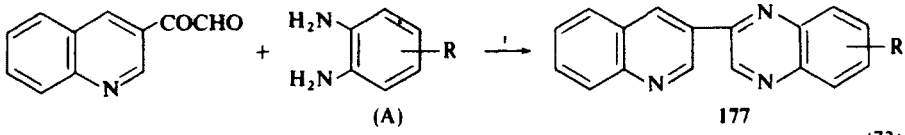


(72)

176

Q = 2-quinolyl
i, AcOH, boil, 1 h; ref. 1215

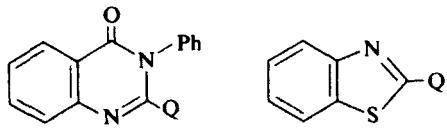
3-Glyoxalylquinoline, prepared by the oxidation of 3-acetylquinoline with selenium dioxide, has been condensed with *o*-phenylenediamine and with the substituted *o*-phenylenediamines indicated in equation 73 to give the 2-(3′-quinolyl)quinoxalines (**177**).[1216]



(73)

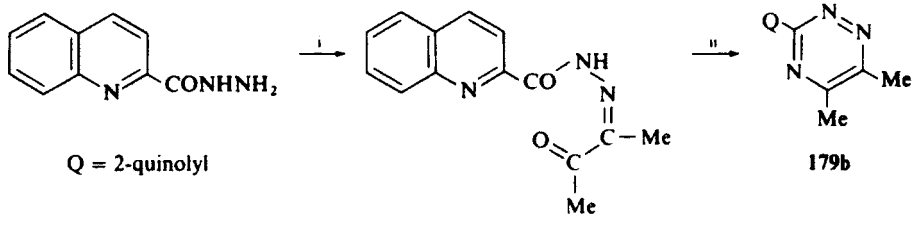
R = H, 4-Me, 4-Cl, 4-NO_2, 4-CO_2H, 3,4-benzo (A = 1,2-diaminonaphthalene)
i, Solution in EtOH, heat (water bath), 30 min; ref. 1216

The reaction of 2-methylquinoline with 2 equivalents of anthranilic acid and 3 equivalents of sulphur gave 2-(2′-quinolyl)-3-phenyl-4-(3*H*)-quinazolone (**178a**)[1521] (yield 15–40%); 2-(2′-quinolyl)benzothiazole (**178b**) was also formed as a by-product. Other heterocycles with reactive methyl substituents such as 2- and 4-methylpyridines were also used in place of methylquinoline.



178a **178b**

e. Quinolyltriazines The reaction of the hydrazide of quinoline-2-carboxylic acid with diacetyl gave the hydrazone (**179a**). The hydrazone with excess of ammonia in alcohol at 150 °C under pressure cyclized to give 3-(2′-quinolyl)-1,2,4-triazine (**179b**)[1221] (equation 74).



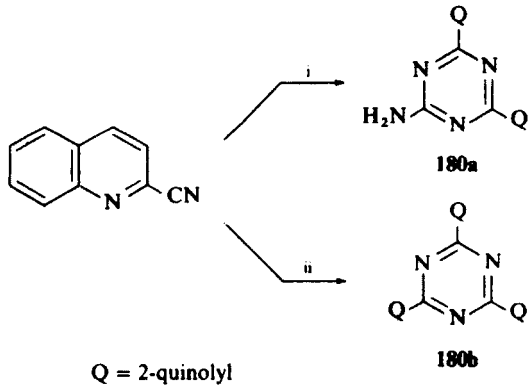
Q = 2-quinolyl

179a **179b**

(74)

i, $(MeCO)_2$; ii, NH_3, EtOH, 150 °C, pressure; ref. 1221

Quinoline derivatives of 1,3,5-triazine have been synthesized from 2-cyanoquinoline,[1222] which when refluxed with guanidine and sodium in ethanol for 15 h gave 2-amino-4,6-bis(2′-quinolyl)-1,3,5-triazine (**180a**). When heated with sodium hydride for 5 h under nitrogen at 160–165 °C 2-cyanoquinoline gave 2,4,6-tris-(2′-quinolyl)-1,3,5-triazine (**180b**). The product was combined with 1.5 mol of water, which was removed at 120 °C *in vacuo* (equation 75).



Q = 2-quinolyl

180a **180b**

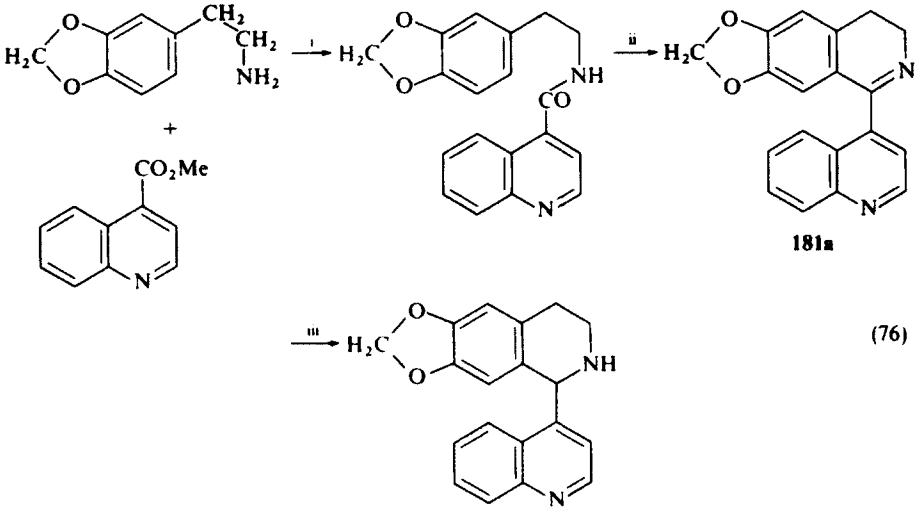
(75)

i, Guanidine $[HN{=}C(NH_2)_2]$, Na, EtOH, reflux, 15 h;

ii, (a) NaH, 5 hr (160–165 °C) under N_2; (b) 120 °C *in vacuo* ($-1.5\,H_2O$);

ref. 1222

f. Isoquinolylquinolines Isoquinolylquinolines have been prepared by Bischler–Napieralski-type syntheses from *N*-homopiperonylamides of quinolinecarboxylic acids by ring closure with phosphoryl chloride.[1217] Equation 76 shows the formation of 4-(6′,7′-methylenedioxy-3′,4′-dihydroisoquinol-1′-yl)quinoline (**181a**). The 6- and 8-substituted quinolines were prepared in a similar manner, and also the 6-methoxy derivative of (**181a**). Zinc and sulphuric acid containing a trace of copper sulphate reduced the isoquinolyl substituents to the tetrahydroisoquinolyl derivatives, e.g. (**181b**) from (**181a**).



181a

181b

(76)

i, Heat, 10 h, 100 °C;

ii, $POCl_3$, 1 h, 120–130 °C (toluene);

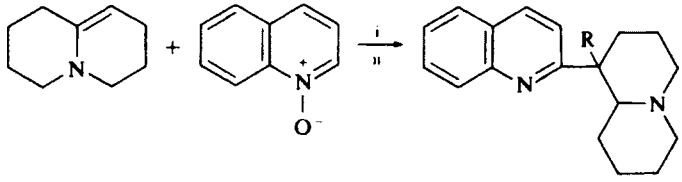
iii, Zn, H_2SO_4, Cu^{2+} (trace)

F. Preparations from Quinoline-1-oxides

Aromatic amines and enamines react with quinoline-1-oxide and an acylating agent to give 2-substituted quinolines. The morpholine enamine of cyclohexanone gave with quinoline-1-oxide and benzyol chloride a 74% yield of 2-(2′-quinolyl)cyclohexanone, which was reduced with sodium borohydride to the cyclohexanol, dehydrated with acetic anhydride to 2-(cyclohexenyl)quinoline and dehydrogenated with selenium at 310–330 °C to give 2-phenylquinoline.[939,1226] 2-(4′-Quinolyl)cyclohexanol was similarly converted to 4-phenylquinoline.[1226] Quinoline-1-oxide with benzoyl chloride and *p*-dimethylaniline gave 58.9% of 2-(*p*-dimethylaminophenyl)quinoline and 10% of carbostyril.[1227] A similar reaction between quinoline-1-oxide, benzoyl chloride and 1,(10)-dehydroquinolizidine in methylene dichloride at room temperature followed by treatment with sodium borohydride gave a 14% yield of 1-(2′-quinolyl)quinolizidine (**182a**) together with other substituted quinolizidines[1228] (see equation 77). Other acylating agents such as acetyl chloride and *p*-toluenesulphonyl chloride have been used in place of benzoyl chloride, usually with reduced yields of the 2-substituted quinolines.[939,1226–1228]

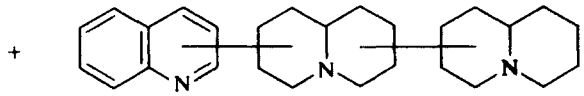
Quinoline-1-oxide or 4-methylquinoline-1-oxide with benzoyl chloride or *p*-toluenesulphonyl chloride in chloroform solution reacted with indole or with substituted indoles having position 3 vacant to give 2-(3′-indolyl) derivatives of quinoline as their hydrochloride salts. The following compounds were prepared by this method: 2-(3′-indolyl)-quinoline, 4-methyl-2-(3′-indolyl)quinoline, 2-(2′-phenylindol-3′-yl)quinoline and 2-(1-methyl-2′-phenylindol-3′-yl)quinoline.[1229]

Quinoline-1-oxide and 1,4-dihydronaphthalene-1,4-endoxide in benzene when heated for 7 h at 80 °C gave a 57% yield of compound (**183**) and 6% of 2-hydroxy-3-(2′-



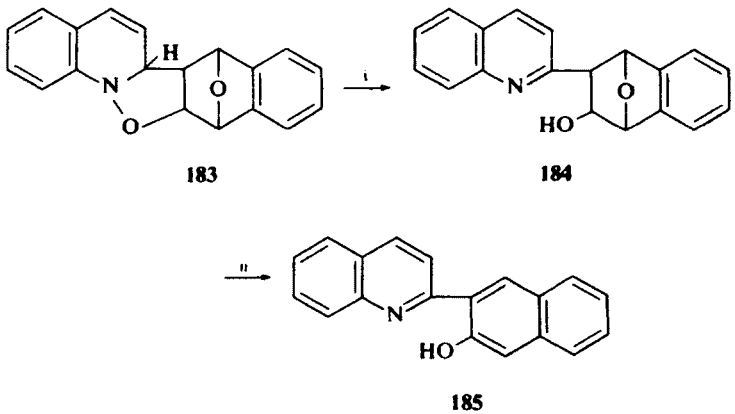
(77)

182, (a) R = H (14%) + (b) R = OH



i, PhCOCl, $CHCl_2$; ii, $NaBH_4$, EtOH

quinolyl)-1,2,3,4-tetrahydronaphthalene-1,4-endoxide (**184**). With methanol and concentrated hydrochloric acid, compound (**183**) was converted into compound (**184**) (92%) and compound (**184**), after treatment with polyphosphoric acid, gave 2-hydroxy-3-(2'-quinolyl)naphthalene (**185**)[1230] (equation 78).



183 **184**

(78)

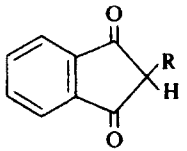
185

i, MeOH, HCl, reflux, 1½ h (92%);

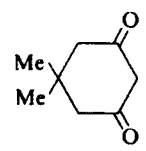
ii, polyphosphoric acid, 20 h at room temp., then 2 h at 60 °C (55%);
ref. 1230

The diketones dibenzoylmethane, benzo[*d*]cyclopenta-1,3-dione (**186**) and its 2-methyl (**187**), 2-phenyl (**188**), 2-*p*-methoxyphenyl (**189**) and 2-*p*-bromophenyl (**190**) derivatives and 5,5-dimethylcyclohexa-1,3-dione (**191**), when heated with quinoline-1-oxide in acetic anhydride, gave the 2-quinolyl derivatives (**192**)–(**198**), respectively.[1231]

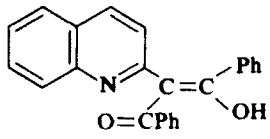
A re-investigation of the reaction of diketen with quinoline-1-oxide[1232] showed that the derivative (**199**) was formed and was converted by the reaction sequence shown in Scheme 26 to 2-(2',6'-dimethylpyrid-3'-yl)quinoline (**200**), which was also prepared via the Grignard reagent (**201**).[1232] This corrects an earlier report[1233] which assigned structure (**202**) to the γ-pyrone derivative instead of (**199**).



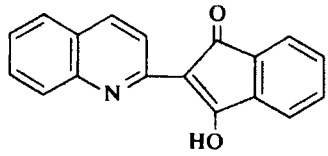
186, R = H; **187**, R = Me; **188**, R = Ph;
189, R = *p*-$MeOC_6H_4$; **190**, R = *p*-BrC_6H_4



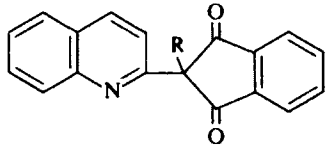
191



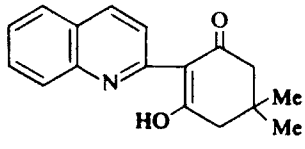
192



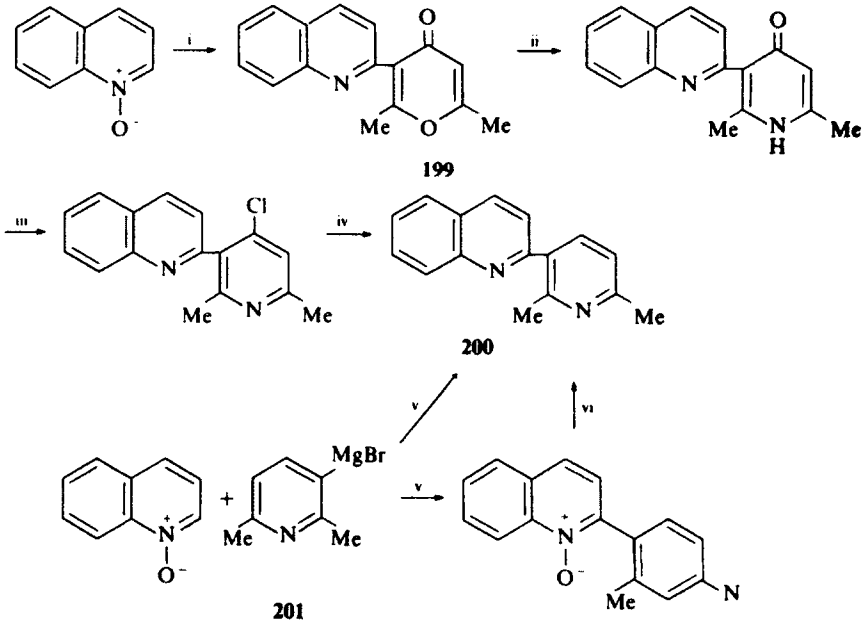
193



194, R = Me; **195**, R = Ph;
196, R = *p*-$MeOC_6H_4$; **197**, R = *p*-BrC_6H_4



198



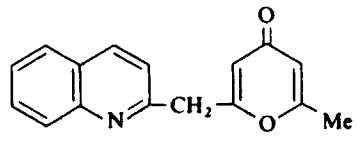
199

200

201

i, Diketen; ii, NH_3; iii, $POCl_3$; iv, H_2, Pd/C;
v, Grignard synthesis; vi, H_2, Raney Ni

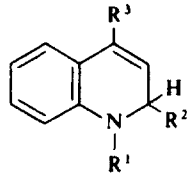
SCHEME 26



202

G. Miscellaneous Methods of Preparation

The preparation of a series of 1-acyl(or 1-aroyl)-2-(2′ or 3′-indolyl)-1,2-dihydroquinolines (**203**) by the reaction of indole or 2- or 3-methylindoles and an acid chloride on quinoline has been described.[1237] Compounds prepared by this method are given in Table 34.

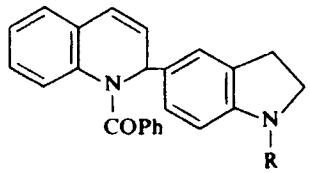


203

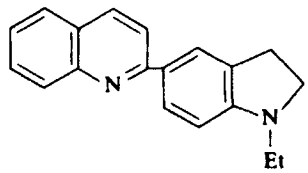
TABLE 34. 1-Acyl-2-indolyl Substituents on Quinoline Derivatives in Formula (**203**)

R^1	R^2	R^3
PhCO	3′-Indolyl	H
PhCO	2′-Me-3′-indolyl	H
PhCO	3′-Me-2′-indolyl	H
p-$MeC_6H_4SO_2$	3′-Indolyl	H
MeCO	3′-Indolyl	H
2,4-$(NO_2)_2C_6H_3CO$	3′-Indolyl	H
PhCO	3′-Indolyl	Me

The dihydro compounds were hydrogenated over PtO_2 to the tetrahydro compounds and were described as readily convertible into the aromatic compounds. 1-Methyl-2-(3′-indolyl)quinolinium iodide was also prepared by the action of indole, sodium and methanol on 1-methylquinolinium iodide. When heated at 250–270 °C/0.005 mmHg the quaternary salt gave 2-(3′-indolyl)quinoline.[1237] 1-Benzoyl-2(1′-methyl-5′-indolinyl)-1,2-dihydroquinoline (**204a**) was prepared by the action of benzoyl chloride and 1-methyl-2,3-dihydroindole on quinoline; the (1′-ethyl-5′-indolinyl) analogue (**204b**) was prepared similarly. Hydrolysis of compound (**204b**) gave the quinoline derivative (**205**).[1238]

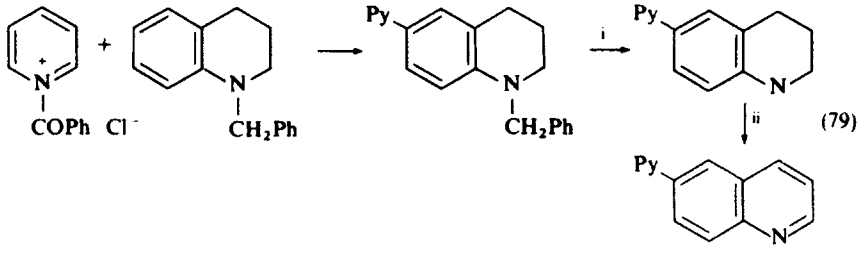


204a, R = Me
204b, R = Et



205

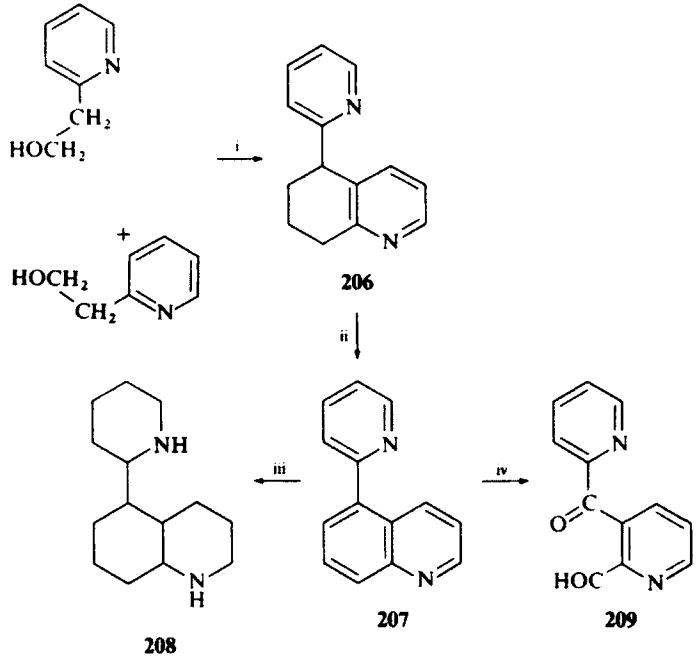
Indole, when refluxed for 30 h in anhydrous dimethylformamide with quinolinium sulphate, gave a 5% yield of 2-(3'-indolyl)quinoline.[1239] The reactions shown in equation 79 were used to prepare 6-(4'-pyridyl)quinoline.[1240]



Py = 4-pyridyl

i, H_2/PtO_2, 60 h, room temp. and atmospheric pressure;
ii, heat, 30 h, with anhydrous $CuCl_2$ in pyridine

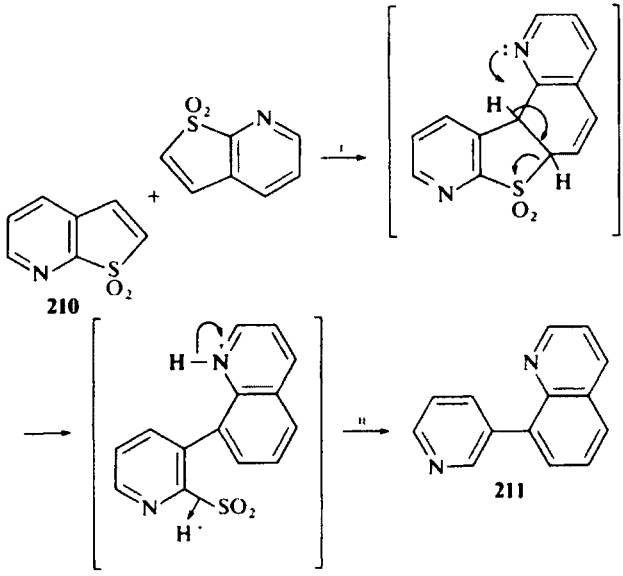
The less familiar process of the closure of the carbocyclic ring to form a quinoline occurs in the self-condensation of 2-(2'-pyridyl)ethanol in polyphosphoric acid at 200 °C to give 5-(2'-pyridyl)-5,6,7,8-tetrahydroquinoline (**206**), which was oxidized by selenium dioxide to the quinoline (**207**) and reduced by hydrogenation to the fully saturated ring structure (**208**). Potassium permanganate opened the carbocyclic ring to give compound (**209**)[1242] (Scheme 27).



i, Polyphosphoric acid, 200 °C; ii, SeO_2; iii, H_2/Pt ($+8H_2$); iv, $KMnO_4$

SCHEME 27

A similar self-condensation of thieno[2,3-*b*]pyridine 1,1-dioxide (**210**) gave, with elimination of sulphur dioxide, 8-(3′-pyridyl)quinoline (**211**) (equation 80). The structure of (**211**) was established by p.m.r. using lanthanum shift reagents.[1243]



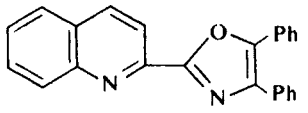
210

211

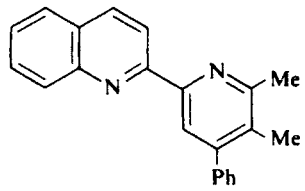
(80)

i, Reflux in xylene, 50 hr (−SO_2); ii, −SO_2, H· migration

In a study of the mechanism of the acid-catalysed hydrolysis of Reissert compounds the action of hydrochloric acid on 1-benzoyl-2-cyano-1,2-dihydroquinoline was found to give, in addition to quinaldinic acid and benzaldehyde, an unidentified yellow solid, benzoin quinaldinate and 2-(2′-quinolyl)-4,5-diphenyloxazole (**212**).[1244]



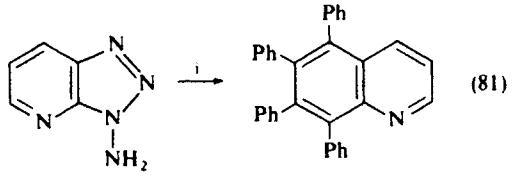
212



213

The Ullmann reaction between 6-bromo-2,3-dimethyl-4-phenylpyridine and 2-bromoquinoline by heating with copper powder for 40 h gave 2,3-dimethyl-4-phenyl-6-(2′-quinolyl)pyridine (**213**).[1245] When the methyl ester of 9-bromoanthracene-10-carboxylic acid was refluxed with copper(I) cyanide and quinoline, 9-(2′-quinolyl)anthracene was isolated in addition to the main product 9-cyanoanthracene.[1246]

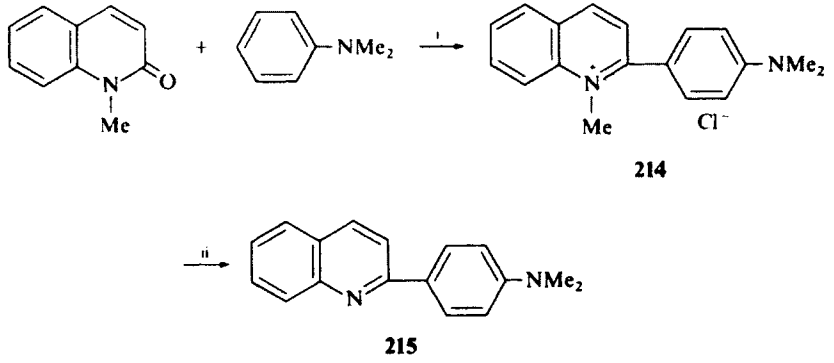
5,6,7,8-Tetraphenylquinoline was isolated in low yield when 3-aminotriazolo[4,5-*b*]-pyridine was oxidized by lead tetraacetate in the presence of tetraphenylcyclopentadienone ("tetracyclone") as a result of the trapping of the 2,3-pyridyne intermediate[1247] (equation 81).



(81)

i, Oxidation by $Pb(OAc)_4$ in presence of "tetracyclone"; ref. 1247

1-Methyl-2-(1*H*)-quinolone reacted with phosphoryl chloride and dimethylaniline to give 76.2% of 2-(4'-dimethylaminophenyl)-1-methylquinolinium chloride (**214**) and 2.6% of the free base (**215**).[1248] The corresponding thioquinolone gave only the quaternary product in low yield. When compound (**214**) was heated at 224–229 °C for 3 min the free base (**215**) (82.6%) was formed. The 2-(4'-dimethylaminophenyl)quinoline (**215**) was quaternized with methyl iodide at the dimethylamino group and (**214**) could not be prepared from (**215**) (equation 82).



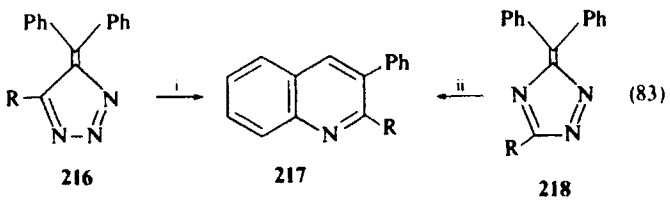
214

(82)

215

i, $POCl_3$; ii, heat, 224–229 °C, 3 min; ref. 1248

Photolysis of 4(5)-benzhydrilidene-5(4)-phenyl-4*H*(5*H*)-1,2,3-triazole (**216a**) gave 2,3-diphenylquinoline (**217a**). The 5(4)-*p*-chlorophenyl analogue (**216b**) gave 2-*p*-chlorophenyl-3-phenylquinoline (**217b**). Photolysis of both 3-benzhydrilidene-5-phenyl-1,2,4-triazole (**218a**) and the 5-*p*-chlorophenyl analogue (**218b**) gave only 2,3-diphenylquinoline.[1249] The products were identified by nmr and mass spectrometry and by an independent synthesis by the Pfitzinger method (equation 83).



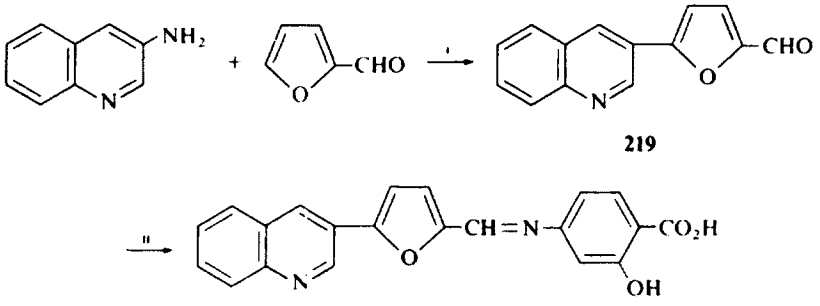
(83)

216 **217** **218**

(a), R = Ph; (b), R = *p*-ClC_6H_4

i Photolysis; ii, photolysis (**217a** formed from both **218a** and **218b**)

A series of Schiff bases derived from 5-(3'-quinolyl)-2-furfural (**219**) have been prepared as insect repellants;[1250a] 3-aminoquinoline was diazotized and coupled with furfural to give 5-(3'-quinolyl)-2-furfural (**219**), which was condensed with a series of aromatic amines. Equation 84 illustrates the use of 4-aminosalicylic acid to give (**220**).



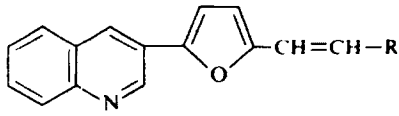
219

(84)

220

i. Diazotization and coupling; ii. + 4-amino salicyclic acid

Other combinations of substituents on the phenyl group were 4-OH, 4-CO_2H, 4-CO_2Me and 2,5-(OH)Cl. The 5-(3'-quinolyl)furfural (**219**) also reacted with the Wittig reagents $RCH_2\overset{+}{P}Ph_3X^-$ (R = substituted furyl, X = halogen) to give compounds of type (**221**).[1250b]



221

R = 5-NO_2-2-furyl or 5-(CO_2Et)-2-furyl

In the preparation of bis-2-quinolylmethane from 2-chloro- or 2-bromoquinoline and 2-methylquinoline, 2-(2'-naphthyl)quinoline was isolated as a by-product[1077] (see Section IV.1.A). 3-Phenylquinoline was prepared by catalytic dehydrogenation of 3-(1'-cyclohexenyl)quinoline.[1319]

2. Physical Properties and Uses

A. General Physical Properties

Some physical properties of individual aryl- and heteroarylquinolines are listed in Tables 49–52.

a. Dipole Moments The dipole moments of phenylquinolines measured in benzene at 25 °C were found to be consistent with the hypothesis that they arise principally from *N*-hybridization. The phenyl and quinolyl rings were found to be nearly coplanar. Mesomeric effects contribute, in addition to the calculated classical electrostatic interactions.[1251] The results of further determinations of the dipole moments of 2-, 3-, 4-, 6-, 7- and 8-phenylquinolines and 2,6-diphenylquinoline from their dielectric constants, specific volumes and refractive indices in benzene at 25 °C and the apparent group

moment of the phenyl substituent have been discussed in terms of the conjugation between the phenyl groups and the heterocyclic ring and the moments induced in the phenyl group.[1252]

The structures of eight indolylquinolines including 2-(3′-indolyl)quinoline and 2-(5′-indolyl)quinoline have been studied from considerations of their dipole moments and mass spectra. Internuclear conjugation resulting in increased double bond character of the bonds joining the rings was indicated, and appeared to give rise to stereoisomerism.[1253]

b. THERMAL STABILITY Studies of the thermal stabilities of organic molecules with the object of finding fluids stable at 550 °C included 6-phenylquinoline, 8-phenylquinoline and 2,2′-biquinolyl. In general, substituents that enhanced the resonance stabilization without causing bond weakening as a result of electron-repelling effects had the greatest stabilizing influence.[1254] Polyphenylquinolyl ethers have been shown to possess good thermal and oxidative stability with no weight loss in air after 100 h at 300 °C.[1282–1285]

c. HYDROGEN BONDING AND ACIDITY The intramolecular hydrogen bonding of 2- and 4-(1*H*)-benzimidazol-2′-ylquinoline have been studied by ultraviolet absorption measurements and the results correlated with the pK_a values of the benzimidazolyl *N*—H moiety.[1255]

d. PICRATE FORMATION BY PYRIDYLQUINOLINES In a study of the picrates formed from pyridylquinolines, pyridylquinaldines, and pyridyllepidines, it has been shown that when the N–N distance is equal to or less than 5.2 Å only monopicrates are formed, but when this distance is greater than 5.8 Å dipicrates are usually formed, although 6-methoxy-5- or -7-(2′-pyridyl)quinoline and some lutidylquinolines, which might be expected to give dipicrates, give only monopicrates.[1196]

B. Spectroscopic Properties

a. ELECTRONIC SPECTRA The following ultraviolet absorptions [λ_{max} (nm),ε ($l\ mol^{-1}\ cm^{-1}$)] of the 2-, 3- and 4-phenylquinolines are among those reported for a range of phenyl-substituted pyridines and quinolines:[1256] 2-phenylquinoline (285.5, 33,000); 3-phenylquinoline (250, 51,300), (280, 13,700); 4-phenylquinoline (230, 34,700), (285.5, 7100). The spectrum of 4-phenylquinoline is similar to that of 1-phenylnaphthalene and the spectra of 2- and 3-phenylquinolines are similar to those of 2-phenylnaphthalene and show bathochromic displacement of parallel-polarized ^1L_b and ^1B_b naphthalene bands. Studies of the ultraviolet absorption spectra of 4-quinolyl-2,6-lutidines indicate that even in the absence of substituents, such as ethoxycarbonyl, at positions 3 and 5 of the pyridine ring, little or no conjugation or coplanarity is possible between the pyridyl and quinolyl rings. Coplanarity was found to be possible with 4-phenyl-2,6-lutidine but was prevented by ethoxycarbonyl substituents at positions 3 and 5.[1257] From an analysis of the spectra of quinoline, 2- and 4-phenylquinolines and their 1-oxides, it was concluded that the N—O bond in quinoline-1-oxide is mainly aliphatic in character, in 2-phenylquinoline it is partly aliphatic and partly aromatic and in 4-phenylquinoline it is strongly aromatic.[1258]

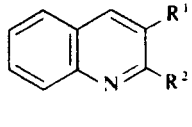
Phenylcinchoninic acids and their analogues when separated on paper chromatograms with 60% ethanol as developing solvent showed a violet fluorescence when wet, yellow when dry and blue on addition of sulphuric acid. The violet and yellow fluorescences were attributed to the quinoline ring and the hydroxycarbonyl group at position 4 and the blue fluorescence with sulphuric acid to the quinoline ring. The presence of these derivatives could be detected by this relationship.[1259] Examination of the solvent effects

on the fluorescence characteristics of a series of 2-(2′-thienyl)quinolines showed fluorescence from an excited state which is mainly $\pi \rightarrow \pi^*$ in character.[1260]

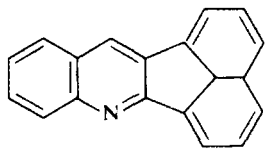
A study of the emission spectra of 2-phenylquinoline and some derivatives showed that as conjugation between the quinolyl and phenyl rings was increased, accompanied by increased rigidity of the molecule, fluorescence became an important mode of decay and the photoreactivity of the system was increased.[1261,1262]

b. NUCLEAR MAGNETIC RESONANCE SPECTRA ^{1}H-nmr data have shown that in 1-phenylquinolinium salts the phenyl substituent lies in a plane almost at right-angles to the plane of the quinolyl ring and so causes shielding of a proton at position 2 or of the protons on a methyl substituent at position 2. On the other hand, in benzo[*f*]quinoline systems a proton at position 4 or protons of methyl substituents at position 4 are deshielded.[336] Comparisons of the chemical shifts of protons in the ^{1}H-nmr spectra of 4-methyl-2-phenylquinoline, its conjugate acid and 1-methyl quaternary salts have shown that the 2-phenyl substituent is rotated 55° out of the plane of the quinolyl ring.[1263]

c. MASS SPECTRA Mass spectra of the *Haplophyllum* alkaloids dubamine (**166**), robustine (**167a**), ψ-fagarine (**167b**) and dictamnine (**167c**) (see Section V.1.A) have been recorded and the fragmentation patterns established. Spectra from the first three alkaloids show intense M^+ peaks.[1264] High-resolution mass spectra of 2-phenyl- (**222a**) and 2,3-diphenylquinoline (**222b**), 2-C_6D_5-quinoline (**222c**) and naphtho[1,8-*b*]quinoline (**223**) and their 1-oxides have been recorded. The only major peaks from (**222**) and (**223**) are from the M^+ and $(M-1)^+$ ions, reflecting the stability of these structures. The 1-oxides have major peaks at M^+, $(M-16)^+$ and $(M-17)^+$. The 1-oxide of 2-phenylquinoline has fragments showing loss of H and CO.[1265] The fragmentation patterns of 2-(2′-pyridyl)quinoline and 2,2′-biquinolyl show that whereas the pyridylquinoline rearranged to acridine derivatives the biquinolyl showed very little fragmentation.[1266]



222



223

(a) R^1 = Ph, R^2 = H; (b) $R^1 = R^2$ = Ph; (c) $R^1 = C_6D_5$, R^2 = H

C. X-ray Diffraction

X-ray diffraction data have been suggested as a convenient means for identifying 1,3,4-oxadiazoles, including 2-(2′-quinolyl)-1,3,4-oxadiazole.[1267] Characteristic X-ray powder diffraction patterns of 22 organic bases including solid 2,6-dimethylquinoline, 6-phenylquinoline and 2,2′-biquinolyl have been obtained. A technique for extruding specimens has been described.[301]

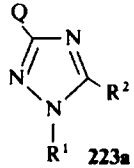
D. Chromatographic Separations

The chromatographic separation and spectrographic identification of phenylquinolines by tlc and gas chromatography, followed by infrared and nmr spectroscopy, has been reported.[1194,1268]

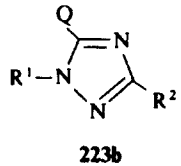
E. Uses of Arylquinolines and Heteroarylquinolines

a. BIOLOGICAL USES 6-Phenylquinoline has been reported as one of a series of quinoline derivatives having cytogenic activity.[259] 2-Phenylquinoline slightly stimulated growth of strains of fungus producing peptide or clavine types of ergot.[1269] A series of 5-(3′-quinolyl)-2-furfural derivatives have been prepared and used as insect repellants for houseflies and cockroaches[1250a,b] [see Section V.1.G, formulae (**220**) and (**221**)]. A German patent[1270] claims wide biological and other useful applications for a series of benzimidazole derivatives including 2-(2′-quinolyl)benzimidazole as pesticides, preservatives, vulcanization additives, pharmaceuticals and intermediates in organic syntheses and for protection against light.

b. MEDICAL, PHARMACOLOGICAL AND PHARMACEUTICAL APPLICATIONS 2-(1*H*)-Indol-3′-ylquinoline was one of a series of 64 indole derivatives studied, most of which were found to possess antifungal activity, although the indolylquinoline was one of the least active of those tested.[1271] A series of pyridyl-substituted tetrazoles including 3-(1*H*)-tetrazol-5′-ylquinoline [see Section V.1.E.c., formula (**174**)] formed a new class of lipolysis inhibitors.[1225] Pyridylquinolines,[1273] thiazolylquinolines[1273] and 20 different phenylquinolines[1274] have been reported to have antispasmodic and antihistaminic activity. 2-(2′-Benzimidazolyl)quinoline has been prepared for its tuberculostatic activity[1214] (see Section V.1.E.b). The various 5-(6′-quinolyl)-1,2,4-triazines indicated by formulae (**223a**) and (**223b**) have been prepared for use in the treatment of gout.[1653a] Trifluoromethylimidazolylquinolines similarly act as xanthine oxidase inhibitors in the

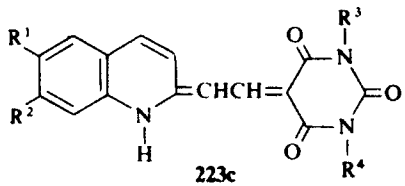


223a



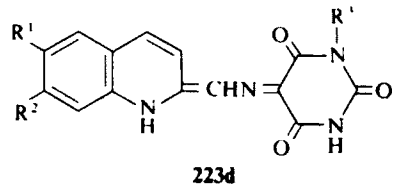
223b

Q = 6-quinolyl (also pyrazinyl, substituted phenyl, picolyl, 2-furyl, pyrimidinyl, 4-pyridazinyl 2-thienyl or 2-naphthyl)
R^1 = H, Me, Ac, $CONMe_2$ or CH_2Ph; R^2 = 4-pyridyl, 2-pyridyl, 4-pyrimidinyl or pyrazinyl



223c

R^1 = H, Me, OMe; R^2 = H; R^3 = Ph, 1-naphthyl, *p*-ClC_6H_4; R^4 = Ph, *p*-tolyl, H, 1-naphthyl; R^1R^2 = benzo



223d

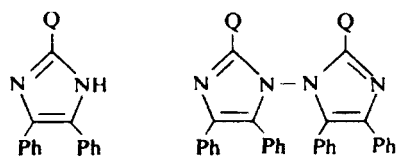
R^1 = Me, OEt, NH_2; R^2 = H; R^3 = Ph, Me, 1-naphthyl; R^1R^2 = benzo

treatment of gout.[1653b] The quinoline alkaloids robustine (**167a**) and dubamine (**166**) (see Section V.1.A, when injected (s.c.) into mice at 50–100 mg kg^{-1} decreased the hypnotic effects of hexenal or chloral hydrate. When injected (i.v.) at 3 mg kg^{-1} they did not show any significant effects on the brain electrical activity and when administered orally at 100–300 or 500–2500 mg kg^{-1}, respectively, they had no apparent toxic effects.[1275] 4-(5′-Nitro-2′-furyl)quinoline-2-carboxylic acid 1-oxide was rated the best of 52 compounds for the treatment of mastitis in cows.[1276]

2- and 4-Quinolyl-9-acridinylmethane (I and II) and 4-quinolyl-9-(2-ethoxy-6-nitro)-acridinylmethane and its iodomethylate (III and IV) were tested for pharmacological activity in mice and rats. They all decreased rectal temperature by 2–3.3 °C. I, II and IV had analgesic activity, and II, III and IV prolonged chloral hydrate-induced sleep. All the compounds had LD_{50} values of 1000 mg kg^{-1}.[1508] Twenty-three derivatives of compounds (**223c**) and (**223d**) prepared (in yields of 50–68%) by condensation of a substituted quinaldine with the appropriate derivative of 5-methylenebarbituric acid or violuric acid were found to suppress the growth of *Staphylococcus aureus* at concentrations of 125–500 μg ml^{-1} for (**223a**) and 3.9–31.25 μg ml^{-1} for (**223b**).[1509]

c. Dyes and Photosensitive Materials Benzoxazolyl-, benzothiazolyl- and benzimidazolylquinolines with a 2-, *o*-, *m*- or *p*-aminophenyl substituent have been prepared for diazotization and coupling (e.g. to β-naphthol) for use as disperse dyes for polyamide fibres[1210,1211,1277,1278] (see Section V.1.E.b). The presence of a benzothiazol-2-yl group on the quinoline nucleus was shown to improve the luminosity and fastness to washing but lowered the light fastness and excitation purity.[1277] Dyes in which the 2-(arylazo)phenyl substituent is replaced by a styryl or carbocyanine residue (with the quinoline nitrogen quaternized) are potentially useful as sensitizers.[1277a] 2-(2'-Quinolyl)indan-1,3-dione is one of the constituents of a photosensitive material for coating on to aluminium plates.[1279]

d. Polymer Technology The quinolyl substituted imidazoles (**224**) and biimidazolyls (**225**) have been used as stabilizers for the inhibition of polymerization of styrene and benzyl methacrylate monomers.[1280,1281]



224 **225**

Q = 2-, 3-, 4-, 5-, 6-, 7- or 8-quinolyl

Phenylated quinoline ethers have been prepared by Friedländer-type condensations of 4,4'-diamino-3,3'-dibenzoyl diphenyl ether[1282,1283] or 4,4'-bis(2''-aminobenzoyl) diphenyl ether[1284,1285] with diacetyl or other bisketomethylene monomers. The polymers were formed by polyphosphoric acid in solvents containing *m*-cresol. They are reported to have good thermal and oxidative stability.

3. Chemical Properties and Reactions

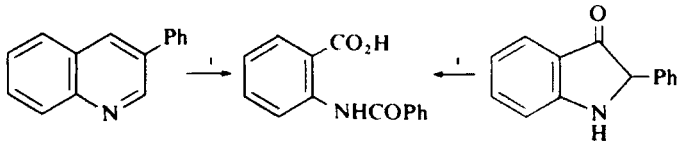
A. Oxidation

Phenylquinolines which also have an alkyl substituent may be converted to the carboxylic acids by oxidation of the alkyl group only. 2-Phenyl-8-methylquinoline was oxidized to 2-phenylquinoline-8-carboxylic acid with potassium dichromate and sulphuric acid, and 2-phenyl-3-methylquinoline with chromic acid, manganese dioxide and sulphuric acid (30%) gave a 66% yield of 2-phenylquinoline-3-carboxylic acid.[1178,1287] An alkyl group attached to the aryl substituent may be oxidized similarly to the carboxylic acid; 2-*p*-tolylquinoline with chromic acid, manganese dioxide and sulphuric acid (40%),[1287] or with chromic acid and acetic acid,[1178] gave 2-phenylquinoline-4'-carboxylic acid, but in other cases the aryl ring may be degraded, e.g. 2-*m*-tolylquinoline

under similar conditions gave quinoline-2-carboxylic acid,[1301] which was also formed from 2-(*p*-hydroxyphenyl)quinoline,[1302] 4-(*m*-hydroxyphenyl)quinoline and 4-(*p*-hydroxylphenyl)-quinoline each gave quinoline-4-carboxylic acid.[1303] Oxidation of 2-(*p*-hydroxyphenyl)-4-methylquinoline with alkaline potassium permanganate gave 4-methylquinoline-2-carboxylic acid, 4-methylpyridine-2,3,6-tricarboxylic acid and pyridine-2,3,4,6-tetracarboxylic acid.[1304, 1305] The attempted electrolytic oxidation of 2-phenylquinoline gave no identifiable products.[1178, 1288] Oxidation of 2-phenylquinoline with potassium permanganate has been reported to give 2-phenylbenzoxazole, which was also formed by oxidation of atophan (2-phenylquinoline-4-carboxylic acid).[1289] An earlier paper described the oxidation of 2-phenylquinoline with potassium permanganate and dilute sulphuric acid to give *N*-benzoylanthranilic acid.[1170]

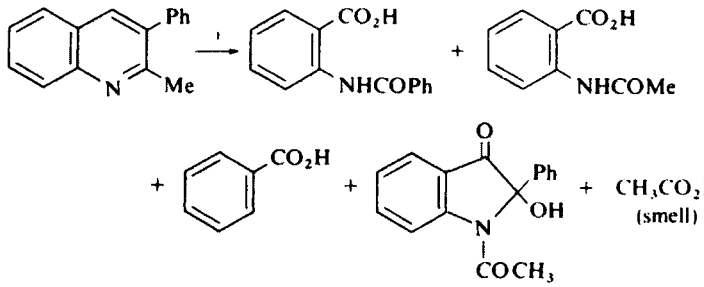
The oxidation of 3-phenylquinoline with potassium permanganate in acetic or sulphuric acid also gave *N*-benzoylanthranilic acid, a reaction which appeared to involve a 1,2-shift of the phenyl substituent. 2-Phenylindoxyl is also oxidized to *N*-benzoylanthranilic acid[1290] (see equation 85).

More recently, the oxidation of 3-phenylquinoline to *N*-benzoylanthranilic acid by cold acidic potassium permanganate has been confirmed and extended to the 2-methyl and 2-ethyl homologues of 3-phenylquinoline.[1291] 2-Methyl-3-phenylquinoline gave, in addition to *N*-benzoylanthranilic acid, *N*-acetylanthranilic acid, benzoic acid and 1-acetyl-2-hydroxy-2-phenyl-(3*H*)-indolinone (see equation 86a). 2-Ethyl-3-phenylquinoline gave benzoic acid and 1-propionyl-2-hydroxy-2-phenyl-(3*H*)-indolinone but no derivatives of anthranilic acid (see equation 86b).



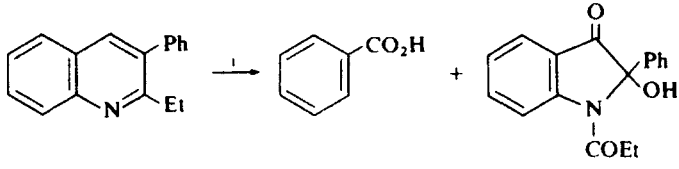
(85)

i, $KMnO_4$ + HOAc or H_2SO_4[1290] or cold dilute acidic $KMnO_4$[1291]



(86a)

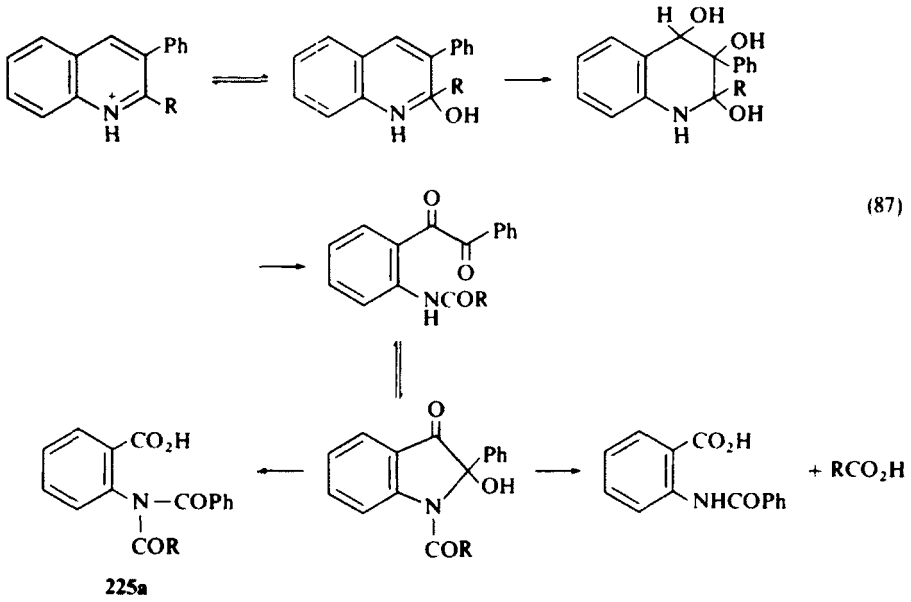
i, Cold dilute acidic $KMnO_4$[1291]



(86b)

i, Cold dilute acidic (H_2SO_4) $KMnO_4$[1291]

These observations, including the apparent 1,2-shift of the phenyl group, have been rationalized by Rees and Sabet,[1291] who suggested the mechanism shown in equation 87.



(87)

225a

Ref. 1291

When R = Me (equation 87), additional hydrolysis of alternate *N*-acyl substituents of (**225a**) would account for all of the products observed in equation 86a. When R = H only benzoic acid and *N*-benzoylanthranilic acids were isolated, owing to the ready hydrolysis and ease of oxidation of *N*-formylanthranilic acid (**225a**, R = H). When R = Et (equation 87) the indolinone is more resistant to hydrolysis on account of steric hindrance.

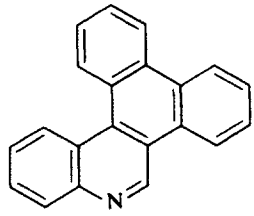
When 2-(6′-tetralyl)quinoline was passed over lead oxide on pumice at 700 °C, 2-β-naphthylquinoline was formed.[814a]

Oxidation of arylquinolines with peracids gives the 1-oxides. 2-Phenylquinoline was oxidized with perphthalic acid to give a 10–12% yield of the 1-oxide. 4-Phenylquinoline under similar conditions gave a 96% yield of its 1-oxide and 2-methyl-4-phenylquinoline gave a 98% yield.[1292] 2-Phenylquinoline was also oxidized with peracetic acid to give the 1-oxide and some *N*-benzoylanthranilic acid. 2-Phenylquinoline-1-oxide was reduced to 2-phenylquinoline with iron(II) sulphate and with sulphur dioxide.[1293] 2-Mesitylquinoline was oxidized to the 1-oxide with perbenzoic acid and 3-methyl-2-phenylquinoline with peracetic acid, and these oxides were not reduced by iron(II) hydroxide.[1294]

Photolysis of solutions of 3,4-diphenylquinoline in dilute hydrochloric acid gave the dibenzo[*a*,*c*]phenanthridine (**226**)[1295]

B. Reduction

The reduction of arylquinolines can involve either or both of the quinoline or substituent aryl ring systems. In a study of the catalytic hydrogenation of Atophan (2-phenyl-



226

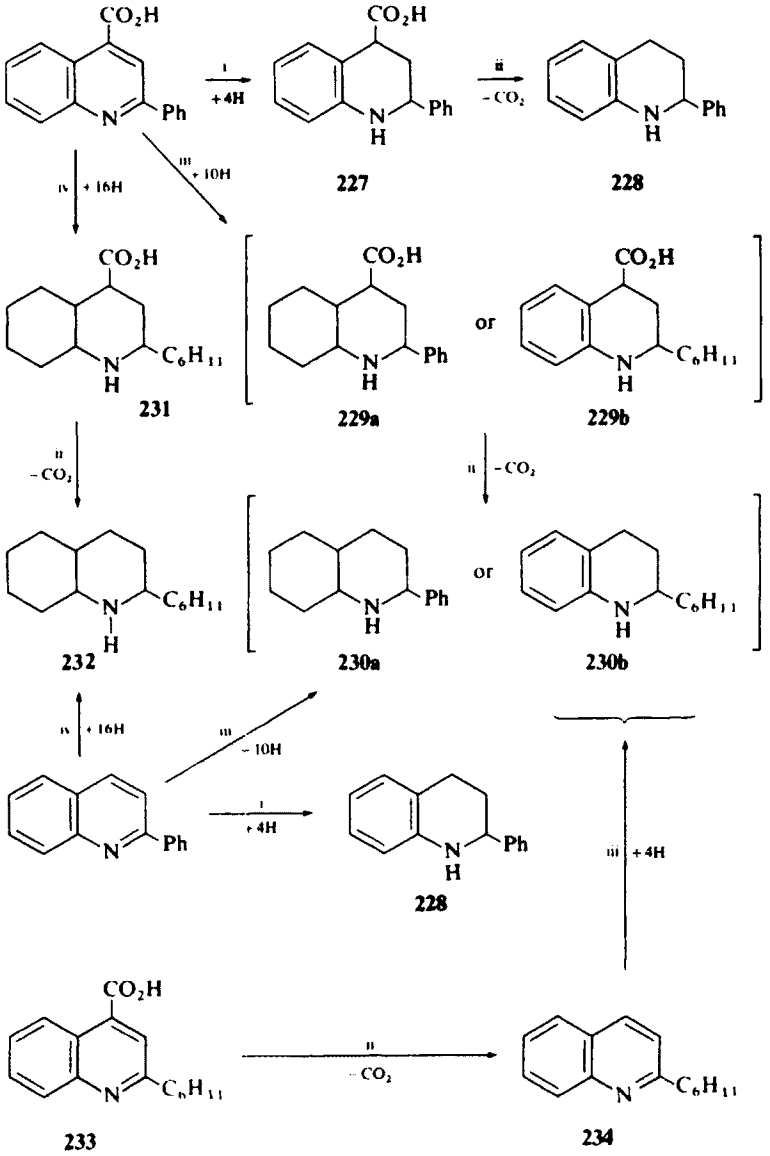
cinchoninic acid) and 2-phenylquinoline with a colloidal platinum catalyst the tetrahydro- (**227**) and (**228**), decahydro- (**229**) and (**230**), and fully saturated perhydro derivatives (**231**) and (**232**) were obtained successively by increasing the hydrogen pressure.[160] The tetrahydro derivatives were secondary amines and therefore had the 1,2,3,4-tetrahydroquinoline ring structure. The perhydro products were clearly 2-cyclohexyldecahydroquinoline or its 4-carboxylic acid. The intermediate decahydro derivatives, however, could have had either the 2-phenyldecahydroquinoline structure (**229a**) or (**230a**) or the 2-cyclohexyl-1,2,3,4-tetrahydroquinoline structure (**229b**) or (**230b**), depending on whether the phenyl substituent or the heterocyclic ring of the quinoline has been reduced. Reduction of synthetic 2-cyclohexylcinchoninic acid (**233**) and its decarboxylation product 2-cyclohexylquinoline (**234**) gave the same decahydroquinoline derivatives as the reduction of Atophan or 2-phenylquinoline, respectively. Thus the heterocyclic ring of quinoline was reduced first, followed by reduction of the phenyl substituent and finally the carbocyclic ring of quinoline (see Scheme 28).

At higher hydrogen pressures (greater than about 1 atm), the decahydro derivative was formed exclusively, even when the reaction was stopped after the absorption of 2 mol of hydrogen, showing that there was an upper threshold pressure above which partial hydrogenation was not possible.

The reduction of 2-phenylquinoline with hydrogen and Raney nickel at 100 atm and 60–70 °C gave (±)-2-phenyl-1,2,3,4-tetrahydroquinoline, which was purified as its acetyl derivative.[1296] Some 2-phenyl-5,6,7,8-tetrahydroquinoline was obtained from the mother liquor from the acetyl purification. A similar result was obtained from 3-phenylquinoline,[514] but 2-methyl-4-phenylquinoline gave 2-methyl-5,6,7,8-tetrahydroquinoline as the main product, with a smaller amount of the 1,2,3,4-tetrahydroquinoline.[516]

The reduction of 2-anisyl- and 2-phenylquinolines with tin and hydrochloric acid gave only small yields of the tetrahydro derivatives.[1297] Hydrogenation with PtO_2 or Pt-black catalysts gave 60–70% yields in 20 h, but reduction with sodium and ethanol gave an almost quantitative yield.[1297] Hydrolysis of the product formed by heating 2-phenylquinoline at 160 °C with diisobutylaluminium hydride[500] or of the potassium radical ions of 2-phenylquinoline[1298] gave 2-phenyl-1,2,3,4-tetrahydroquinoline. 8-Phenylquinoline was reduced by sodium to the (py)-tetrahydro derivative.[1299] Many other examples have been reported of the reduction of arylquinolines to the corresponding 1,2,3,4-tetrahydro derivatives.[1162,1179,1302,1306–1310]

The reduction of 2,3-diphenylquinoline with zinc and ethanolic hydrogen chloride or with sodium and ethanol gave mixtures of the (±)-geometrical isomers of 2,3-diphenyl-1,2,3,4-tetrahydroquinoline, m.p. (a) 130–131 °C and (b) 92 °C.[517a] The proportions of the two isomers formed with zinc and hydrochloric acid was not determined but sodium and ethanol gave 80% of the higher melting isomer (a).[517a] Reduction with tin and hydrochloric acid[517a] or hydrogen and colloidal platinum in acetic acid[1175] gave only the higher melting (±)-isomer (a).



i, H_2/Pt, 1 atm; ii, dry distillation with soda-lime;

iii, H_2/Pt, 2 atm; iv, H_2/Pt, higher pressures

SCHEME 28

The hydrogenation of 2-(2'-furyl)quinoline has been investigated using various catalysts—Raney nickel in ethanol at room temperature, Adams platinum in ethanol and Adams platinum in acetic acid. With the Raney nickel catalyst, 4 mol of hydrogen

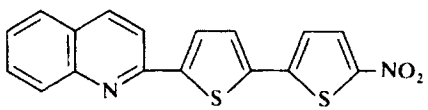
were absorbed with no change in reaction rate after the absorption of the first 2 mol of hydrogen. Five compounds were isolated from the reaction and the main product (76–78%) was a mixture of the stereoisomeric 2-(2'-tetrahydrofuryl)-1,2,3,4-tetrahydroquinolines.[1300]

C. Aromatic Substitutions

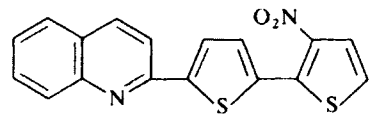
Electrophilic aromatic substitutions (such as nitration) of phenylquinolines occur most easily on the phenyl substituent and subsequently on the carbocyclic ring of the quinoline moiety at positions 5 and 8. If the quinoline is quaternized, electrophilic substitution of the phenyl substituent occurs almost entirely at the *m*-position (i.e. the 3'-position), otherwise a mixture of products is obtained consisting mainly of *p*- and *m*-phenyl-substituted quinolines with the *p*-substituted isomer predominating. Small amounts of *o*-phenyl-substitution products have been reported. Nucleophilic attack, e.g. by metal amides or organolithium compounds, takes place on the quinoline ring preferably at position 2. If this position is free a 2-substitution product is usually formed (see Section I.5.F. f, g and h). If position 2 is already substituted, nucleophilic attack may occur at position 4 or a substituted 1,2-dihydroquinoline may result.

a. Electrophilic Substitutions Nitration of 2-phenylquinoline at 0 °C gave mononitro derivatives which consisted of about 60% 2-(4'-nitrophenyl)quinoline and 30% 2-(3'-nitrophenyl)quinoline. A similar nitration of 2-phenylquinoline methosulphate gave 97% of 2-(3'-nitrophenyl)quinoline methosulphate.[656] The methosulphate of the nitro compound was converted to the methochloride by boiling with hydrochloric acid and to the free base by heating the methochloride at its melting point for 30 min.[656] The nitration of 4-methyl-2-phenylquinoline with fuming nitric acid at 50–60 °C gave mainly 4-methyl-2-(4'-nitrophenyl)quinoline together with other nitro compounds.[1304,1311] When nitrated at −10 °C with nitric acid and sulphuric acid, 3-phenylquinoline gave 3-(4'-nitrophenyl)quinoline as the only pure product isolated. Further nitration gave two dinitro derivatives, the main one of which was shown to be 5-nitro-3-(4'-nitrophenyl)-quinoline.[618] Similarly, 4-phenylquinoline with cold nitric acid (sp. gr. = 1.5) gave a mixture of 4-(3'-nitrophenyl)quinoline and 4-(4'-nitrophenyl)quinoline together with small amounts of dinitration products.[1173] An early report on the nitration of 6-phenylquinoline with fuming nitric acid in acetic acid described the isolation of unidentified mono- and dinitro-6-phenylquinoline.[1309]

Nitration of thienyl- and bithienylquinolines occurs, as might be expected, in the thienyl ring systems. With nitric and sulphuric acids, 2-(2'-thienyl)quinoline gave an 82.5% yield of 2-(5'-nitro-2'-thienyl)quinoline and 2-(2',2''-bithienyl)quinoline gave a mixture of 2-(5''-nitro-2'-,2''-bithien-5'-yl)quinoline (**235a**) and the 3''-nitro analogue (**235b**).[1312a,b]



235a



235b

Sulphonation of 2-phenylquinoline with pyrosulphuric acid ($H_2S_2O_7$) was reported to give a mixture of 4- and 3-(2'-quinolyl)benzenesulphonic acids.[1313a] A later paper[1313b] described the separation of a small amount of monosulphonic acid and the isolation as their barium salts of two unidentified disulphonic acid derivatives of 2-phenylquinoline,

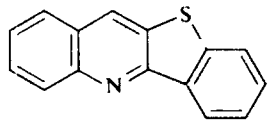
together with other products. Sulphonation of 6-phenylquinoline with cold fuming sulphuric acid gave 4-(6′-quinolyl)benzenesulphonic acid and a further product believed to be sulphonated in the quinoline nucleus.[1309]

b. NUCLEOPHILIC SUBSTITUTIONS 2-Phenylquinoline forms addition compounds with alkali metal amides in liquid ammonia, which regenerate the 2-phenylquinoline by the action of ammonium salts. On standing, secondary addition compounds are formed which can be converted by sodamide or potassamide and an alkali metal nitrate to 4-amino-2-phenylquinoline.[636c,1314] Potassamide alone converts 6- and 8-phenylquinolines into tars but in the presence of potassium nitrate aminophenylquinolines are formed, presumably 2-amino-6- or -8-phenylquinoline.[636d] 2-Amino-8-phenylquinoline has been prepared by the direct amination of 8-phenylquinoline with sodamide.[1316] 2-*p*-Tolylquinoline, however, was not converted to the 4-amino derivative by potassamide and potassium nitrate.[1314]

With phenyllithium, 2-phenylquinoline gives the addition product 2,2-diphenyl-1,2-dihydroquinoline.[126,1317] Treatment of 3-(2′-thienyl)quinoline with butyllithium followed by trimethylchlorosilane gave 3-(5′-trimethylsilylthien-2′-yl)quinoline and 3-(3′-trimethylsilylthien-2′-yl)quinoline as a result of α- and γ-lithiation, respectively. α-Lithiation was favoured by the use of tetrahydrofuran as solvent and γ-lithiation by the use of ether as solvent.[1318] Treatment of 2-ferrocenylquinoline with butyllithium gave the 1,4- rather than the expected 1,2- addition to the quinoline ring.[1333]

D. Formation of Condensed Ring Systems

Among the biaryls which can form a sulphur bridge by the action of hydrogen sulphide and an alumina catalyst at 630 °C are 2- and 3-phenylquinolines. For example, 2-phenylquinoline forms benzothieno[3,2-*b*]quinoline (**236**).[1319]



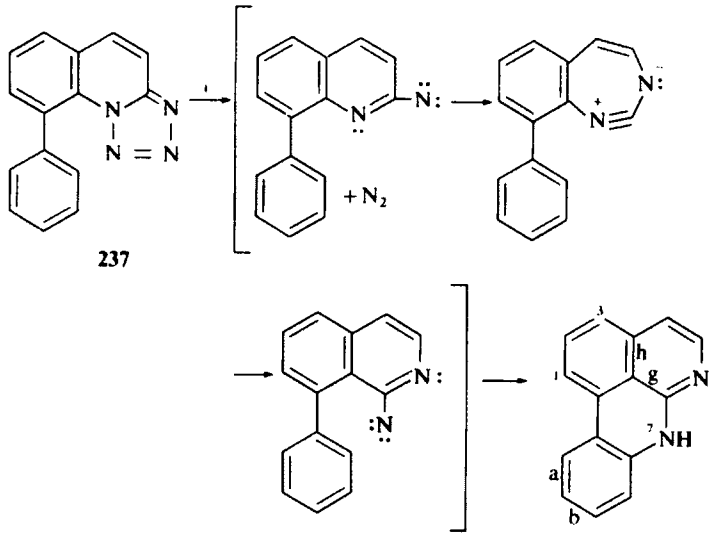
236

When 9-phenyltetrazolo[1,5-*a*]quinoline (**237**), prepared from 2-amino-8-phenylquinoline, was heated to 530 °C at 0.2 mmHg a molecular rearrangement occurred in high yield (82%) to give (7*H*)-pyrido[2,3,4-*gh*]phenanthridine (**238**). The formation of this product is consistent with the ring expansion of 8-phenyl-2-quinolylnitrene followed by ring contraction to 8-phenyl-1-isoquinolylnitrene and ring closure[1316] (see Scheme 29).

When treated with diisopropylaminolithium, $LiN(CHMe_2)_2$, followed by water and potassium permanganate, 3-(1′-imidazolyl)quinoline gave a 56% yield of the cyclo-dimer (**238a**) and 3-(1′-benzimidazolyl)quinoline gave 15% of an analagous product (**238b**) and 8% of the dimer (**238c**).[1654]

E. Miscellaneous Reactions

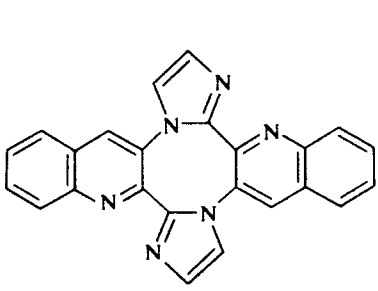
Alkali metals, particularly potassium have been reported to combine with a series of *N*-heterocycles including 2-phenylquinoline to give K^+ ions and *N*-heterocyclic radical anions.[1320] These combinations have been used to metalate other aromatic compounds to give products which were readily alkylated or carboxylated. The reactions are favoured by aprotic dipolar ethers as solvents, e.g. tetrahydrofuran. Thus K^+[2-



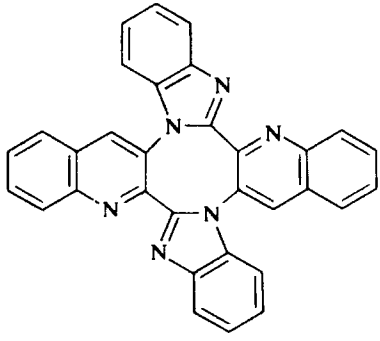
237 238

i, Heat to 530 °C at 0.2 mm Hg ($-N_2$)

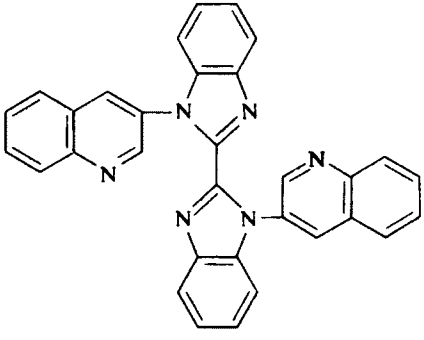
SCHEME 29



238a



238b



238c

phenylquinoline]' metalated diphenylmethane and triphenylmethane and on treatment with carbon dioxide the products gave diphenyl- and triphenylacetic acid, respectively. *N*-Ethylaniline, on metalation followed by treatment with butyl bromide, gave *N*-butyl-*N*-ethylaniline. Many other examples of reactions of these types have been reported.[1320a] Hydrolysis of the alkali metal–*N*-heterocycle combinations gave potassium hydroxide and partially or completely hydrogenated heterocycles.[1320b]

Quaternization of 2-(4′-dimethylaminophenyl)quinoline or the corresponding diethylaminophenyl analogue with methyl, propyl, butyl or isobutyl halides has been investigated and the site of quaternization was found to depend on temperature. At room temperature quaternization of the nitrogen atom of the dialkylamino group was favoured, at 80 °C the reactivities of the two nitrogen atoms were almost equal and at 150 °C only the heterocyclic nitrogen was quaternized. 2-(1′-Methyl-1′,2′,3′,4′-tetrahydro-6′-quinolyl)quinoline formed equal amounts of the two possible mono-quaternary salts at 80 °C and bis-quaternary salts at 150 °C.[1321]

F. Metal Complexes with Aryl- and Heteroarylquinolines

A large number of metal complexes with aryl- or heteroarylquinolines as ligands have been studied and are listed in Table 35. In most cases details of their absorption spectra are given in the references quoted.

VI. Biquinolyls and Polyquinolines

1. Preparation

The biquinolyls are particular examples of heteroarylquinolines in which the substituent is itself a quinolyl function. It follows that the methods described for the preparation of heteroarylquinolines (Section V.1) are generally applicable to the preparation of biquinolyls as indicated below. The identity of the two ring structures, however, favours additional methods which involve some form of dimerization, polymerization or oxidative self-condensation.

A. Preparations Involving the Synthesis of One or More of the Quinoline Rings

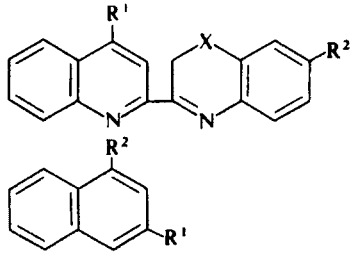
As with the alkyl- and arylquinolines, and other types of heteroarylquinolines, biquinolyls can be synthesized by the many methods which result in the formation of the quinoline ring. These methods have been reviewed in Part I, Chapter 2. Examples of biquinolyls and some polyquinolyls prepared by these methods are given in Table 36.

B. General Methods for Heteroarylquinolines

a. From Hydroxybiquinolyls and Biquinolones The reduction of hydroxybiquinolyls or biquinolones by methods such as distillation with zinc dust has been used to obtain the biquinolyls. 2,3′-Biquinolyl was obtained in this way from an unspecified dihydroxy derivative[1360] from the 4,4′-dihydroxy derivative[1361] and from 2-hydroxy-2,3′-biquinolyl by distillation with zinc dust in a stream of hydrogen.[1362]

b. Decarboxylation Biquinolyl carboxylic acids undergo decarboxylation to the biquinolyls as described for other heteroarylquinoline carboxylic acids (Section V.1.D.c) and, as before, they are particularly important when applied to the 4-carboxylic acids or 4,4′-dicarboxylic acids obtained from the Pfitzinger synthesis. Other examples include 8,8′-biquinolyl from its 5,5′-dicarboxylic acid,[1363] 2,3′-biquinolyl from 4,4′-dihydroxy-

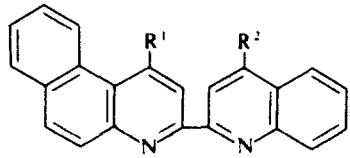
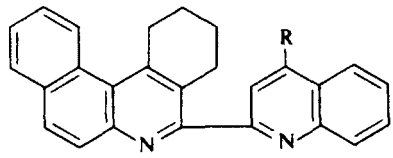
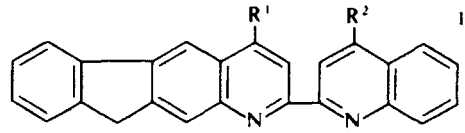
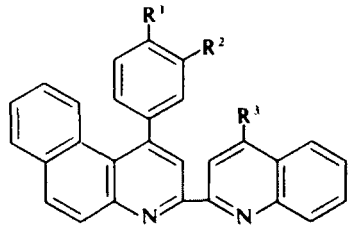
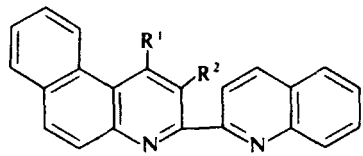
TABLE 35. Metal Complexes of Aryl- and Heteroarylquinolines

Metal species	Ligand	Ref.
Cu^+	2-(2′-Benzimidazolyl)quinoline	1322–3, 1327
	2-(1′-Methylbenzimidazol-2′-yl)quinoline	1323
	2-(2′-Benzimidazolyl)-8-methylquinoline	1323
	2-(1′-Methylbenzimidazol-2′-yl)-8-methylquinoline	1323
	2-(2′-Pyridyl)quinoline	1324
	3-Methyl-2-(2′-pyridyl)quinoline	1324
	2-(1′-Isoquinolyl)quinoline	1324
	 X = NH, S, O; R^1 = Cl, OMe, Ph, NEt_2, NHPh; R^2 = Cl, Me, NO_2, NH_2Ph	1325
	R^1 = 2-pyridyl, 2-quinoxalinyl or 2-substituted-4-thiazolyl; R^2 = Me or Ph	1326
	2,6-Bis(2′-quinolyl)pyridine	1328
Cu^{2+}	2,6-Bis(2′-quinolyl)pyridine	1656
Co^{2+}	2-(2′-Benzimidazolyl)quinoline	1327
	2,6-Bis(2′-quinolyl)pyridine	1328
Fe^{2+}	2,6-Bis(2′-quinolyl)pyridine	1328
Lanthanides^{3+}	2,6-Bis(2′-quinolyl)pyridine	1322
Mn^{2+}	2,6-Bis(2′-quinolyl)pyridine	1328
Ni^{2+}	2,6-Bis(2′-quinolyl)pyridine	1328
	2-(2′-Benzimidazolyl)quinoline	1327
$NbOCl_3$	2-Phenylquinoline	901a
$TiCl_4$	2-Phenylquinoline	901a
Os^{2+}	2-(2′-Pyridyl)quinoline	1329
Ru^{2+}	2-(2′-Pyridyl)quinoline	1329
Pd^{2+}	2-Phenylquinoline	1330
Pd^{2+}	6-Phenylquinoline	905
Pd^{2+}	2-(2′-Thienyl)quinoline	1331
Pt^{2+}	2-(2′-Thienyl)quinoline	1331
Au^{3+}	2-(2′-Pyridyl)quinoline	1334
$CuNO_3$ + P, As or Sb	2-(2′-Pyridyl)quinoline	1335

2,3′-biquinolyl-3,2′-dicarboxylic acid as a result of decarboxylation and reduction when distilled with zinc dust.[1361] More recently very pure 2,2′-biquinolyl was obtained in high yield (78%) from 2,2′-bicinchoninic acid by decarboxylation in paraffin oil at 310–340 °C and 100–200 mmHg,[1364] and similarly in 82% yield,[1365] and also from the 4-monocarboxylic acid.[1366] Decarboxylation of the appropriate 2-carboxylic acids gave 2,3′-[1367] and 3,4′-biquinolyls.[1348]

Biquinolyls are also formed as by-products during the decarboxylation of quinolinecarboxylic acids to quinolines. The distillation of the calcium salt of cinchoninic acid has been reported to give some 3,7′- or 4,7′-biquinolyl,[1369,1370] which was also obtained from the calcium salts of quinoline-2-carboxylic acid[1368] and 3-isopropylquinoline-2-

TABLE 36. Biquinolyls Prepared by Methods Involving the Synthesis of the Quinoline Rings

Biquinolyls prepared	Ref.
A. By Skraup Synthesis	
2,6'-	1302
5,7'-	1336
5,8'-	1336
7,7'-	1336
7,8'-	1336
8,8'-Dimethoxy-6,6'-	1337
7,7'-dimethyl-8,8'-	1338
5,5',7,7'-Tetra-methyl-8,8'-	1338
4,4',5,5'-Tetra methyl-8,8'-	1339
2,2'-Dimethyl-6,6'-	1340
B. By Doebner–Von Miller Synthesis	
2,2',4,4',8,8'-Hexa-methyl-6,6'-	1341
2,2',8,8'-tetra-methyl-6,6'-	1342
Bis-2,2'-(indane-1,3-dione)-6,6'-	1342
C. By Combes Synthesis	
2,2',4,4'-Tetra-methyl-6,6'-	1343
2,2',4,4',8,8'-Hexa-methyl-6,6'-	1343, 1344
D. By Friedländer-type Synthesis	
2,4'-	1345
2,3'-	1346, 1348, 1307, 1359
2'-Methyl-2,3'-	1346
2,2'-	1349, 1358
3,4'-	1348
3-Ethyl-2,2'-	1349
4-Methyl-2,2'-	1349
3-Phenyl-2,2'-	1349
4-Phenyl-2,2'-	1349
3-Propyl-2,2'-	1349
4,4'-Diphenyl-6,6'-(polymeric)	1350
3-(2'-Quinolyl)-4-(2''-quinolyl)-quinoline	1234
E. Pfitzinger synthesis	
2,2'-	1351, 1352, 1366
6,6'-Dimethyl-2,2'-	1351
7,7'-Dimethyl2,2'-	1351
8,8'-Dimethyl-2,2'-	1351
5,5'-Dimethyl-2,2'-	1351
2,6'-	1354
[2,6';2',6''-Terquinoline]	1354
2-(CO_2Et)-4-(CO_2H)-3,2'-	1355
F. By Other Methods	
	1356
R^1 = H or Ph; R^2 = H or Ph	
	1356
R = H or Ph	
	1357
R^1 = H or Ph; R^2 = H or Ph	
	1353
R^1 = H, NO_2, Br, OMe, Ph, biphenylyl, Ac, C_6H_4COMe, OH; R^2 = H, SO_3Na; R^3 = H, Ph	
	1511
R^1 = H, R^2 = CO_2H, or R^1 = CO_2H, R^2 = I	
4-Arylamino-2,2'-	1476

carboxylic acid.[454] Salts of 2-phenylquinoline-4-carboxylic acid when distilled gave some 2,2'-diphenyl-4,4'-biquinolyl in addition to the main product 2-phenylquinoline.[1168a]

C. Action of Alkali Metals or Amides on Quinolines

When quinoline is heated with sodium, e.g. for 5–6 h on a water bath and finally at 160 °C, 2,3'-biquinolyl is formed.[1302,1360,1370–1375] Under similar conditions 6-, 7- and 8-methylquinolines form 6,6'-, 7,7'- and 8,8'-dimethyl-2,2'-biquinolyls, respectively.[1376] In the course of the arylation of quinoline with indole, and other aromatic compounds, in the presence of activated sodium powder (or numerous other metals) about 15% of 2,3'-biquinolyl was formed in addition to the expected aryl- or heteroarylquinolines;[1205] 2,3'-biquinolyl was also formed as a by-product in the photo-stimulated reaction of lithioacetone with 2-chloroquinoline in liquid ammonia at −33 °C.[1378]

Under different conditions the reaction with quinoline may take a different course. When quinoline in ether was treated with a dispersion of sodium in xylene at −40 °C for 20 min and then poured on to solid carbon dioxide the disodium salt of 1,1',4,4'-tetrahydro-4,4'-biquinolyl-1,1'-dicarboxylic acid was obtained.[1377]

Studies by Chichibabin and co-workers on the preparation of aminoquinolines by the reaction of sodamide on quinoline showed that the main products at temperatures of 80–150 °C were 2,3'-biquinolyl ($C_{18}H_{12}N_2$) and a 'biquinoline' (dihydro derivative of biquinolyl) ($C_{18}H_{14}N_2$). The latter was isolated as yellow leaflets (m.p. 185 °C) and formed red salts with mineral acids. Both the free base and the salts were readily oxidized to 2,3'-biquinolyl.[1379,1380] The formation of yellow bases from quinoline and substituted quinolines and sodamide which gave brick-red hydrochlorides have also been described elsewhere;[1381] they were found to sensitize silver chloride and silver bromide photographic emulsions and were active as photographic developers. The product from quinoline was characterized as 1,2,3,4,1',2',3',4'-octahydro-2,3'-biquinolyl ($C_{18}H_{20}N_2$)[1381] as opposed to the dihydro derivative described by Chichibabin and co-workers. When treated with diisopropylaminolithium, $(Me_2CH)_2NLi$, in ether, quinoline dimerized to give 2,2'-biquinolyl.[1382]

D. Ullmann Reaction

The Ullmann reaction, in which an aromatic halogen compound is heated with copper bronze to give a biaryl, and related methods, have been used for the preparation of biquinolyls. When 6-iodoquinoline was heated with copper powder at 220 °C 6,6'-biquinolyl was formed.[1383] 4,4'-Biquinolyl was prepared from 4-bromoquinoline[1441] and 8,8'-diethyl-2,2'-biquinolyl from 8-ethyl-2-bromoquinoline;[1394] also a small yield of 4,4'-dimethyl-2,2'-biquinolyl was formed from 2-chloro-4-methylquinoline when heated with copper bronze for 2 h at 218 °C.[1393] The distillation of di-8-quinolylmercury with copper powder gave 8,8'-biquinolyl.[1384] A small yield of 6,6'-dimethoxy-8,8'-biquinolyl was formed by the Ullmann reaction from 8-iodo-6-methoxyquinoline,[1385] and 2,2'-dimethoxy-4,4'-dimethyl-3,3'-biquinolyl was obtained from 3-bromo-2-methoxy-4-methylquinoline by the action of copper bronze in boiling diphenyl ether.[1386] A series of 2-hydroxyquinolines prepared by the Knorr synthesis were converted to 2-bromoquinolines with phosphoryl bromide ($POBr_3$) and then to biquinolyls by a variation of the Ullmann reaction in which the bromoquinolines in 5% methanolic potassium hydroxide were heated with $Pd/CaCO_3$ and hydrazine hydrate. In this way the following 2,2'-biquinolyls were obtained (with yields given in parentheses): 2,2'-biquinolyl (44.7%), 4,4'-dimethyl- (50%), 4,4',6,6'-tetramethyl- (56.5%), 4,4',7,7'-tetramethyl- (47.3%), 4,4',8,8'-tetramethyl- (25%), 4,4'-diphenyl- (10.7%), 4,4'-diphenyl-6,6'-dimethyl- (19.8%),

4,4'-diphenyl-7,7'-dimethyl- (19.7%), 4,4'-diphenyl-8,8'-dimethyl- (38.9%), 4,4'-dimethyl 6,6'-dimethoxy- (41.8%), 4,4'-diethyl- (51.2%), 4,4'-diethyl-6,6'-dimethyl- (48.4%), 4,4'-diethyl-7,7'-dimethyl- (18.5%), 4,4'-diethyl-8,8'-dimethyl- (14.5%),[1387] and 6,6'-dimethyl-4,4'-diphenyl- (24.0%).[1468] Subsequently the following chlorinated-2,2'-biquinolyls were also obtained by the same method from chlorinated 2-bromoquinolines: 4,4'-dimethyl-6,6'-dichloro- (44%), 4,4'-dimethyl-7,7'-dichloro- (47%), 4,4'-dimethyl-8,8'-dichloro- (30%), 4,4'-dichloro- and 4,4'-dibromo-.[1388] These products showed that biaryl formation occurred preferentially through a 2-bromo substituent rather than a 6-, 7- or 8-chloro substituent or even a 4-chloro- or 4-bromo substituent. Other, including earlier, reports of the use of this method describe the preparation of 7,7'-biquinolyl,[1390,1391] 8,8'-dimethyl-2,2'-biquinolyl and 8,8'-diphenyl-2,2'-biquinolyl,[1394] 5,5'-biquinolyl, 2,2'-dimethyl-6,6'-biquinolyl,[1408] 3,3'-biquinolyl, 2,2'-biquinolyl[1390] and 4,4'-biquinolyl[1441] from their respective bromo derivatives. In the last case some 2,7'-biquinolyl was also formed, which was shown to be identical (mixed melting point) with that prepared by Von Miller and Kinkelin.[1162]

A series of arylgold compounds, including 2- and 8-quinolylgold and 4-(2'-quinolyl)-phenylgold, have been prepared for use as gold sources for printed circuits, decoration and general gold plating. On heating to about 350 °C at 0.1 mmHg they decompose to metallic gold and the appropriate biquinolyl. The following biquinolyls were formed by this method: 2,2'-; 8,8'; 2,2',4,4'-tetramethyl-7,7'-; 2,2'-dimethyl-4,4'- and also 4,4'-bis(2''-quinolyl)biphenyl.[1389]

E. Thermal and Catalytic Dehydrogenation

When quinoline vapour is passed through an iron tube heated to a dull red, some 3,7'- or 4,7'-biquinolyl is formed,[1414,1415] and when heated in a sealed glass tube to 325–335 °C with a catalyst of nickel deposited on alumina, quinoline was dehydrogenated to 2,2'-biquinolyl in 15% yield.[1396] When quinoline was heated with selenium in a sealed tube at 280–300 °C for 5 h a 10% yield of 2,3'-biquinolyl was obtained.[1397] Hydrogenation of the methyl ester of quinoline-2-carboxylic acid over palladium black gave the dimethyl ester of 1,2,3,4,1',2',3',4'-octahydro-4,4'-biquinolyl-2,2'-dicarboxylic acid in addition to the expected 1,2,3,4-tetrahydro derivative of the original ester.[1416]

Catalytic dehydrogenation of quinoline[1392] and of 4-methylquinoline[1393] gave 2,2'-biquinolyl and 4,4'-dimethyl-2,2'-biquinolyl (30% yield), respectively. 6-Methylquinoline gave only a 1% yield of 6,6'-dimethyl-2,2'-biquinolyl and no biaryls were obtained from 7-methyl- or 8-methylquinolines.[1393] 4,4'-Dimethyl-2,2'-biquinolyl was also prepared by catalytic dehydrogenation of lepidine and was shown to form a Cu^+ complex with a higher molar absorptivity (7020 l mol^{-1} cm^{-1}) than the biquinolyl complex (6220 l mol^{-1} cm^{-1}). The absorption maximum was also changed from 546 to 550 nm.[1398]

A free radical reaction between 4-nitroquinoline-1-oxide and 4-hydroxyquinoline-1-oxide gave 4,4'-dihydroxy-3,3'-biquinolyl, which was converted to 3,3'-biquinolyl by catalytic reduction of the 4,4'-dichloro derivative.[1395]

When treated with degassed Raney nickel (W7-J),[1399] quinoline and methylquinolines all gave 2,2'-biquinolyls together with a complex mixture of other products including methylindoles, carbazole, methylanilines, tetrahydroquinolines and other methylquinolines.[1400,1401,1407] 4-Methylquinolines with a vacant 2-position gave the highest yields of 2,2'-biquinolyls, but even quinolines with a 2-methyl substituent gave traces of 2,2'-biquinolyls.[1400] Using a Raney cobalt catalyst, prepared by the method used for Raney nickel, a small amount (less than 0.1%) of 2,2'-biquinolyl was obtained from 2-mercaptoquinoline.[1402] A 5% palladium on charcoal catalyst has also been effective in the formation of biquinolyls from quinolines,[1403–1405] normally by heating under reflux

for 24 h, but higher temperatures were sometimes necessary. The compounds prepared included 2,2'-biquinolyl itself and the 8,8'-dimethyl- and 4,4'-diphenyl derivatives. Conversions of 11–21% were achieved and most of the unchanged quinolines could be recovered.[1403]

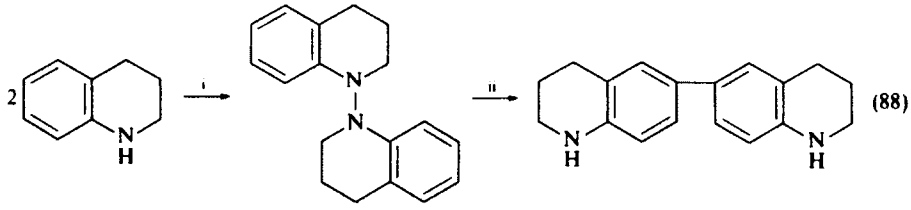
In a comparison of the efficiencies of Group VIII metals and copper as catalysts for the conversion of quinolines to biquinolyls, only palladium and rhodium on charcoal were effective in the formation of 2,2'-biquinolyls, and some 2,3'-isomer and two triquinolyls were also formed from quinoline by the rhodium catalyst.[1072,1406] Quinoline, 6-methylquinoline and 7-methylquinoline were converted to the corresponding 2,2'-biquinolyls at their boiling points, and benzo[*f*]quinoline reacted similarly at 320–330 °C. The methylquinolines suffered some demethylation and quinoline was methylated at positions 2 and 4. 2-Methylquinoline gave bis(2-quinolyl)-methane, tris(2-quinolyl) methane and 1,2-bis(2'-quinolyl)ethane.[1072] 2,2'-Biquinolyl has also been prepared in low yield (less than 0.1%) by a mechanico-chemical process by treating quinoline with one third of its weight of activated nickel powder in a controlled-temperature ball mill at 230 ± 10 °C for 2 h.[1409]

The formation of 2,2'-biquinolyl in 46.5% yield was achieved by heating quinoline with powdered aluminium or zinc and mercury(II) chloride for 8 h at 190–200 °C in an inert atmosphere and finally refluxing the product with more quinoline and nitrobenzene.[1203b,1410] This method has also been extended to the preparation of the following biquinolyls:[1411] 4,4'-dimethyl-2,2'-; 7,7'-dimethyl-2,2'-*; 8,8'-dimethyl-2,2'-*; 2,3'-; 4,4'-dimethyl-2,3'-; 4,4'-; 2,2'-dimethyl-4,4'-; and 2,4'.

The preparation of a palladium–charcoal catalyst by reduction of palladium chloride ($PdCl_2$) with formaldehyde has been patented, which gives 95–96% yields of 2,2'-biquinolyl when refluxed with quinoline for 18 h and a 60% yield of 4,4'-dimethyl-2,2'-biquinolyl from lepidine.[1412,1413] The catalyst was also modified by the incorporation of platinum, which affected the yields of the products. The addition of some of the heterocycle-1-oxide facilitated the dehydrogenation and enabled the reaction to progress under milder conditions.[1413]

F. Miscellaneous Methods

The oxidation of 1,2,3,4-tetrahydroquinoline with potassium permanganate and acetone gave 1,2,3,4-1',2',3',4'-octahydro-1,1'-biquinolyl which, with 2 N hydrochloric acid was converted into the octahydro-6,6'-biquinolyl as a result of a benzidine rearrangement[1416] (equation 88).



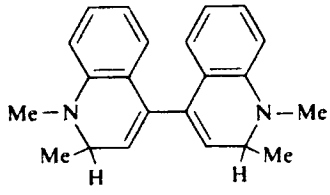
(88)

i, $KMnO_4$, acetone; ii, 2 N HCl (benzidine rearrangement)

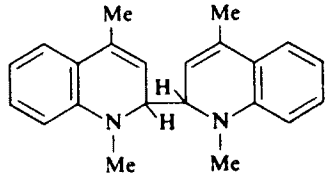
The electrolysis of a 10% solution of 1-methylquinolinium iodide at a platinum cathode with 10% sodium carbonate solution as the anode electrolyte gave a dimethyl-

* The melting points reported for these two products correspond to those for the corresponding 2,3'-biquinolyls.

dihydrobiquinolyl, but the position of union of the quinoline rings was not established.[1417] The electrolysis of quinolinium perchlorate and some methylquinolinium perchlorates at the potentials of the first d.c. polarographic reduction waves gave dimeric products, and 2- and 4-methylquinolinium salts gave 4,4'- or 2,2'-biquinolyl derivatives, respectively. The nmr spectra of the dimers from 2-methyl- and 4-methylquinolinium perchlorates indicated that their structures were (**239**) and (**240**). No neutral radical species were detected by esr during electrolysis.[1418]



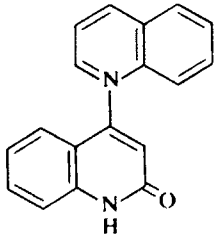
239



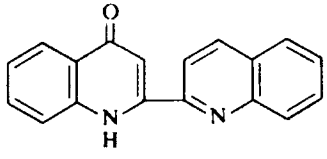
240

When heated for 3 h with calcium hydride at 220 °C, quinoline gave 3,3'-biquinolyl.[1419] 2,2'-Biquinolyl was among the basic products formed during the thermal decomposition of benzyl phenyl ether in quinoline.[140] 3,6,8-Tribromo-5-nitroquinoline, on boiling with sulphuric acid, gave 3,6,8,3',6',8'-hexabromo-5,5'-biquinolyl, which was also formed by heating 3,6,8-tribromoquinoline with nitric acid and sulphuric acid.[1420] The dry distillation of quinoline-8-sulphonic acid has been reported to give the 3,7'- or 4,7'-biquinolyl.[1421a]

When quinoline-1-oxide was treated for 9 h at 70 °C with potassium *t*-butoxide with oxygen bubbling through the solution the products isolated were 1-hydroxycarbostyril (41%), 2-2'-biquinolyl (34%) and 2,2'-biquinolyl-1-oxide (10%). The last two compounds could be interconverted by reduction of the 1-oxide by catalytic hydrogenation or by oxidation of the biquinolyl with 1 equivalent of perphthalic acid.[1422] Quinoline-1-oxide reacts with dimethylsulphoxonium methylide to give 2,2'-biquinolyl. In the presence of benzenesulphonyl chloride, however, a mixture of 2-quinolone and a quinolylquinolone believed to be either 4-(4'-quinolyl)-2-(1*H*)-quinolone (**241**) or 2-(2'-quinolyl)-4-(1*H*)-quinolone (**242**) was obtained.[1423]



241



242

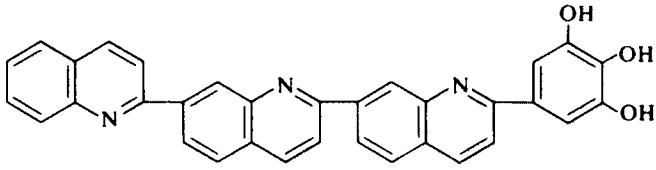
When quinoline was treated with acetyl chloride or benzoyl chloride at 20–130 °C in a dry organic solvent such as benzene, the *meso*-form of the *NN'*-diacyl-1,1',2,2'-tetrahydro-2,2'-biquinolyl was obtained. Subsequently the *dl*-form was also isolated.[1424]

The action of iron(III) chloride on 8-hydroxyquinoline in dilute neutral solution gave 8,8'-dihydroxy-5,5'-biquinolyl. In acidic solution chlorination was the main reaction.[1425]

Oxidation of quinoline with potassium persulphate gives a small yield (of the order of 0.1%) of 2,2'-biquinolyl.[1426] A low yield of about 1% of 2,2'-biquinolyl was also obtained by irradiation of quinoline under nitrogen for 48 h in a cooled quartz tube by unfiltered ultraviolet light from a high-pressure mercury arc. The unchanged quinoline was recovered.[1427] Exposure of 2-methylquinoline and acetophenone to sunlight for several months was reported to give 2,2'-dimethyl-6,6'-biquinolyl.[1428]

G. Preparations of Polyquinolines and Biquinolyl Polymers

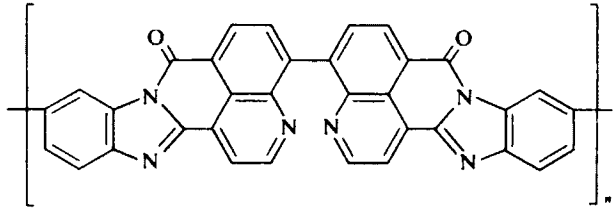
The substituted terquinoline 2-{2'-[2"-(3",4",5"-trihydroxyphenyl)-7"-quinolyl]-7'-quinolyl}-quinoline (**243a**) has been prepared by heating the anilide of anthranilic acid with excess of paraldehyde to give 2-(2'-aminophenyl)quinoline, which was again heated with anthranilic acid followed by excess of paraldehyde and the product so formed was heated with gallic acid and excess of paraldehyde.[1429]



243a

The polymerization of quinoline in the presence of catalytic amounts of alkyl halides at 250 °C or above has been described and the various molecular weight fractions of the product were examined by infrared spectroscopy.[1430]

The condensation of 2,2'-dimethyl-6,6'-biquinolyls [see Section I.5.I.c equation 46, formula (**85**), X = direct bond] with the anydrides of aromatic tetracarboxylic acids gives polymeric 6,6'-biquinolylphthalones [formula (**87**), X = direct bond.][828,1431,1492] Thermally stable polymers prepared from the dianhydride of 8,8'-biquinolyl-4,4',5,5'-tetracarboxylic acid and 3,3'-diaminobenzidine (**243b**) have been described.[1518]



243b

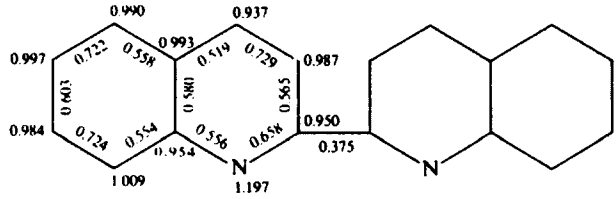
2. Physical Properties and Uses

A. General Physical Properties

Known biquinolyls are listed in Table 51, which also includes some of their physical properties. Biquinolyls in general can be distilled at high temperatures with only slight decompositions; 2,3'-biquinolyl sublimes. They are insoluble in water and only slightly

soluble in common organic solvents, including hot ether, benzene and chloroform.[1456] Solutions of 6,6'-biquinolyl[1456] and its 4-methyl derivative[1457] in acids have a blue fluorescence.

The dipole moment of 2,2'-biquinolyl (0.68 D) has been determined and discussed in terms of the vector addition of individual bond dipoles.[1432] The following ionization potentials for a series of biquinolyls have been determined:[1433] 2,2'-, 7.93; 2,3'-, 7.97; 6,6'-, 7.97; and 1,2-dihydro-2,3'-, 6.81 eV. 2,2'-Biquinolyl was one of the aromatic compounds studied for thermal stability in a search for fluids stable at 550 °C.[1254] The stability of biquinolyls is confirmed by their lack of fragmentation in the mass spectrometer (see below), which also suggests that isomers with *trans*-annular bonds in positions other than 2 should have greater stability.[1449] A study has been made of the protonation constants (σ) and ionization constants (pK) of 2,2'-biquinolyl and some derivatives.[1434,1435] An investigation of the mechanism of the solvent extraction of organic bases from strongly acidic media in the unionized form or as ion pairs includes 2,2'-biquinolyl (see Section I.4.Ha,).[369] The π-electron distribution and bond orders of 2,2'-biquinolyl and some phenyl and isopropyl derivatives of 2,2'-biquinolyl have been calculated;[1436] the results for 2,2'-biquinolyl are shown in formula (**244**).



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π-Electron densities (e) and bond orders (ethylene = 1.0, benzene = 0.677) for 2,2'-biquinolyl; ref. 1436

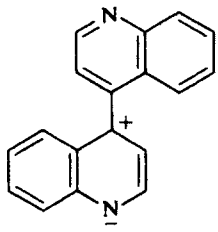
The mechanical and thermal properties of a series of sixteen polyquinolylphenyl ethers have been measured. They possess good thermal and oxidative stability and form tough flexible films when cast from chloroform or *m*-cresol solutions.[1284,1285,1442,1443]

B. Optical Activity of Biquinolyls

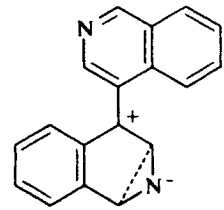
An attempt to resolve 8,8'-biquinolyl through its salt with (+)-camphorsulphonic acid was unsuccessful,[1437] but 4,4'- and 5,5'-biquinolyls were resolved through their (+)-tartrates. For 4,4'-Biquinolyl $[\alpha]^{17.5} = 205°$ and for the (+)-tartrate $[\alpha]_D^{18} = -52.3°$; for 5,5'-biquinolyl $[\alpha]_D^{20.5} = 1.3°$ and for the (+)-tartrate $[\alpha]_D^{20} = -3.24°$. The rates of racemization at room temperature were 4,4'-biquinolyl 24 h and 5,5'-biquinolyl 18 h.[1438,1439]

The possibility of racemization occurring as a result of electrophilic attack at a carbon of the inter-annular bond to form a tetrahedral configuration in the transition state (which would facilitate free rotation) has been discussed. Evidence in favour of the mechanism is provided by the increase in optical stability which results from the introduction of electron-withdrawing substituents (including heterocyclic nitrogen) in positions conjugated with the atoms joining the two rings and the reduction of optical stability when electron-donating substituents are present. This would explain the greater optical stability of the 4,4'- and 5,5'-biquinolyls in which the nitrogen can stabilize a positive charge at position 4 or 5 by a conjugative mechanism (**245**), compared with the

4,4'- and 5,5'-biisoquinolyls, where only the inductive effect of the ring nitrogen can operate (**246**).[1440, 1441] It would also explain the probably lower optical stability of the 8,8'-biquinolyl noted above.[1437]



245



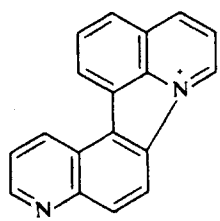
246

C. Spectroscopic Properties

The ultraviolet absorption spectrum of 2,2'-biquinolyl has been reported[1444] and the values of pK_{BH^+} (4.25) and $pK_{BH^{2+}}$ (−0.2) have been determined from the spectrum.

The most significant feature of the mass spectra of biquinolyls is the lack of fragmentation. Except for 8,8'-biquinolyl, discussed below, the molecular ion (M^+) gives the strongest peak, followed in intensity by the peak from the $(M-1)^+$ ion.[1445-1449, 1266] The peak at $m/e = 128$ of 2,2'-biquinolyl has been shown, from the $^{12}C/^{13}C$ isotope ratios, to consist of M^{2+} (17.3% of base peak) and [M − quinolyl·]$^+$ (7.5%), whereas the peak at $m/e = 128$ from 6,6'- and 8,8'-biquinolyls was entirely produced by M^{2+}.[1449] This suggested that the fission of the inter-annular bond is facilitated by the proximity of the heterocyclic nitrogen atoms.

The fragmentation of 8,8'-biquinolyl differs from that of the other symmetrical isomers in the intensity of the $(M-1)^+$ peak which becomes the base peak. This is believed to be the result of stabilization by a pentacyclic structure (**247**). Other unsymmetrical biquinolyls having at least one ring joined at C-8 could possibly form similarly stabilized $(M-1)^+$ ions, but 8,8'-biquinolyl could be distinguished from the other symmetrical isomers by its mass spectrum.[1449] Full details of the mass spectrum of 2,2'-biquinolyl have been reported.[1411]



247

The following assignments have been made[1571n] for the observed ^{1}H-nmr spectrum of 2,2'-biquinolyl, δ p.p.m. downfield from TMS (solvent = $CDCl_3$): 6H or 7H = 7.50; 7H or 6H = 7.60; 5H = 7.81; 8H = 8.18; 3H = 8.26; 4H = 8.82.

D. X-ray Diffraction Analysis

Crystal structures of 2,2'-biquinolyl[301,1450-1452] and 8,8'-biquinolyl[1453] have been published. The 2,2'-biquinolyl molecule is planar with a *trans*-configuration. The bond lengths are C—N (average) 1.38 Å, C—C ring (average) 1.46 Å,[1450] C—C between rings 1.492(3) Å.[1452] The configuration of 8,8'biquinolyl is also *trans*, the angle between the two halves of the molecule being 96.8°. The length of the bond between the rings is 1.495(2) Å.[1453]

E. Chromatographic Separations

The separation of biquinolyls from other bases has been achieved by paper chromatography[1454] and thin-layer chromatography (tlc).[383,1455,1614] Whatman No. 4 paper impregnated with formamide and formic acid was used with mobile phases containing heptane, benzene, trichloroethylene, chloroform, methyl butyl ketone and heptanol for the analysis of mixtures containing 2,2'-biquinolyl.[1454] Mixtures of 2,2'-biquinolyl, 4,4'-dimethyl-2,2'-biquinolyl, quinoline and 4-methylquinoline were separated on silica gel G with carbon tetrachloride–isopropanol–formic acid (30 : 8 : 2) as the mobile phase. Spots were developed with Dragendorff's reagent and the areas of the spots were related to the amounts of the individual components within the range 5–20 μg.[383] The separation of mixtures of 2,2'-biquinolyl and 4,4'-dimethyl-2,2'-biquinolyl obtained by dehydrocondensations of quinoline with W-alka type Raney nickel catalyst was achieved on Kieselguhr G with the solvent mixture benzene–methanol–formic acid (15 : 4 : 1).[1455]

F. Uses

The yellow base obtained (together with aminoquinolines) when quinoline is heated with sodamide and reported to be 1,2,3,4,1',2',3',4'-octahydro-2,3'-biquinolyl[1381] acts as a sensitizer for silver chloride and silver bromide emulsions and also as a photographic developer.

2,2'-Biquinolyl in conjunction with prepolymers prepared from mixtures of diethynylbenzenes is a possible constituent of a heat-hardenable, oxidation-resistant resin which forms no volatile compounds during the hardening process.[1458]

Probably the most important applications of 2,2'-biquinolyl and substituted 2,2'-biquinolyls depend upon their ability to form chelate compounds with metal ions, which, as a result of their intense absorption in the visible (and in some cases the ultraviolet) region of the spectrum, are suitable as spectrophotometric reagents for the determination of the metals, in trace amounts, especially copper as Cu^{+} or Cu^{2+}.[1324,1335,1353,1357,1392,1398,1459-1480] For further details see also Table 38.

The chelating properties of 2.2'-biquinolyl have also led to its use as an indicator for the direct titration by acids with organomagnesium and lithium compounds in organic solvents,[1481] and it is also listed as one of the agents which can influence the sorption of metal ions (e.g. those of Cu, Co, Ni, Mn, Zn, Cd and Pb) by silver halides or silver thiocyanate when coprecipitated.[1482]

3. Chemical Properties and Reactions of Biquinolyls

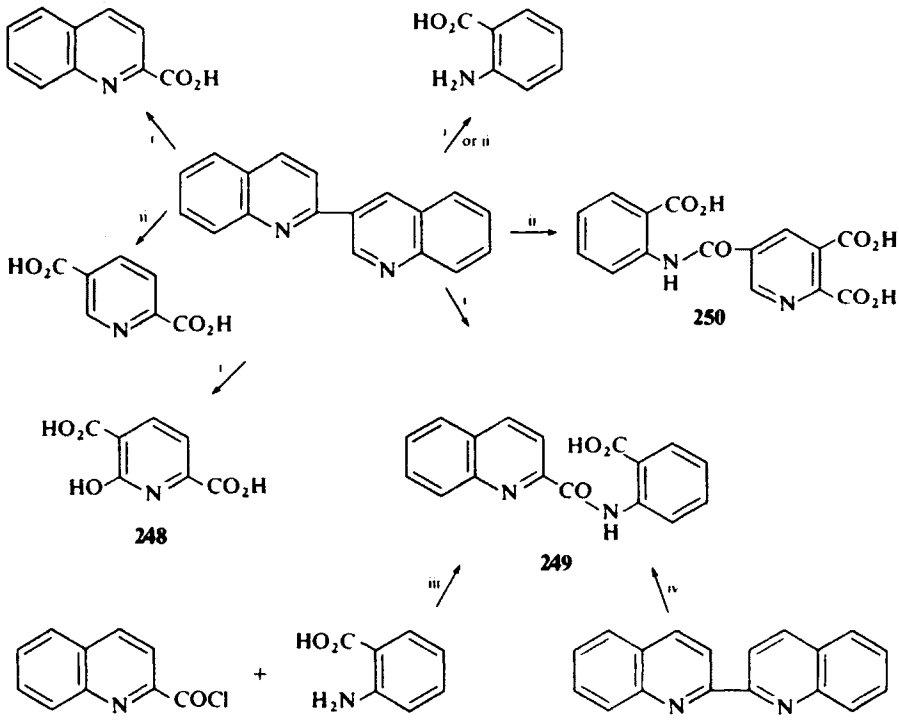
A. Oxidation

An early paper by Weidel and Strache[1483] described the oxidation of 2,3'-biquinolyl with potassium permanganate in acetic acid. The degradation products isolated were quinoline-2-carboxylic acid, anthranilic acid, 'Kyklothraustinsaure' [*N*-(2-quinolinoyl)-

anthranilic acid] (**249**) and 6-hydroxyisocinchomeronic acid (6-hydroxypyridine-2,5-dicarboxylic acid) (**248**). In alkaline solution the degradation products isolated were pyridine-2,5-dicarboxylic acid, anthranilic acid and 'pyridanthrilsaure' [pyridine-2,3,5-tricarboxylic acid-5-(2'-carboxyanilide)] (**250**). All of the products are readily derived by degradation of 2,3'-biquinolyl, except (**249**), the formation of which would require a rearrangement of the basic molecular skeleton, although (**250**) is clearly derived from a 3-quinolyl fragment.

The structure of compound (**249**) has been confirmed on the basis of its molecular formula and a mixed melting point by synthesis from quinaldinyl chloride and anthranilic acid,[1484] and it has also been isolated from the products of oxidation of 2,2'-biquinolyl with both potassium permanganate and chromic acid[1484] (see Scheme 30). The 3,7'- or 4,7'-biquinolyl prepared by Fischer and Loo was oxidized with chromic acid in acetic acid to give quinoline-7-carboxylic acid, but with chromic acid and dilute sulphuric acid 5-(or 4)-(7'-quinolyl)pyridine-3-carboxylic acid was formed.[1421]

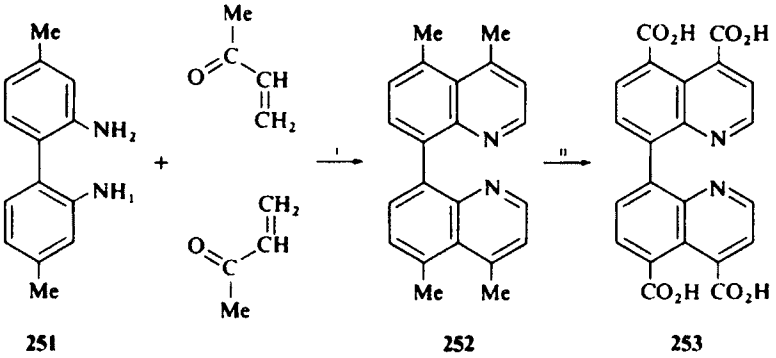
Alkyl side-chains attached to biquinolyls can be oxidized to carboxyl groups (hydroxycarbonyl). Thus 5,5'-dimethyl-8,8'-biquinolyl with chromic acid and sulphuric acid gave a mixture of 5-methyl-8,8'-biquinolyl-5'-carboxylic acid and 8,8'-biquinolyl-5,5'-dicarboxylic acid by oxidation of one or both of the methyl groups.[1363] The mono- and dicarboxylic acids were both decarboxylated on distillation at reduced pressure.



i, $KMnO_4$ in acetic acid; ii, $KMnO_4$, alkali (ref. 1483); iii, roomtemp., 12 h, pyridine solution; iv, oxidation, $KMnO_4$ or CrO_3 (ref. 1484)

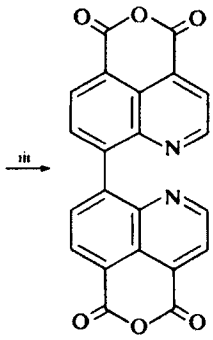
SCHEME 30

Similarly, 4,4',5,5'-tetramethyl-8,8'-biquinolyl (**252**) [prepared from 2,2'-diamino-4,4'-dimethylbiphenyl (**251**) by condensation with methyl vinyl ketone in the presence of iron(III) chloride and zinc chloride] when oxidized by sodium dichromate gave 8,8'-biquinolyl-4,4',5,5'-tetracarboxylic acid (**253**). This acid, when heated with acetic anhydride for 20 min at 120 °C, gave the dianhydride (**254**)[1339] (see equation 89).



251 **252** **253**

(89)



254

i, $FeCl_3$–$ZnCl_2$ (SKraup); ii, $Na_2Cr_2O_7$, H_2SO_4; iii, Ac_2O, distillation at reduced pressure

The oxidation of 4,4'-dimethyl-2,2'-biquinolyl by potassium permanganate and potassium hydroxide in pyridine solution gave 4'-methyl-2,2'-biquinolyl-4-carboxylic acid in about 20% yield.[1486]

Oxidation of biquinolyls with peracids give either mono- or di-*N*-oxides, or a mixture of both. 2,2'-Biquinolyl with 1 equivalent of perphthalic acid gave the 1-oxide, from which the parent compound was recovered by catalytic hydrogenation.[1422] On reaction with hydrogen peroxide and acetic acid at 70–80 °C for 8 h, 2,2'-biquinolyl-1,1'-dioxide was formed.[1387c] The unsymmetrical 3,2'-biquinolyl gave either the 1-oxide or the 1,1'-dioxide, depending upon the reaction conditions (i.e. the 3-quinolyl moiety was oxidized preferentially).[1487] The reactivities of the two oxide substituents in the dioxide could be distinguished, as the 1-oxide group was readily deoxygenated by heating with carbon disulphide in dimethylformamide but the 1'-oxide group was resistant to reduction under

these conditions. Nitration of the 1-oxide did not give a γ- or α-nitro compound. The last two reactions were taken to indicate that the 1-oxide has some nitrone-like properties.[1487]

B. Reduction

When 6,6'- and 2,3'-biquinolyl were reduced with tin and hydrochloric acid, sodium and ethanol or by catalytic hydrogenation the 1,2,3,4,1',2',3',4'-octahydro derivatives were formed. Reduction of 6,6'-biquinolyl with hydrogen iodide and phosphorus, however, gave the 5,6,7,8,5',6',7',8'-octahydro-6,6'-biquinolyl.[1488]

C. Substitution Reactions

Early work on the sulphonation of biquinolyls with fuming sulphuric acid indicated that both mono- and disulphonic acids were formed but the products were not characterized. Thus with fuming sulphuric acid at 180–190 °C, 2,3'-biquinolyl gave a monosulphonic acid and two disulphonic acids,[1360,1370] 2,6'-biquinolyl gave a monosulphonic acid[1302] and 6,6'-[1456] and 6,8'-biquinolyls[1485] gave disulphonic acids. The 3,7'- (or 4,7')-biquinolyl prepared by Fischer and Van Loo, when treated with a 10-fold excess of fuming sulphuric acid at 180 °C, gave a disulphonic acid.[1421b] Treatment of 6,6'-biquinolyl with bromine in hydrochloric acid[1456] or ethanol[1489] gave a bromine addition product which, on heating to 180–200 °C, gave an unspecified monobromo-substitution product. 6,8'-Biquinolyl with 6 mol of bromine in an aqueous medium gave an unspecified dibromo derivative.[1485]

D. Miscellaneous Reactions

A Reissert reaction between 2,3'-biquinolyl, potassium cyanide and benzoyl chloride resulted in an addition to the 3'-quinolyl moiety to give 1'-benzoyl-2'-cyano-1',2'-dihydro-2,3'-biquinolyl, which on standing with concentrated hydrochloric acid for 2 days gave the 2,3'-biquinolyl-2'-carboxylic acid, and this on decarboxylation gave the original 2,3'-biquinolyl.[1367] 6,6'-Biquinolyl with the positions α- to nitrogen unsubstituted in both rings gave under similar conditions a double Reissert addition compound 1,1'-dibenzoyl-2,2'-dicyano-1,1',2,2'-tetrahydro-6,6'-biquinolyl. With concentrated hydrochloric acid 6,6'-biquinolyl-2,2'-dicarboxylic acid was formed.[1493]

Treatment of 3,2'-biquinolyl-1-oxide with nucleophiles in the presence of acylating agents, e.g. sulphuryl chloride, benzoyl chloride and potassium hydroxide, or benzoyl chloride and potassium cyanide, gave 2- and 4-chloro derivatives, 2-hydroxy and 2-cyano derivatives, respectively. Similar results were obtained with acylating agents and ethanol–triethylamine, ethyl cyanoacetate and 1-morpholinocyclohexene.[1535]

Methyl substituents at active positions on biquinolyls behave in a manner similar to those on quinoline and readily take part in condensations. An example is the formation of polybiquinolylphthalones [Section I.5.I.c] (equation 46, formula (**87**), X = direct bond).[828,1431,1492]

E. Complexes with Halogens and Organic Compounds

A series of polyhalide complexes formed with organic bases included 2,2'-biquinolyl.$HICl_2$.ICl. This was prepared by dissolving [2,2'-biquinolyl.$HICl_2$] in 1,2-dichloroethane and adding a 4–5-fold excess of iodine monochloride (ICl). Addition of carbon tetrachoride displaced the new complex, which was stable at room temperature and decomposed slowly on exposure to atmospheric moisture. It was soluble in most organic solvents other than carbon tetrachloride.[1494]

The complexes of biquinolyls with phenols shown in Table 37 have been prepared. Their compositions were determined from the nitrogen content and in some cases by thermal analysis.

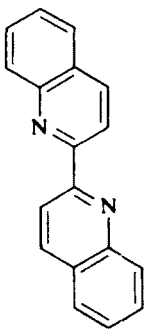
TABLE 37. Complexes Between Biquinolyls and Phenols

Biquinolyl (A)	Phenol (B)	Ratio A : B	Reference
2,3'-	Pyrogallol	1 : 1	1495a
	Phloroglucinol	1 : 1	1495a
	2,4-Dinitrophenol	1 : 1	1495a
	2,6-Dinitrophenol	1 : 1	1495a
	2,6-dibromo-4-nitrophenol	1 : 1	1495a, b
	2-Chloro-4-nitrophenol	—	1495b
	2,6-Dichloro-4-nitrophenol	—	1495b
6,6'-	Pyrogallol	1 : 1	1495a
	2,4-Dinitrophenol	1 : 1	1495a
	2,6-Dinitrophenol	1 : 1	1495a
	2,6-Dibromo-4-nitrophenol	1 : 2	1495a, b
	Hydroquinone	1 : 1	1495a
	p-Nitrophenol	1 : 2	1495a
	m-Nitrophenol	1 : 2	1495a
	sym-Trinitrotoluene	1 : 1	1495a

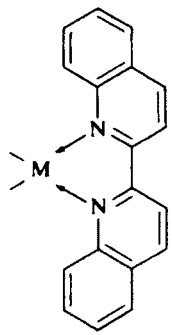
F. Complexes with Metals and Metal Compounds

The ready formation of metal chelate compounds by biquinolyls, particularly 2,2'-biquinolyl with copper ions (Cu^+ and Cu^{2+}), has been referred to above in connection with their application to chemical analysis by colorimetric techniques. Table 38 gives a summary of the complexes reported between biquinolyls and metal compounds.

Zero-field splitting of the triplet states of 2,2'-biquinolyl free and complexed with zinc indicate a change in geometry from the planar *trans*-configuration (**255**) in the free state[1451](see Section VI.4.B) to the *cis*-configuration (**256**) when complexed.[1491]



255



256

It has been reported that the reaction of the pentacarbonylmanganese anion, $[Mn(CO)_5]^-$, and the pentacarbonylrhenium anion, $[Re(CO)_5]^-$, with $XM(CO)_3L$ (X = Cl,Br,I; L = one of a number of bidentate ligands including biquinolyl) may give metal–metal bonded complexes, $M_2(CO)_8L$ (M = Mn or Re).[1490]

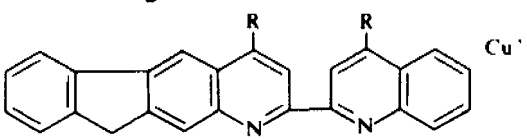
TABLE 38. Complexes Between Biquinolyls and Metal Ions or Metal Compounds

Biquinolyl (L)	Metal or metal compound	Composition of complex	Notes	Ref.
2,2'- 3-Me-2,2'-	Cu^+	—	Purple complex. Soluble in amyl alcohol. Used in microanalysis	1324
2,2'-	$CuNO_3(ZPh_3)_3$, Z = P, As or Sb	$CuNO_3(ZPH_3)(L)$	$[Cu(PPh_3)_2L]NO_3$ also formed under mild conditions	1335
2,2'-	Cu^+	—	Purple complex. Detection of 1 part per 10^8 Cu described.	1392
	$CuCl_2$	$L[CuCl_2]$	Orange-red crystals	1392
	$CuSO_4$	$L[CuSO_4]$	Green crystals	1392
	$CoCl_2$	$L[CoCl_2]$	Grass-green crystals	1392
4,4'-Me_2-2,2'-	Cu^+	—	Study of effects of substituents	1459
4,4'-Ph_2-2,2'-	Cu^+	—	on spectrophotometric constants	1459
3-Et-2,2'-	Cu^+	—	of complex. 4,4'-Ph_2-2,2'-	1459
3-Me-2,2'-	Cu^+	—	biquinolyl most efficient	1459
4-Me-2,2'-	Cu^+	—	($\lambda_{max.}$ = 559 nm; ε = 9020)	1459
3-Ph-2,2'-	Cu^+	—		1459
4-Ph-2,2'-	Cu^+	—		1459
3-Pr-2,2'-	Cu^+	—		1459
2,2'-	Cu^+	$[L_2Cu]^+$	$\lambda_{max.}$ = 540 nm; molar absorptivity = $(5.5 \pm 0.06) \times 10^{-25}$	1460
2,2'-	Cu^+		Effect of added methyl substituents	1398
4,4'-Me_2-2,2'-	Cu^+	—	on absorption spectrum studied	
2,2'-	Cu^+	$[L_2Cu]^+$	Comparison of sensitivities for	1461a, b
4,4'-Me_2-2,2'-	Cu^+	$[L_2Cu]^+$	spectrophotometric analysis.	1461a, b
4,4'-Et_2-2,2'-	Cu^+	$[L_2Cu]^+$	Maximum sensitivity reported for	1461a, b
4,4'-Ph_2-2,2'-	Cu^+	$[L_2Cu]^+$	6,6'-Me_2-4,4'-Ph_2-2,2'-biquinolyl	1461a, b
4,4',6,6'-Me_4-2,2'-	Cu^+	$[L_2Cu]^+$	complex after extraction with	1461a, b
4,4',7,7'-Me_4-2,2'-	Cu^+	$[L_2Cu]^+$	isoamyl alcohol. $\lambda_{max.}$ = 554 nm;	1461a, b
4,4',8,8'-Me_4-2,2'-	Cu^+	$[L_2Cu]^+$	ε = 11,030	1641a, b
6,6'-Me_2-4,4'-Ph_2-2,2'-	Cu^+	$[L_2Cu]^+$	8,8'-Substituted biquinolyls	1461a, b
7,7'-Me_2-4,4'-Ph_2-2,2'-	Cu^+	$[L_2Cu]^+$	and 1,1'-oxides did not give	1461a, b
8,8'-Me_2-4,4'-Ph_2-2,2'-	Cu^+	$[L_2Cu]^+$	complexes with Cu^+ owing to steric	1461a, b
4,4'-Et_2-6,6'-Me_2-2,2'-	Cu^+	$[L_2Cu]^+$	hindrance	1461a, b

TABLE 38 (*cont.*)

Biquinolyl (L)	Metal or metal compound	Composition of complex	Notes	Ref.
4,4'-Et_2-7,7'-Me_2-2,2'-	Cu^+	$[L_2Cu]^+$	8,8'-Substituted biquinolyls	1461a, b
4,4'-Et_2-8,8'-Me_2-2,2'-	Cu^+	$[L_2Cu]^+$	and 1,1'-oxides did not give	1461a, b
6,6'-$(OMe)_2$-4,4'-Me_2-2,2'-	Cu^+	$[L_2Cu]^+$	complexes with Cu^+ owing to steric hindrance	1461a, b
4,4'-Me_2-3,3'-$(CH_2)_n$-2,2'- (n = 0, 1, 2, 3)	Cu^+, Cu^{2+}	—	Increasing bridge length reduced absorptivity and λ_{max}	1462a, b
6,6'-Me_2-4,4'-Ph_2-2,2'-	Cu^+ and Cu^{2+}	—	Complexing abilities studied for	1463,
7,7'-Me_2-4,4'-Ph_2-2,2'-	Cu^+ and Cu^{2+}	—	analytical purposes.	1466,
8,8'-Me_2-4,4'-Ph_2-2,2'-	Cu^+ and Cu^{2+}	..	6,6'-Me_2-4,4'-Ph_2-2,2'-biquinolyl	1468,
4,4'-Ph_2-2,2'-	Cu^+ and Cu^{2+}	—	most sensitive for Cu^+ and Cu^{2+}	1469
2,2'-	Cu^{2+}	$CuLX_2$, X = Cl, Br and NO_3; $CuL_2(ClO_4)_2$	Magnetic susceptibilities and magnetic moments measured. $CuL_2(ClO_4)_2$ (brown) + $H_2O \rightarrow$ $CuL_2(ClO_4)_2H_2O$(green)	1465
2,2'-	Cu^+	—	Determination of Cu (10^{-5}%) in NaCl described	1467
2,2'-	Cu^+	$CuX(PPh_3)L$ X = Cl, Br, I; $CuI(PBu_3)L$; $(CuIL)_2$		1470
2,2'-			Hückel M.O. studies	
3,3'-Ethylene-2,2'-	Cu	—	Polarography of complexes and	1471a–d
3,3'-Ethylene-4,4'-Ph_2-2,2'-			ligands. Structures of complexes	
3,3'-Ethylene-4,4'-Me_2-2,2'-				
3,3',4,4'-H_4-derivative of above				
2,2'-	Cu	—	Analytical method described for determination of Cu in silicate rocks	1472
4-$(CONH_2)$-2,2'-	Cu^+	$[L_2Cu]^+$	Spectrophotometric study	1473
4-$(CONEt_2)$-4'-Ph-2,2'-				

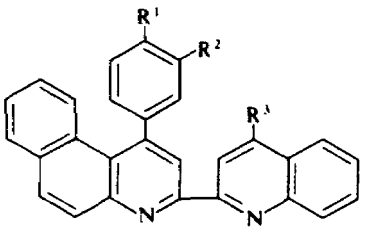
4-(CONHPh)-4′-Ph-2,2′- 4-(CO_2H)-4′-Ph-2,2′- 4-($CO_2C_5H_{11}$)-4′-Ph-2,2′-	Cu^+	$[L_2Cu]^+$	Spectrophotometric study	1473
2,2′-	Cu^{2+}	$[CuL_2ClO_4]ClO_4$	Esr and visible spectra given.	1474
3,3′-(CH_2)$_2$-4,4′-Me_2-2,2′-	Cu^+		Discussion of structure	
2,2′-	Cu^{2+}	$[CuL_2(NO_3)]NO_3$	Esr, ir and uv spectra and electrical conductivity measured. M.O. coefficients calculated and bonding discussed	1475
3,3′-(CH_2)$_2$-4,4′-Me_2-2,2′-	Cu^{2+}	$[CuL_2(NO_3)]NO_3$		
3,3′(CH_2)$_2$-4,4′-Ph_2-2,2′-	Cu^{2+}	$[CuL_2(NO_3)]NO_3$		
4-(NHPh)-2,2′-	Cu^+	—	Highly coloured complexes formed	1476
4-(NH-α-Naphthyl)-2,2′-	Cu^+			
2,2′-	Cu^+	$(CuL_2D)^+$, D=bromophenol blue or cresol red	Extraction kinetics and electrical conductivity in presence of added dyes studied	1477
2,2′-	Cu^+ and Cu^{2+}	—	Determination of Cu^{2+} by oxidation of Variamine Blue and complexation of Cu^+ formed	1478
2,2′-	Cu^+	—	Extraction of ion pairs formed by Cu^+ complex and anions of sulphophthalein dyes	1480
2,2′-	Cu^{2+}	$CuL(NO_3)_2$	Esr, ir and uv spectra and electrical conductivity measured and structures discussed	1479
3,3′-($CHMeCH_2$)-2,2′-	Cu^{2+}	$CuL(NO_3)_2$		
3,3′-($CHPhCH_2$)-2,2′-	Cu^{2+}	$CuL(NO_3)_2$		



R = H, Ph

			Colour intensities of complexes studied but found to be less than those from 2,2′-biquinolyl	1357

TABLE 38 (*cont.*)

Biquinolyl (L)	Metal or metal compound	Composition of complex	Notes	Ref.
 R^1 = H, NO_2, Br, OMe, Ph, PhPh, Ac, $C_6H_4COMe.OH$; R^2 = H, SO_3Na; R^3 = H, Ph	Cu^+	—	Uv spectra studied	1353
2,3'-	MX_3; M = As, Sb, Bi; X = Cl, Br	$L_3[MX_3]_2$		1496
6,6'-	MX_3; M = As, Sb, Bi; X = Cl, Br	$L[MX_3]$		1496
2,2'-	Be, Mg, Ca, Sr, Zn	ML_2	Esr study	1497
2,2'-	$Cd(C_6F_5)_2$	$Cd(C_6F_5)_2L$		1498
2,2'-	$NaAuCl_4$	$AuLCl_3$	Orange complex. Non-conducting in $PhNO_2$. Structure discussed	1334
2,2'-	Ph_2Hg	Ph_2HgL		1499
2,2'-	Mn^{2+}	$[MnLOH]^+$	Effect of complexes on decomposition of H_2O_2 studied	1500
2,2'-	Os, Ru	$OsL_3(ClO_4)_2$, $RuL_3(ClO_4)_2$	Luminescence and absorption spectra studied	1329b

2,2'-	$Ag^{2\bullet}$	$[AgL_2]^{2+}$	Electrooxidation of $AgNO_3$ and $AgClO_4$ in presence of L gave indication of formation of Ag^{2+}. Complexes isolated with 2,2',2''-terpyridyl and with 4,4'-Me_2-2,2'-bipyridyl but not with 2,2'-biquinolyl	1501
2,2'-	Zn^{2+}	(3,4-Toluenedithiolato-2,2'-biquinolyl)Zn	Visible spectrum studied	1502
2,2'-	$NiCl_2$	$(NiLCl_2)_2$	Triclinic structure determined by X-ray diffraction	1655
2,2'-	$NiBr_2$	$NiLBr_2$	Monoclinic structure determined by X-ray diffraction. Magnetic properties studied	1655

VII. Tables of Physical Properties

TABLE 39. Alkylquinolines

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.) m.p. (°C)	References
MONOALKYLQUINOLINES					
2-Methyl-	−2 to −1	247.6/760 135.5/26 118/10 86–87/1	n_D^{20} 1.6126 d_4^{20} 1.0585	195 Chloroplatinate, 228–229 (230–241)	1, 240, 459 542, 1557, 1632, 1667–1683
3-Methyl-	16–17	259.55/760 138.5–139.5/21 122/16	n_D^{20} 1.6171 d_4^{20} 1.0673	190 Chloroplatinate, 249	1, 127, 240, 431, 515, 804b, 1667, 1676, 1684–1693
4-Methyl-	9–10	264.2/760 133/15 105–107/2	n_D^{20} 1.6206 d_4^{20} 1.0868	220 Chloroplatinate, 226–230	1, 75, 77, 81, 240, 429, 446, 495, 765, 818, 1623, 1676, 1677, 1678, 1692, 1694–1708
5-Methyl-	19	262.7/760 129/15 85/1	n_D^{20} 1.62195 d_4^{20} 1.0832	223	34, 76, 163, 208, 240, 1625, 1676, 1692, 1709–1712
6-Methyl-	*ca.* −22	258.6/760 148/87 84–85/1.5	n_D^{20} 1.6157 d_4^{20} 1.0654	235 (245)	88, 240, 427, 1676, 1690, 1692, 1712–1714
7-Methyl-	39	257.6/760 144/18	n_D^{20} 1.6150 d_4^{20} 1.0609	245 (237) Chloroplatinate, 223–224	1, 61, 109, 150, 240, 449, 1676, 1692, 1709–1716
8-Methyl-		247.75/760 143/34	n_D^{20} 1.6164 d_4^{20} 1.0719	205	1, 240, 1676, 1690, 1692, 1713, 1714, 1717–1719
2-Ethyl-		245–246 145–146/27 123–126/5 76–78/0.5	n_D^{23} 1.5979 n_D^{25} 1.586 d^{17} 1.050	149–151 (157) Chloroplatinate, 188	128, 129, 171, 172, 213a, 215, 216, 223, 559, 1070, 1177, 1551, 1554, 1557, 1603, 1632, 1720–1725
3-Ethyl-		265–267 135–138/12 111/1.5	n_D^{20} 1.6160 n_D^{20} 1.5988 d_4^{20} 1.0508	197–198.5	72, 347, 514, 1685, 1689, 1693, 1725–1727

4-Ethyl-		271–274 143–145/8–9		200 (191 – 92, 209) Chloroplatinate, 204	74, 171, 172, 173, 174, 206, 213a, 223, 347, 1551, 1697, 1703, 1728–1731
5-Ethyl-					601
6-Ethyl-		258–258.5/745 140–142/12 135–138/14	n_D^{25} 1.6009 d^{25} 1.043	205–206	347, 1732–1734
7-Ethyl-	32–33	128–129/6	n 1.6012	240–241	601, 1676, 1734
8-Ethyl-		256 132–135/20 119/10	n_D^{25} 1.6020 d_4^{20} 1.0499	154–156 (146)	12, 227, 1733
2-*n*-Propyl-		274–275 142–145/13 130 – 31/10 105/5 91–93/1 85–87/0.1	n_D^{23} 1.5886 d_4^{17} 1.038	163–164.5	126a, 186, 201, 346, 533, 559, 735, 925, 926, 1557, 1632, 1720, 1721, 1723, 1735–1737
3-*n*-Propyl-		137–140/11		174 – 75	347, 676, 1727
4-*n*-Propyl-		280–285 159/16 110–111/1.35		209–210 Chloroplatinate, 198	93, 126a, 135, 173, 174, 205, 206, 347, 1697, 1738
6-*n*-Propyl-		140/7	n 1.5878 n_{He}^{20} 1.589 $d_4^{15.8}$ 1.0257 d_4^{20} 1.066	173.5–174.5	347, 1734, 1739
7-*n*-Propyl-		145–147/7	n 1.5900	191–193	1734
8-*n*-Propyl-		142/15		142 Chloroplatinate, 196	347, 1740
2-Isopropyl-		255 124–125.5/7 82/0.7 74–78/0.5	n_D^{20} 1.5834	158 Chloroplatinate, 195	94, 119, 206, 215, 216, 223, 347, 1177, 1554, 1557, 1603, 1723, 1741, 1742
3-Isopropyl-	*ca.* 10	275–280/715		206–207	454, 1743
4-Isopropyl-		96/0.5		172–173 Chloroplatinate, 204	73, 93, 94, 152a, 215, 223, 1741

TABLE 39 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.) m.p. (°C)	References
6-Isopropyl-		143/12	n_D^{20} 1.5884	197.5–198	1609a, 1744
7-Isopropyl-				205–206 Chloroplatinate, 219–220	73
8-Isopropyl-		133–134/11	n_D^{20} 1.5934	199.5–200	1744
?-Isopropyl- (unknown)				160–161	1745
2-*n*-Butyl-		153/14	n_D^{23} 1.5799	163 (143)	122, 124, 128, 129,
		139–143/5	n_D^{20} 1.5699	Chloroplatinate, 163.5	138, 212, 213a,
		104–105/0.3	d_4^{20} 1.003		346, 559, 1071b,
		94–98/0.7	d_4^{18} 1.020		1632, 1720, 1721, 1723, 1735, 1737, 1746–1748
3-*n*-Butyl					1749
4-*n*-Butyl				185–189	151, 1697
6-*n*-Butyl-		161–164/12	*n* 1.5802	162	1734
7-*n*-Butyl-		152–154/6	*n* 1.5828	180	1734
2-Isobutyl-		270–271	n^{16} 1.5766	162–163	187, 215, 216, 926,
		157/23			1177, 1609b, 1750
		148–150/14			
3-Isobutyl-		114/2		160	1685
4-Isobutyl-		103/0.25		168.5–170	348, 1738
2-*sec*-Butyl-		118–121/3–5		164–165	150, 206, 216,
		102–106/1			1723
4-*sec*-Butyl-					150
2-*t*-Butyl-				172–173	151, 216, 1604, 1751
2-*n*-Pentyl-		150–155/11		126–127 (107.5–109)	65, 66, 138, 559,
		140–142.5/4			1071b, 1673, 1680,
		120–122/0.5			1747, 1752
3-*n*-Pentyl-		179/16			
		69–72/0.005–0.001	n_D^{17} 1.5715 n_{He}^{20} 1.575 d_4^{20} 1.000 d_4^{17} 1.0048	155–156	514, 1684, 1739

4-*n*-Pentyl-		155–158/9		161–162	1753
2-(2-Methylbutyl)-		149/9			562, 1754
4-(1-Ethylpropyl)-				133–133.5	126a
2-*n*-Hexyl-		298–300	n^{18} 1.5620	112	1071b, 1747, 1750
		131–133/0.5			
2-(3,3-Dimethylbutyl)-					346
2-*n*-Heptyl-		190–191/15	n_D^{23} 1.5675	101–102 (137)	137, 165, 1071b
		118–122/0.2	n_D^{20} 1.5499		
2-*n*-Nonyl-		230–232/25	$n_D^{16.5}$ 1.5470	96	1517, 1750
		167/1			
4-*n*-Nonyl-		158–159/0.01			1143
2-(3-Ethylheptyl)-				Hydrochloride, 247.5–249	711
2-*n*-Decyl-				65	1071b
2-*n*-Undecyl-	42	237–238/17	$n_D^{20.5}$ 1.5478	87	165, 1071b, 1755, 1756
		233/14			
2-*n*-Dodecyl-	30	185–186/0.5		83.5	1071b
6-Dodecyl-		196–198/0.5	*n* 1.5345	131	1734
2-*n*-Tridecyl-	31–32	*ca.* 246/10			1757
2-*n*-Pentadecyl-	38	263–264/13		90	165
2-*n*-Heptadecyl-	49			92	165
MONOALKYLQUINOLINES—ISOTOPIC VARIATIONS					
2-(Methyl-*t*)				194.8–196.4	1758
2-(Methyl-d_3)-					347
2-(Methyl-^{13}C)-		116–122/15			350b, 1759
2-Methylquinoline-2-^{13}C		130–140/18			1585
2-(Methyl-^{14}C)-		116–120/15			1681
3-(Methyl-*t*)-				190.4–191.6	1758
4-Methylquinoline-2-*d*					126c, 347
6-Methylquinoline-^{15}N					1586
8-(Methyl-*d*)-					347
8-(Methyl-d_3)-					350b
2-(Ethyl-2-*d*)-		58–59/0.15			126a, b
2-(Ethyl-1,1-d_2)-					347
2-(Ethyl-2,2,2-d_3)-					347
8-(Ethyl-2,2,2-d_3)-					347

TABLE 39 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.) m.p. (°C)	References
2-(Propyl-2-*d*)-		80–82/0.1			126a
2-(Propyl-2-*d*)quinoline-4-*d*					126a
2-(Propyl-3,3,3-d_3)-					347
8-(Propyl-3,3,3-d_3)-					347
2-(Isopropyl-2,2,2-d_3)-					347
2-(Isopropyl-2,2,2,-2',2',2'-d_6)-					347
DIALKYLQUINOLINES					
2,3-Dimethyl-	70.5	273 261/730		235 Chloroplatinate, 230	3, 15, 49, 74, 127, 304, 515, 517a, b, 1169, 1676, 1760–1765
2,4-Dimethyl-		264–265 143/15 104.5–105.5/4	n_D^{20} 1.6075 d_4^{20} 1.0558	196 Chloroplatinate, 229	3, 128, 193, 197a, 197b, 204, 217, 222, 543, 609, 1623, 1632, 1676, 1678, 1683, 1696, 1699, 1761, 1766–1774
2,5-Dimethyl-	61	264–265 80–85/1		223	459, 1676, 1775
2,6-Dimethyl-	60	266–267 (259–261) 165/55 152–155/13 106–107/4		191–2	183, 240, 610, 630, 1169, 1340, 1536, 1676, 1679, 1683, 1693, 1770, 1776–1778
2,7-Dimethyl-	61	264–265 115–116/7		196	459, 610, 1676, 1693, 1775, 1779
2,8-Dimethyl-	23.2–23.6	255.3/760 93–95/2	n_D^{20} 1.6022 d_4^{20} 1.0394	210 Chloroplatinate, 207	1, 4, 109, 459, 1340, 1536, 1674, 1679, 1780
3,4-Dimethyl-	73–74	290/737		221 Chloroplatinate, 234–240	89, 517b, 1676, 1730, 1781–1783

3,5-dimethyl-				220	79, 1676, 1687
3,6-Dimethyl-	58	270–271.5		253	1676, 1687, 1693
3,7-dimethyl-	80	270–271.5 101–103/1		244	1676, 1687, 1693
3,8-Dimethyl-		269/751	n_D^{20} 1.6063 d_{20}^{20} 1.0524	210	49, 1676, 1687, 1693
4,5-Dimethyl-	78			233	1676
4,6-Dimethyl-		273–274 (280) 140–141/12 103 – 15/0.4	n_D^{20} 1.6100 d_4^{20} 1.0577	249 Chloroplatinate, 238	77, 90, 91, 1676, 1690, 1695, 1696, 1699, 1706, 1707, 1730, 1782–1784
4,7-Dimethyl-		283/750 140–141/15 95–100/2		235–236 Chloroplatinate, 227	91, 1569, 1676, 1785
4,8-Dimethyl-	57–57.5	258–259/758 134–135/12		229 Chloroplatinate, 226–227	77, 91, 240, 1676, 1690, 1706, 1730, 1778
5,6-Dimethyl-	50			201	1676, 1712, 1786
5,7-Dimethyl-	22	273–275		249	63, 347, 635, 1676
5,8-Dimethyl-	5.7–5.8	265/736 162/42 158/31	d^{21} 1.070	192–193 (186) Chloroplatinate, 234	17, 77, 347, 350a, 433b, 443, 1676, 1787
6,7-Dimethyl-	58			278	347, 433b, 1676, 1712, 1786, 1788
6,8-Dimethyl-		269 133–134/14	d^{25} 1.0665	230 Chloroplatinate, 235	77, 86, 87, 347, 627, 1676, 1690
7,8-Dimethyl-		267/759	n_D^{20} 1.6160	198	347, 1569, 1676
2-Ethyl-3-methyl-	57–58	268–269/711 138–142/12		195 Chloroplatinate, 249	169, 177b, 197a, 458, 1687, 1722, 1789–1794
2-Ethyl-4-methyl-		270–275 126–129/10	n_D^{20} 1.5941 d_{20}^{20} 1.027	167–168 (159) Chloroplatinate, 219	1632, 1795
2-Ethyl-6-methyl-	59–60	270/718		244–245	453
2-Ethyl-8-methyl-		Oil		154–156	213a, b

TABLE 39 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n, d*	Picrate (and other derivs.) m.p. (°C)	References
3-Ethyl-2-methyl-	74–74.5			229–229.5	96, 1747, 1751, 1796
3-Ethyl-4-methyl-		177–180/29	n_D^{20} 1.6033	209–210	1797, 1798
3-Ethyl-6-methyl-		284–285.5	n_D^{20} 1.5955 d_{20}^{20} 1.0298	247	1693
3-Ethyl-7-methyl-		282–283	n_D^{20} 1.5947 d_{20}^{20} 1.0304	224.5	1693
4-Ethyl-2-methyl-	108	150–153/14		219 Methiodide, 246	151, 193, 197a, b, 217, 1799
4-Ethyl-3-methyl-		172–173/27–28 154–156/10		199–200 Chloroplatinate, 230	74, 1800, 1801
4-Ethyl-8-methyl-				Hydrochloride, 187–189	213a, b
6-Ethyl-2-methyl-		276–279		Methiodide, 214	1670
6-Ethyl-4-methyl-		84/0.2	n_D^{20} 1.5968	225–226	1802
6-Ethyl-8-methyl-		273–275			1803, 1804
8-Ethyl-2-methyl-		263–263.5/755	n_D^{25} 1.5870 d_4^{20} 1.0175	169	12
8-Ethyl-3-methyl-		263/746	n_D^{25} 1.5946		6, 15
8-Ethyl-6-methyl-				156–158	67
2,4-Diethyl-		286–287/760		177–178	151, 215, 216, 217, 1551, 1805
3,4-Diethyl-		177–178/25		179 Chloroplatinate, 230	74
5,7-Diethyl-		250/20		190–191.5	1806
6,8-Diethyl-		144/12	$n_D^{23.3}$ 1.5850	142	1807
x,x-diethyl-[a]		282.8–284.8		Chloroplatinate, 217	171, 172

[a] Later considered[1805] as 2,4-diethylquinoline.

2-Methyl-3-*n*-propyl-	34	115–116/0.1		224–227	1054a, 1808a, b, 1809
2-Methyl-4-*n*-propyl-				199–201	125, 126a, b, 151
3-Methyl-2-*n*-propyl-	59			Chloroplatinate, 228	74, 1792
4-Methyl-2-*n*-propyl-(?)				196–198	206
6-Methyl-2-*n*-propyl-		131–134.5/3–4		2,4,6-Trinitro-*o*-cresolate, 172.5–173.5	206
2-Isopropyl-7-methyl-		139–142/7	n_D^{20} 1.5788		1742
3-Isopropyl-2-methyl-	No data				1810
4-Isopropyl-2-methyl-	No data				151, 153
5-Isopropyl-8-methyl-		230–232/190 175/35	n_D^{27} 1.5798 $d_4^{26.2}$ 1.0287	166–168	261, 1811, 1812
3-Ethyl-2-*n*-propyl		291/720 182–184/23 160/12 101–108/0.2	n_D^{25} 1.5774	167–168	156, 197a, 458, 1789, 1813–1816
3-Ethyl-4-*n*-propyl-		167–169/10		173–174	1800, 1801
2-*n*-Butyl-3-methyl-		105–106/0.15		181–182	1054a, 1792, 1809
2-*n*-Butyl-4-methyl-		115–117/?			152a, 1637, 1817
3-*n*-Butyl-2-methyl-	61–62			210–212	1673, 1747
3-*n*-Butyl-4-methyl-		142–143.5/1	n_D^{20} 1.5803	162.5–164	1797
4-*n*-Butyl-2-methyl-	No data				152a
6-*n*-Butyl-8-methyl-	No data				261
2-Isobutyl-3-methyl-	No data				1810
2-Isobutyl-6-methyl-		180/20	n^{16} 1.5766	156	1750
2-*sec*-Butyl-4-methyl-	No data				1637
3-*sec*-Butyl-2-methyl-	No data				1054b
2,4-Di-*n*-propyl-		309/760		120–121	151, 152a, 1569
x,*x*-Di-*n*-propyl-		329		189–190	1818
2,4-Diisopropyl-		299/760		156–157	151, 215, 216, 1569
x,*x*-Diisopropyl-		300–320		226–228	1745
3-Methyl-2-*n*-pentyl-	No data				1792
6-Methyl-2-*n*-pentyl-		300–302		188–189	1755
2-*n*-Butyl-4-ethyl-		Oil			213a
3-Ethyl-2-isobutyl-		298–300		160–161	1755
2-*n*-Hexyl-3-methyl-	No data				1792
2-*n*-Hexyl-6-methyl-		218–220/60		114	1750

TABLE 39 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.) m.p. (°C)	References
2-*n*-Butyl-3-*n*-propyl-		335–340 136–137/0.2		146–147	1789, 1809
4-*n*-Butyl-3-*n*-propyl-		186–190/10		166–167	1800
2-Isobutyl-3-*n*-propyl-	No data				1810
2-Isobutyl-3-isopropyl-		295–295/709		182–183 Chloroplatinate, 219	454, 458, 1810, 1819–1821
2,4-Di-*n*-butyl-		335/760		135–136	151, 1569
2-*n*-Butyl-3-*sec*-butyl-		131–132/0.15		145–146	1054b
2-*n*-Heptyl-3-methyl-	No data				1792
2-*n*-Heptyl-6-methyl-		200/13	n_D^{15} 1.5700	137	165
2-(1-Propylbutyl)-3-methyl-		126–127/0.15		150–151	1054a, 1809
2-*n*-Pentyl-3-*n*-propyl-		134–135/0.3		139–140	1054b
2-*n*-Octyl-3-methyl-	No data				1792
3-*n*-Butyl-2-*n*-pentyl-		345–350		156–157	1789
3-*n*-Butyl-4-*n*-pentyl-		215–218/8.5		137–139	1800
2-*n*-Nonyl-3-methyl-	No data				1792
2-*n*-Decyl-3-methyl-	No data				1792
2-*n*-Hexyl-3-*n*-pentyl-		355			169, 458
6-Methyl-2-*n*-undecyl-		238–239/12	n_D^{21} 1.5490	114	165
8-Methyl-2-*n*-undecyl-		235–238/14		76	1755
6-Dodecyl-3-methyl-	No data				874, 1822
2-*n*-Heptyl-3-*n*-hexyl-	No data				1790
3-Methyl-2-*n*-pentadecyl	55			105–106	1755
6-Methyl-2-*n*-pentadecyl	46	271–272/13		92	165
2-*n*-Heptadecyl-6-methyl-	54	302–303/18		129	165
DIALKYLQUINOLINES—ISOTOPIC VARIATIONS					
4-Methyl-2-(methyl-d_3)-					350a
6-Methyl-2-(methyl-d_3)-					350a
4-Methyl-8-(methyl-d_3)-					350a
5-Methyl-8-(methyl-d_3)-					350a
8-Methyl-5-(methyl-d_3)-					350a

TRIALKYLQUINOLINES

2,3,4-Trimethylquinoline	94–95	285 156–158/12 153–155/9		225–226 Chloroplatinate, 215	217, 516, 1569, 1823–1825
2,3,6-Trimethylquinoline	86–87	285		212	90
2,3,8-Trimethyl-	55–56	280/747		242–245	47, 49
2,4,5-Trimethyl-	77			194–195	217, 1826
2,4,6-Trimethyl-	43–45 65.5 (+1 H_2O)	286.9/742 146–148/13.5		200–201 Chloroplatinate, 220	193, 197a, 197b, 447, 543, 609, 1766, 1767, 1768, 1774, 1799, 1824, 1825, 1827–1829
2,4,7-Trimethyl-	48 (+1 H_2O)	282.9/742 116–117.5/2 103–104/1.5	n_D^{20} 1.5997 d^{20} 1.0337	234–236 Chloroplatinate, 272	217, 1767, 1768, 1826, 1829, 1830 1574
2,4,8-Trimethyl-	42	275.8/740 112–114/3	n_D^{30} 1.5855	193 Chloroplatinate, 275	2, 217, 1766, 1767, 1768, 1799, 1829, 1830 1569, 1831, 1832
2,5,6-Trimethyl-	No data				
2,5,7-Trimethyl-		286.6/746 107–108/1.2	n_D^{20} 1.5980	204.5–205.5	1829
2,5,8-Trimethyl-		250.4/746 144–146/15	n_D^{21} 1.5941	181–182 (177–178.5)	610, 1829
2,6,7-Trimethyl-	73–74			221–222	1569, 1831, 1832
2,6,8-Trimethyl-	46	266–267/780 267.4/746 94–95/1.27		187–189 Chloroplatinate, 206–207	183, 184, 451, 630, 1674, 1679, 1690, 1829, 1833–1835
2,7,8-Trimethyl-	41	276.1/740 144–146/15		186	1829
3,4,6-Trimethyl-	67	*ca.* 300 168–170/20		236	1778, 1782, 1836
3,4,7-Trimethyl-	78			229	1569, 1676
3,4,8-Trimethyl-	56	*ca.* 295		225	1782
3,5,6-Trimethyl-	No data				1569
3,5,8-Trimethyl-	61–62			210–211	1743
3,6,7-Trimethyl-	111–112			245–246	1569
3,6,8-Trimethyl-	31–32	105–106/0.5		222–223	1743, 1837
3,7,8-Trimethyl-	66–67			204–205	1743

TABLE 39 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.) m.p. (°C)	References
4,5,6-Trimethyl-	No data				1569
4,5,7-Trimethyl-	78–79			248–249	1569
4,5,8-Trimethyl-		282–284/757 155/13		187–188	77, 1569, 1838
4,6,7-Trimethyl-	95–96	162–164/10		266–267 Ethiodide, 241–242	1569, 1839
4,6,8-Trimethyl-	56.5–57	270–280		208–209	77, 1707, 1838, 1840
4,7,8-Trimethyl-	57 58			219–220	1569, 1841
5,6,7-Trimethyl-	83	174–177/24		216	1842
5,6,8-Trimethyl-	42–43	285–287			534, 1843
4-Ethyl-2,3-dimethyl-		302/749	n_D^{25} 1.5982 d_4^{20} 1.0511	220–221	11
8-Ethyl-2,3-dimethyl-	36.5	284.6/755	n_D^{20} 1.5940 d_4^{20} 1.017	220	6, 15, 52, 53
3-Ethyl-2,4-dimethyl-		137–138/1.2	n_D^{20} 1.6009	Methosulphate, 203–206	1823
6-Ethyl-2,4-dimethyl-		299–300/742	n_D^{25} 1.5860	190–191	435
7-Ethyl-2,4-dimethyl-		302–304/771	n_D^{20} 1.5890	197–198 (210)	601, 1844
8-Ethyl-2,4-dimethyl-		288/747 148/13	n_D^{22} 1.5988 n_D^{25} 1.5846 d_4^{20} 1.017	168–169	8, 1845
3-Ethyl-2,6-dimethyl-	51	284–293		178	1846
4-Ethyl-2,6-dimethyl-		169–171/20		Tartrate, 173	193
2-Ethyl-3,5-dimethyl-	No data				453, 1687
2-Ethyl-3,6-dimethyl-	54	287–288/720		177	453, 1687, 1795
4-Ethyl-3,6-dimethyl-	68–69			205–206	1801
2-Ethyl-3,7-dimethyl-	40–41	288–292		222–223	453, 1569, 1687
2-Ethyl-3,8-dimethyl-	44	279–280/717		187	453, 1687, 1795
2-Ethyl-4,6-dimethyl-		285–290	n_D^{20} 1.5889 d_{20}^{20} 1.0236	193 Chloroplatinate, 203	1795

2-Ethyl-4,8-dimethyl-		275–280	n_D^{20} 1.5849 d_{20}^{20} 1.0011	147 Chloroplatinate, 217	1795
4-Ethyl-6,7-dimethyl-	No data				1569
2,3-Dimethyl-8-*n*-propyl-	14.5–15.5	299.5	n_D^{25} 1.57780 d_4^{20} 0.9996	198–199	7, 52, 53
2,4-Dimethyl-3-*n*-propyl-		137–138/0.9	n_D^{20} 1.5882	Methosulphate, 187–190	1823
2,4-Dimethyl-8-*n*-propyl-		298/747	n_D^{20} 1.5748 d_4^{20} 0.9992	Chlorozincate, 225–226	9
8-Isopropyl-2,5-dimethyl-		179/16			1847
5-Isopropyl-2,8-dimethyl-	78.2	186/16 170/25		142	820, 1811, 1812, 1847
5,7-Diethyl-2-methyl-		250/20		147–148.5	1806
2,6-Diethyl-3-methyl-		313.5/748	n_D^{25} 1.5834 d_4^{20} 1.0049	152–153	435
2,8-Diethyl-3-methyl-	18.5–19.5	298/754	n_D^{25} 1.5778 d_4^{20} 1.0014	194–195	435
5,7-Diethyl-3-methyl-(?)	No data				1806
5,7-Diethyl-4-methyl-		250/20		209–210.5	1806
6,8-Diethyl-4-methyl-		102/1	n_D^{20} 1.5838	189–191	1802
3-*n*-Butyl-2,4-dimethyl-		149–150/1	n_D^{20} 1.5788	Methosulphate, 182–185	1823
6-*sec*-Butyl-2,4-dimethyl-		321	n_D^{20} 1.5660	142	10
6-*t*-Butyl-2,4-dimethyl-		204–205/35	$n_D^{15.5}$ 1.5740	130	1848
8-*sec*-Butyl-2,4-dimethyl-		310	n_D^{20} 1.5669 d_4^{20} 0.9824	148–150	10
6-*n*-Butyl-2,8-dimethyl-		149–151/2	n_D^{20} 1.5690	134–135	1835
3-Ethyl-6-methyl-2-*n*-		174/15	n_D^{25} 1.5773		1813
2,4-Dimethyl-3-*n*-pentyl-		164–165/0.8	n_D^{20} 1.5701	Methosulphate, 191–195	1823
3-*n*-Hexyl-2,4-dimethyl-		182–184/1.8	n_D^{20} 1.5662	Methosulphate, 197–199	1823
2-Isobutyl-3-isopropyl-6-methyl-		178/18		173	1821
x,*x*,*x*-Tripropyl-		348		133–134	1818
3-*n*-Heptyl-2,4-dimethyl-		186–188/1.5	n_D^{20} 1.5598	Methosulphate, 203.5–205	1823

TABLE 39 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.) m.p. (°C)	References
2,4-Dimethyl-3-*n*-octyl-		182–183/0.6	n_D^{20} 1.5545		1823
3-*n*-Butyl-6,8-di-*n*-propyl-				110–112	68, 69
6-*n*-Butyl-3,8-di-*n*-propyl-				130–131	69
2,4-Dimetyl-3-*n*-nonyl-		206–208/1.8	n_D^{20} 1.5510	Methosulphate, 207.5–209	1823
3-*n*-Pentyl-6,8-di-*n*-propyl-				115–116	68, 69
6-*n*-Pentyl-3,8-di-*n*-propyl-				103–104	69
8-*n*-Pentyl-3,6-di-*n*-propyl-				130–132	69
3-*n*-Decyl-2,4-dimethyl-		214–216/1.6	n_D^{20} 1.5458	Methosulphate, 211.5–213	1823
TETRAALKYLQUINOLINES					
2,3,4,6-Tetramethyl-	150				1848
2,3,4,7-Tetramethyl-	119–120 (79)	188–190/28		217–218	1569, 1848
2,3,4,8-Tetramethyl-	77–78			240	7
2,4,5,7-Tetramethyl-	59			234–235	1569, 1849
2,4,5,8-Tetramethyl-	48	168–172/12		163–164	516, 1829, 1849–1851
2,4,6,7-Tetramethyl-	79–80			239–240	1569, 1852
2,4,6,8-Tetramethyl-	86–87	284–285		208–209	1569, 1852
2,4,7,8-Tetramethyl-	30–31	295.5/742		181–182	1569, 1829, 1854
2,5,6,8-Tetramethyl-	28	297–300		179 Chloroplatinate, 248	185, 458
3,4,5,8-Tetramethyl-	83–84				1850, 1855
3,4,6,7-Tetramethyl-	124–125			251–252	1569, 1850
3,4,6,8-Tetramethyl-	89			210	1782
8-Ethyl-2,3,4-trimethyl-	52–53	320	n_D^{34} 1.5798	216	1856
4-Ethyl-2,3,8-trimethyl-		310–311/748	n_D^{25} 1.5918 d_4^{20} 1.0240	178	11, 52

5-Ethyl-2,4,8-trimethyl-	32			153	1857
2-Ethyl-3,6,7-trimethyl-	113–114			228–229	1569
2-Ethyl-3,6,8-trimethyl-	62	291		183	90, 1837
2,3,4-Trimethyl-8-*n*-propyl-	69–70	330	n_D^{70} 1.5618 n_D^{44} 1.5731 n_D^{20} 1.5790	211–211.5	52, 53, 1858
8-Isopropyl-2,3,4-trimethyl-	106–107	327/750		165–166	13
5-Isopropyl-2,4,8-trimethyl-		177–178/22		181–183	1811, 1812
4,8-Diethyl-2,3-dimethyl-		319/752	n_D^{20} 1.5871 d_4^{25} 1.008	174–175	14
5,8-Diethyl-2,4-dimethyl-		178–180/15	n_D^{21} 1.5792	133	1859
6,8-Diethyl-2,4-dimethyl-		180/20	n_D^{21} 1.6670	167	1807
5-*t*-Butyl-2,4,8-trimethyl-		210–215/35	n_D^{16} 1.5720	100–101	1848
4-Ethyl-2,3-dimethyl-8-*n*-propyl-		327/752	n_D^{20} 1.5751 d_4^{25} 1.003	Nitrate, 161	14
3-Ethyl-6,8-dimethyl-2-*n*-propyl-		130–135/0.5			1837
PENTAALKYLQUINOLINES					
2,3,4,5,8-Pentamethyl-	82–83 (54)	172/13		165	1848, 1850, 1855
2,3,4,6,7-Pentamethyl-	145–146			227–228	1569, 1850, 1855
2,3,4,6,8-Pentamethyl-	100	195/28			1848
2,4,5,6,7-Pentamethyl-	94–95			204–205	1842
2,4,5,6,8-Pentamethyl-	75	182–183/15		183–184	1569, 1766, 1848
3,4,5,6,8-Pentamethyl-	102–103				1850, 1855
HEXAALKYLQUINOLINES					
2,3,4,5,6,8-Hexamethyl-	83	207–208/28		162–163	1569, 1848

TABLE 40. Cycloalkylquinolines

Compound	M.p. (°C)	B.p. (°C/mmHg)	n	Picrate, m.p. (°C)	References
2-Cyclopropyl-		145–148/17 65–70/0.01	n_D^{21} 1.6266	175	1755, 1860, 1861
4-Cyclopropyl-	No data				1861
2-Cyclopentyl-		163/10 76–80/0.05		152–154	119, 127
6-Cyclopentyl-	No data				378
2-Cyclohexyl-		180–183/20 165–168/10 120/3		162	127, 151, 160, 1554, 1557, 1735, 1862, 1863
3-Cyclohexyl-	No data				378
4-Cyclohexyl-		160–164/7		205–207	151, 1735, 1862
2-Cyclooctyl-[a]		180–190/2			1864
4-Cyclooctyl-[a]		180–190/2			1864
4-Cyclopropyl-2-methyl-	No data				151
4-Cyclopentyl-2-methyl-		170–175/3			1864
2-Cyclohexyl-4-methyl-		177–179/4		178	1735, 1863
4-Cyclohexyl-2-methyl-		173/5		206	152a, 1735
7-Cyclohexyl-2,4-dimethyl-	77–78				1866
2-Cyclohexylmethyl-				146.5–147.5	559
2-(2-Cyclohexylethyl)-3-methyl-	52–53			178.5–180	1865
2,4-Dicyclopropyl-		120/0.001			1861
2,4-Dicyclohexyl-	No data				151, 1864

[a] Mixture of 2- and 4-isomers, not separated.

Note: A few quinolyl derivatives of cyclohexanone and of cyclohexanol (and certain cyclopentane derivatives) have also been reported. For details see refs. 939, 1226, 1950, 1966 and 2107.

TABLE 41. Cyclopolyalkylenequinolines (Cycloalkenoquinolines)

Note on nomenclature and numbering: In order to avoid the use of different numbering systems for the various ring sizes included in this table, compounds have generally been referred to as cyclopolyalkylenequinolines rather than cycloalkenoquinolines, the numbering system used is that of the first name mentioned, alternative names being shown in parentheses.

Compound	M.p. (°C)	B.p. (°C/mmHg)	n	Picrate (and other derivs.) m.p. (°C)	References
DIMETHYLENEQUINOLINES					
2,3-Dimethylenequinoline (2,3-cyclobutenoquinoline)	96.8–97.4			236–237	306, 1867, 1868
4,5-Dimethylenequinoline [4,5-dihydrocyclopenta(*d,e*)quinoline]	94–95				80
TRIMETHYLENEQUINOLINES[a]					
2,3-Cyclopentenoquinoline (2,3-trimethylenequinoline)	59–61	106–108/0.25		203–204 Chloroplatinate, 235	306, 349, 940 1760, 1762, 1869–1873
Derivatives of 2,3-cyclopentenoquinoline:					
3-Methyl-		113–117/0.64		182.5–184.5 Hydrochloride, 164–166	1874, 1875
9-Methyl-	66.5 (62)	150–151/2			1876–1878
7-Phenyl-	115				305
9-Phenyl-	135–136			192–193	940, 1879
3-Benzyl-	82	205–206/2			1878
3-Triphenylmethyl-	221–222				1880
3-Methylene-	103–105				1874, 1875
3-Benzylidene-	138 (119–120)	228–229/2			1878, 1881, 1882
3-Diphenylmethylene-	161.5–162				1874, 1880
2,9-Dimethyl-		125/0.5			1876, 1877
3,9-Dimethyl-		119/0.45			1876, 1877
3-Benzyl-9-methyl-	95	225–226/2			1876–1878

[a] A number of derivatives of (1*H*)-, (3*H*)- and (4*H*)-2,3-cyclopenta(*b*)quinoline have also been prepared. For details see refs. 927, 940, 1874, 1880 and 1890.

TABLE 41 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	n	Picrate (and other derivs.) m.p. (°C)	References
9-Methyl-3-phenyl-	91	221–222/2			1878
3-Cyclopentylidene-9-methyl-	123–125.5				1876, 1877
3-Benzylidene-9-methyl-	149 (170)	239–240/2			1876–1878
9-Methyl-1,2-diphenyl-	130				1877
2,2',3,3'-Tetrahydro-3,-3'-bi-(1*H*)-cyclopenta(*b*)-quinoline	208–209				1881
9,9'-Dimethyl-2,2',3,3'-tetrahydro-3,3'-bi-(1*H*)-cyclopenta(*b*)quinoline	213–215				1877
2,3-Dihydro-2,2'-bi(1*H*)-cyclopenta(*b*)quinoline	192–192.5				1881
3,4-Trimethylenequinoline (3,4-cyclopentenoquinoline)				216–217	1883, 1884
2-Phenyl-3,4-trimethylenequinoline	74			205 Hydrochloride, 200+	1884, 1885
5,6-Trimethylenequinoline (5,6-cyclopentenoquinoline)	43–44.5	162–163/11		190–191	1886, 1887
2-Methyl-5,6-trimethylenequinoline	53–54			193–194	1888
6,7-Trimethylenequinoline (6,7-cyclopentenoquinoline)	79.5–81 (58)	168/12		269–271	696, 1886, 1887
2-Methyl-6,7-trimethylenequinoline	93–95			202–203	1888
7,8-Trimethylenequinoline (7,8-cyclopentenoquinoline)	51–53	165–168/high vacuum 118/0.5		211–212	1886, 1889

2-Methyl-7,8-trimethyl-enequinoline	89			190–191	1889
TETRAMETHYLENEQUINOLINES[a]					
1,2,3,4-Tetrahydro acridine (2,3-tetra-methylenequinoline, 2,3-cyclohexenoquinoline)	59–60	115/15		220–222 (208–209) Chloroplatinate, 233–235	96, 158, 306, 481, 1760, 1762, 1871, 1872, 1882, 1891–1894
Derivatives of 1,2,3,4-tetrahydroacridine:					
2-Methyl-	87–88	180/15		199–200	1869, 1873
3-Methyl-	76–77 (70–71)	195/15		185–186	1869, 1893, 1895, 1896
4-Methyl-		140–160/0.05			1897
5-Methyl-	77–78	190/20		215–216	1893, 1894
6-Methyl-	100–101	208/25 108/0.01		189–190	1891, 1893, 1894, 1898
7-Methyl-	61–62			189.5–190.5	1891, 1893, 1894
9-Methyl-	66–68 (71)				1876, 1877, 1899
3-Ethyl-	46–47.5			174–176	1900
7-Ethyl-		Oil	n_D^{22} 1.6008		1901
8-Ethyl-	38.5–40			160–162	1900
9-*n*-Propyl-		167/2	n_D^{20} 1.6040		1899
2-Cyclohexyl-	101			221	1902
4-(1-Cyclohexenyl)-	80–82			215–217	158
5-Phenyl-	85–86 (78–81)				482, 1901, 1903
7-Phenyl-	130			246–247	305, 1893
9-Phenyl-	142–143			193–194	1879
4-Benzyl-		180–185/0.1		Hydrochloride, 205–207	1904
4-Cyclohexylidene-	44–46			205–207	158
4-Benzylidene-	103–104			176–178	1869
4-(4-Nitrobenzylidene)-	145–146				701
4-(4-Dimethylamino-benzylidene)-	133–134				701
3,9-Dimethyl-	72–74			193	1869, 1876, 1877
4,9-Dimethyl-		161/1.5			1876, 1877
5,8-Dimethyl-	38–39			187–188	1893

[a] A series of derivatives of 1,2-dihydroacridine has also been prepared. For details see ref. 1823.

TABLE 41 (*cont.*)

Compound	M.p. (°C)	B.p.(°C/mmHg)	n	Picrate (and other derivs.) m.p. (°C)	References
2-*t*-Butyl-9-methyl-	80				1876, 1877
2-Cyclohexyl-7-methyl-	152				1902
4-(1-Cyclohexenyl)-9-methyl-	94				1876, 1877
9-Methyl-4-phenyl-	129				1876, 1877
9-Methyl-4-(4-methyl-2-quinoyl)-	70				1877
4,4-Dibenzyl-	153–154				1904
4-Isopropyl-1,9-dimethyl-		156/0.55			1876, 1877
4-Isopropylidene-1,9-dimethyl-	76–77				1876, 1877
7,8,9,10-Tetrahydrophenanthridine (3,4-tetramethylenequinoline, 3,4-cyclohexenoquinoline)	64			212–213	1884, 1905–1907
Derivatives of 7,8,9,10-tetrahydrophenanthridine:					
1-Methyl- (?)	57			231–232	1905, 1908
2-Methyl-	73.5			231–232	1905, 1906
3-Methyl- (?)		215/20		230–231	1905, 1908
4-Methyl-	80–81			203–204	1905, 1906
6-Methyl-	85			215–218	1884
8-Methyl-	45			196–197	1905, 1906
2-Phenyl-	122–123			235	1905
6-Phenyl-	79			206–207 Hydrochloride, 240–242	1884, 1907
1,4-Dimethyl-	63–64			181–182	1905, 1906
2,4-Dimethyl-	50–51			212–213	1905, 1906
6,9-Dimethyl-	78			208	1869
2-Methyl-6-phenyl-	83			174–176	1907

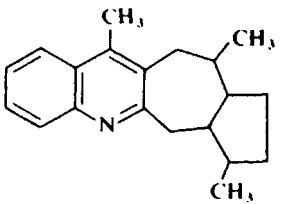
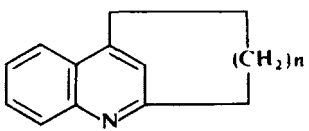
5,6-Tetramethylenequinoline [5,6-cyclohexenoquinoline, 7,8,9,10-tetrahydrobenzo-(*f*)-quinoline]	158	183–185/12		207	1909
2-Methyl-5,6-tetramethylenequinoline	57			190	1910, 1911
2,4-Dimethyl-5,6-tetramethylenequinoline		214–216/17	$n_D^{21.5}$ 1.6125	223–224	1912
8-Ethyl-2,4-dimethyl-5,6-tetramethylenequinoline	50			97	1912
6,7-Tetramethylenequinoline [6,7-cyclohexenoquinoline, 6,7,8,9-tetrahydrobenzo(*g*)quinoline]	71–72	187/11		269.5	1909
2-Methyl-6,7-tetramethylenequinoline	45			206	1910, 1911
7,8-Tetramethylenequinoline [7,8-cyclohexenoquinoline, 7,8,9,10-tetrahydrobenzo(*h*)-quinoline]	26			186	1913
2-Methyl-7,8-tetramethylenequinoline	55			199	1914
2,4-Dimethyl-7,8-tetramethylenequinoline	49	196–200/15		201	516
PENTAMETHYLENEQUINOLINES					
2,3-Pentamethylenequinoline (2,3-cycloheptenoquinoline)	93 (82)			200.5–202 Chloroplatinate, 214	158, 221a, 306, 1760, 1762, 1869, 1872, 1898
4-Methyl-2,3-pentamethylenequinoline	94				1876, 1877
6-Methyl-2,3-pentamethylenequinoline	105			189–190	1755
6-Phenyl-2,3-pentamethylenequinoline	106				305
11-Methyl-6-phenyl-2,3-cycloheptenoquinoline	113.5				1877

TABLE 41 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	n.	Picrate (and other derivs.) m.p. (°C)	References
3,4-Pentamethylene-quinoline	67–68			193–194	1883, 1884
2-Phenyl-3,4-penta methylenequinoline		Oil		206–208 Hydrochloride, 210–215	1884
HEXAMETHYLENEQUINOLINES					
2,3-Hexamethylene-quinoline (2,3-cyclo-octenoquinoline	59	130–135/0.1		212	158, 278, 306, 1915 1916
4-Methyl-2,3-hexa-methylenequinoline		159/0.75			1876, 1877
6-Methyl-2,3-hexa-methylenequinoline	102			185–186	1917
6-Phenyl-2,3-hexa-methylenequinoline	78				305
6-(4-Biphenylyl)-2,3-hexa-methylenequinoline	147				305
HIGHER POLYMETHYLENEQUINOLINES					
2,3-Heptamethylenequino-line (2,3-cyclononeno-quinoline	55			179–180	1917
6-Methyl-2,3-hepta-methylenequinoline	79			183–184	1917
2,3-Octamethylenequino-line (2,3-cyclodeceno-quinoline)	92				1917
6-Methyl-2,3-octa-methylenequinoline	93			202	1917
2,3-Decamethylenequino-line (2,3-cyclododeceno-quinoline)	75			185	164

6-Methyl-2,3-decamethylenequinoline	61	238/11	196	164
6,7-dimethyl-2,3-decamethylenequinoline	93		221	164
2,3-Undecamethylenequinoline (2,3-cyclotridecenoquinoline)	80		175	1918
2,3-Dodecamethylenequinoline (2,3-cyclotetradecenoquinoline)	76		159	928
2,3-Tridecamethylene-Quinoline (2,3-cyclopentadecenoquinoline)		197/0.1	169–171	278
6-Methyl-2,3-tridecamethylenequinoline	Wax		165	928
2,3-Tetradecamethylenequinoline (2,3-cyclohexadecenoquinoline)			173	928
4-Methyl-2,3-tetradecamethylenequinoline	62.5–64			1876, 1877
2,3-Pentadecamethylenequinoline (2,3-cycloheptadecenoquinoline)	Wax		172	928
2,3-Heptadecadienoquinoline [7,8,9,10,11,12,-15,16,17,18,19,20-dodecahydro(6*H*)-cycloheptadeca(*b*)quinoline]		Oil	161	928
2,3,6,7-Bis(tetramethylene)quinoline [1,2,3,-4,7,8,9,10-octahydrobenz(*b*)acridine]	146	380/15	208	1919

TABLE 41 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	n,	Picrate (and other derivs.) m.p. (°C)	References
	144				1877
META-BRIDGED COMPOUNDS[c]					
					
n					
8	44–45			166.5–167.5	221a, b
10	62–63			Hydrochloride, 230–234	221a, b, 1920

[c] Many functional derivatives of the benzopyridinophanes mentioned have also been reported. For details see refs. 221a, b, 257, 258, 1920–1924

TABLE 42. Aralkylquinolines

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate, (and other derivs.), m.p. (°C)	References
BENZYLQUINOLINES				
2-Benzyl-		230/14	158–159	98, 127–129,
[2-(1-phenylmethyl) quinoline]		212–213/12 156/1 145–150/0.04		140, 141, 155, 560, 1554, 1557, 1558, 1925–1928
3-Benzyl-	67–68	226/19 170–190/3	182–183	98, 110, 224, 1929, 1930
4-Benzyl-	52–52.5	222–223/19 180–190/2	178–179	136, 140, 141, 155, 219, 220, 615, 1731, 1931
5-Benzyl-	81–83	186–190/12	204 Hydrochloride, 172–174	98, 1932
6-Benzyl-	79–80 (48–49)	139–142/1	207–208	1932–1935
7-Benzyl-	63–65		181 Hydrochloride, 146–147	98, 1932
8-Benzyl-	54–55	144–147/0.3	134 Hydrochloride, 146–149	98, 1932
2-Benzyl-3-methyl-	66	187–192/15	184	1928
2-Benzyl-4-methyl-	No data			155
3-Benzyl-6-methyl-	69–70		197–198	1929
3-Benzyl-8-methyl-	61–62	155–158/0.1	219–221	1929
4-Benzyl-2-methyl-	63		185	175
6-Benzyl-8-methyl-	55	163/0.3		98, 1934, 1936
2-(4-Methylbenzyl)-		250–263/52	167–167.5	1606
4-(3-Methoxybenzyl)-			Hydrochloride, 163–165	218
4-(4-Aminobenzyl)-	130–132			615
4-(4-Bromobenzyl)-		167/2	188	615
4-(4-Methoxybenzyl)-			*p*-Toluene-sulphonate, 153–156	218
4-(4-Nitrobenzyl)-	135.5			615
4-{[(2-Quinolyl)methyl] benzyl}- [2,2'-(4-phenylenedimethylene)diquinoline)	135–136			1937
4-(3,4-Dimethoxybenzyl)-			Hydrochloride, 209–211	218
4-(3,4-Dimethylbenzyl)-			Hydrochloride, 207–209	218
4-(3,4,5-Trimethoxybenzyl)-			Hydrochloride, 166–168	218
6-(4-Chlorobenzyl)-	191.5–192			1934
6-(2,4-Dichlorobenzyl)-			167–168	1934
6-(3,4-Dichlorobenzyl)-			164–165	1934

TABLE 42 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
8-(4-Methoxybenzyl)-		174–176/0.25		1932
8-(3,4-Dimethoxybenzyl)-	102–103	188–189/0.3	Hydrochloride, 145–151	1932
8-(3,4-Methylenedioxybenzyl)-	71–72	194–196/0.3	Hydrochloride, 133–135	1932
2-(2-Hydroxybenzyl)-3-methyl-	168			1938
2-(2-Methoxybenzyl)-3-methyl-	Needles			1938
3-(2-Aminobenzyl)-2-methyl-	166–167			1939
4-(3,4-Dimethoxybenzyl)-2-methyl-			Hydrochloride, 243–245	218
2,4-Dibenzyl-		230–245/3	193	143, 155, 1558
PHENYLETHYLQUINOLINES				
(1-Phenylethyl) derivatives:				
None				
(2-Phenylethyl) derivatives:				
2-Phenylethyl-	29–30	216–218/13	134–135	101, 121, 124,
[2-(2-phenylethyl)-quinoline]		189–191/3		127, 135, 202,
		165–167/1		224, 559, 616, 1032, 1557, 1928
4-Phenylethyl-	100–101		192–193 (183–186)	101, 202, 224, 616, 1029
2-Methyl-4-phenylethyl-	61–62.5			1940
3-Benzyl-2-phenylethyl-	98		198	1928
2-(3-Aminophenylethyl)-	165–166		226–228	711
2-(3-Carboxyphenylethyl)-			214–216	711
2-(3-Cyanophenylethyl)-	198–199			711
2-(4-Aminophenylethyl)-	107–109			616, 711
2-(4-Methoxyphenylethyl)-	57.5–58.5 (44.5)	184/0.3		121, 616
2-(4-Nitrophenylethyl)-	105–106		190–192	616
2-(4-Carboxyphenylethyl)-	185–187			711
2-(2,3-Dimethoxyphenylethyl)-			Hydrochloride, 194	121
2-(3,4-Dimethoxyphenylethyl)-	52		Hydrochloride, 177	121, 725
2-(2-Hydroxy-3-methoxyphenylethyl)-	139			121
2-(4-Hydroxy-3-methoxyphenylethyl)-	147			121
2-(3-Methoxy-2-pentyloxyphenylethyl)-	59	212–215/0.3		121
4-(4-Dimethylaminophenylethyl)-	110–111.6			1052
4-(2-Hydroxyphenylethyl)-	180–181			1941
4-(3-Hydroxyphenylethyl)-	209			1941
4-(4-Hydroxyphenylethyl)-	175–177			101, 1941

TABLE 42 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
4-(4-Methoxyphenyl-ethyl)-	92.5–93.5			616
2,4-Diphenylethyl-	54	232–234/0.6	198–201 Styphnate, 183	224
HIGHER MONOPHENYLALKYLQUINOLINES				
2-(4-Phenylbutyl)-	34–37	220–221/7–8	123–124	103, 616
DIPHENYLMETHYLQUINOLINES				
2-Benzhydryl-[2-(diphenylmethyl)-quinoline, diphenyl-(2-quinolyl)methane]	81–82	185–210/2		226a, b, 560
2-(4,4'-Diacetoxy-benzhydryl)-	110–115			1943
2-(4,4'-Diaminobenz-hydryl)-	180			1555
2-(4,4'-Dihydroxybenz-hydryl)-	247		Benzene-sulphonate, 138	276, 1545, 1555, 1943
2-(4-Amino-4'-Hydroxy-benzhydryl)-	205			1555
2-(4-Hydroxy-4'-methoxybenzhydryl)-	206			1555
2-(4,4'-Dihydroxybenz-hydryl)-6-methyl-	239–240			276, 1943
2-(4,4'-Dihydroxy-3,3'-dimethoxy-benzhydryl)-	177			1943
2-(4,4'-Dihydroxy-3,3'-dimethyl-benzhydryl)-	264–265			276, 1943
4-Benzhydryl-	158 (146–147)			131, 132, 136
4-Benzhydryl-2-methyl-	174			131, 132
4-Benzhydryl-2-phenyl-	159			131, 132
4-Benzhydryl-2,6-dimethyl-	202			131, 132
4-Benzyhydryl-6-methyl-2-phenyl-	231			131, 132
4-Benzhydryl-8-methyl-2-phenyl-	216			131, 132
4-(4,4'-Dihydroxybenz-hydryl)-	296			1545
4-(4,4'-Dimethoxybenz-hydryl)-	202–205			1943
4-(3,3'-Dibenzyl-4,4'-dihydroxybenz-hydryl)-	187–190			1943
4-(4,4'-Dihydroxy-3,3'-diphenylbenz hydryl)-	198–200			1943
4-(4,4'-Dihydroxy-5,5'-diisopropyl-2,2'-dimethylbenzhydryl)-	220–223			1943

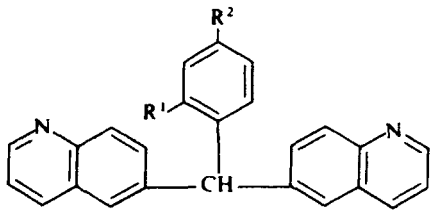
TABLE 42 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
5- and/or 7-(4,4'-dimethylaminobenzhydryl)-	185–186			1104
6-Benzhydryl-	103–104 (129–130)			1933, 1935, 1947
6-(4,4'-Dimethylaminobenzhydryl)-	165			565, 1104, 1948
7- and/or 5-(4,4'-dimethylaminobenzhydryl)-	185–186			1104
8-(4,4'-Dimethylaminobenzhydryl)-	179–180			1949
DIPHENYLETHYLQUINOLINES				
2-[1,1-Bis(4-hydroxyphenyl)ethyl]-[1,1-bis(4-hydroxyphenyl)-1-(2-quinolyl)-ethane]	228			276, 277, 1943
2-(2,2-Diphenylethyl)-(2-benzhydrylmethylquinoline)	119–121		217	766a, 766c, 1944
2-(2,2'-Diphenylethyl)-3-methyl- (?)	121–122			1765
2-(2,2'-Diphenylethyl)-6-methyl-	128		212	1942, 1945
2-[2-Phenyl-2-(4-chlorophenyl)ethyl]-	91.5–92.5			766c
2-[2,2-Bis(4-dimethylaminophenyl)ethyl]-	130–132		Methiodide, 153–155	705, 837
2-[2,2-Bis(4-dimethylaminophenyl)ethyl]-6-methyl-	152			837
4-(2.2-Diphenylethyl)-	130–131			766a
DIPHENYLPROPYLQUINOLINES				
2-(1,3-Diphenylisopropyl)-[2-dibenzylmethylquinoline, 1,3-diphenyl-2-(2-quinolyl)propane]	74		Methiodide, 204	1946
4-(1,3-Diphenylisopropyl)-	95–96		194–196	224
2,4-Bis(1,3-Diphenylisopropyl)-	104	220–240/0.1	175.5–176.5	224
TRIPHENYLMETHYLQUINOLINES				
2-Trityl-(2-triphenylmethyl)-	191–192			560, 1195
6-Trityl-	182–183			1933, 1935

TABLE 43. Heteroaralkylquinolines

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
(a) QUINOLINE DERIVATIVES				
DIQUINOLYLMETHANES				
Di-(2-quinolyl)methane	107 (red/light brown form) 102–103 (colourless form)		239 Dipicrate, 210	1072, 1075b–e 1077, 1083, 1087, 1925, 1950
Bis(4-phenyl-2-quinolyl)methane	No data			1102
(2-Quinolyl)-4-quinolylmethane	104			1076
Di(4-quinolyl-2-benzothiazolyl-methane	264			207
Di(6-quinolyl)methane	160		195–197	1080
Bis(2-methyl-6-quinolyl)methane	142	*ca.* 310/15	234	1082
Bis(4-methyl-6-quinolyl)methane	No data			1951
Bis(2-phenyl-6-quinolyl)methane	205			1082
Bis(2,4-dimethyl-6-quinolyl)methane	148			1343
Bis(2,4,8-trimethyl-6-quinolyl)methane	142			1343
Di(6-quinolyl)phenyl-methane			199 Chloroplatinate, 230	1088

Derivatives of di(6-quinolyl)phenylmethane:

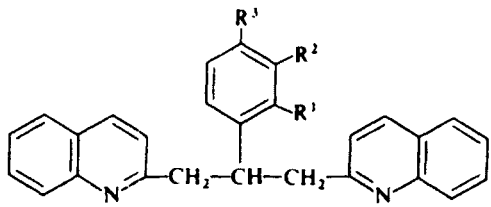


R^1	R^2			
H	H	157–160°		1088
H	$N(CH_3)_2$	168–170		1088
H	OH	263+		1088
H	OCH_3	No data		1088
H	NO_2	108		1088
OH	OH	240+		1088
TRIQUINOLYLMETHANES				
Tri(2-quinolyl-methane		203–204 (exists in colourless and red forms)	239 Dipicrate, *ca.* 212	1072, 1075a, b, 1925

TABLE 43 (*cont.*)

Compound	M.p (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
Benzyltri(2-quinolyl)-methane [2-phenyl-1,1,1-tri-(2-quinolyl)ethane]	202		Perchlorate, *ca.* 236	1107
Tri(6-quinolyl)-methane	202			1117
DIQUINOLYLETHANES				
1,2-Di(2-quinolyl)-ethane	166–167		Dipicrate, 275–280	653, 1070, 1072, 1073, 1078a, 1079, 1090, 1097, 1403, 1404, 1628a, 1953
1,2-Bis(4-methyl-2-quinolyl)ethane	167–168		Dipicrate, 255–259	653
1,2-Di(4-quinolyl)-ethane	182			1070, 1097
1,2-Bis(2-methyl-4-quinolyl)ethane	199–200.5			1726
1,2-Di(6-quinolyl)-ethane	124			1952
TETRAQUINOLYLETHANES				
1,1,2,2-Tetra(2-quinolyl)ethane	267			1076
DIQUINOLYLPROPANES				
2-Phenyl-1,3-di-quinolyl)propane (benzylidene-diquinaldine)	90–92 106.5–107.5 (exists in two crystal forms)		Chloroplatinate, *ca.* 240 Dimethiodide, 179 (183–200)	775, 1109, 1628b

Derivatives of 2-phenyl-1,3-di(2-quinolyl)propane.



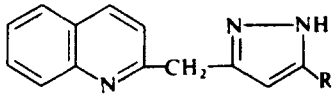
R^1	R^2	R^3			
Cl	H	H	106		1096
OH	H	H		Dihydrochloride, 188	1096
H	NO_2	H	154	Dimethiodide, 202–204	1628b
H	H	$N(CH_3)_2$	138–139	Dihydrochloride, 202 Trihydrochloride, 150	699, 1096

TABLE 43 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
R^1 R^2 R^3				
H H OH	210		Dihydrochloride, 190	1096
H H OCH_3			Dihydrochloride, 122	1096
H H NO_2	165		Dimethiodide, 201–203	1628b
H H CH_3	121		Dimethiodide, 201–203	1628b
2-Phenyl-1-(2-quinolyl)-3-(4-quinolyl)propane	107–108		Dimethiodide, 175–176	1628b
2-Phenyl-1,3-di(4-quinolyl)propane benzylidene-dilepidine)	109–124 (110–127)		Chloroplatinate, 265+ Dimethiodide, 234–235	775, 1628b
2-(3-Nitrophenyl-1,3-di(4-quinolyl)-propane	227–232			767
2-(4-Nitrophenyl-1,3-(4-quinolyl)-propane	237–240			767
TRIQUINOLYLPROPANES				
1,2,3-Tri(2-quinolyl)-propane	136			1073
1,2-Di(2-quinolyl-3-(4-quinolyl) propane	134		Tripicrate, 233–235	1097
1,2,3-Tri(4-quinolyl)-propane	174–175			1097
HIGHER QUINOLYLALKANES				
1,4-Di(2-quinolyl)-butane	98		224	1680
1,6-Di(4-quinolyl)-hexane	97–98			1086
1,6-Bis(2-methyl-4-quinolyl)hexane	146.5–148			647
(b) OTHER MONOHETEROCYCLIC DERIVATIVES[a]				
METHANE DERIVATIVES				
2,6-Dimethyl-3-(2-thienylmethyl)-quinoline	40			1954
2-(2-Pyridylmethyl)-quinoline	66–67			1075c, 1083
4-(2-Pyridylmethyl)-quinoline	63–64			1075c
2-[(6-Methyl-2-pyridyl)methyl]-quinoline	No data			1955

[a] This list may not be exhaustive.

TABLE 43 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
2-[(4-Chloro-6-methyl-2-pyridyl)methyl]-quinoline[b]	—			1232, 1956
2-(9-Acridylmethyl)-quinoline	160–161			1508, 1957
4-(9-Acridylmethyl)-quinoline	240–242			1508, 1957
4-[(2-Ethoxy-6-nitro-acridin-9-yl)methyl]-quinoline	252–254			1508
2-(6-Phenanthridylmethyl)-quinoline	165			1076, 1103
Derivatives of 2-[(pyrazol-3-yl)methyl]quinoline: 				
R				
C_6H_5	168.5–170			594
4-Cl-C_6H_4	175–179			594
3,4-Cl_2-C_6H_3	166–168			594
3,4,5-Cl_3-C_6H_2	165–167			594
2-[(2-Hydroxy-4-phenyl-pyrimidin-6-yl)-methyl]quinoline	265–267			594
3-[(5-Amino-1,3,4-oxadiazol-2-yl)-methyl]-2,4-dimethyl quinoline	284			1958
3-[(5-Amino-1,3,4-oxadiazol-2-yl)-methyl]-2-methyl-4-phenylquinoline	267			1958
3-[(5-Amino-1,3,4-oxadiazol-2-yl)-methyl]-2-methyl-4-(4-methylphenyl)-quinoline	267			1958
ETHANE DERIVATIVES				
2-[2-(2-Thienyl)ethyl]-quinoline		170–173/93		139
6-Methyl-3-[2-(2-thienyl)ethyl]quinoline		210/13.5	175	1954
2-[2-(2-Pyridyl)ethyl]-quinoline	46–47	168–172/1.4	Dihydrochloride, 236–239	108, 139
2-[2-(3-Pyridyl)ethyl]-quinoline	66–67		Dihydrochloride, 244–247	108
2-[2-(4-Pyridyl)ethyl]-quinoline		178–181/3	Dihydrochloride, 215–218	108

[b] This compound was later shown[1232] to be 2-(4-chloro-2,6-dimethylpyrid-3-yl)quinoline (see Table 51).

TABLE 43 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
4-[2-(2-Pyridyl)ethyl]-quinoline	95.5–96		Dihydrochloride, 252–254	799
4-[2-(3-Pyridyl)ethyl]-quinoline	98.5–99.5		Dihydrochloride, 238–241	799
4-[2-(4-Pyridyl)-ethyl]quinoline	137–137.5		Dihydrochloride, 262–268	799
PROPANE DERIVATIVES				
2-[3-(4-Pyridyl)-propyl]quinoline		182–184/1	Dipicrate, 210–211	133
4-[3-(4-Pyridyl)-propyl]quinoline		185–187/1	Dipicrate, 214–215	133
OTHER HETEROCYCLIC DERIVATIVES				
Di-2-(2-benzothiazolyl)-2-quinolylmethane	190			207
Di-2-(2-benzothiazolyl)-4-quinolylmethane	239			207

TABLE 44. Alkenylquinolines

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.), m.p. (°C)	References
2-Vinyl- (2-ethenyl-)		120–123/3 120–125/7 104/3 91–92/0.8 63–65/0.01	n_D^{20} 1.6490 d_{25}^{25} 1.0705	Chloroplatinate, 182	126a, 712, 714, 716, 718, 935, 964, 965, 1044, 1860, 1959
Poly-(2-vinyl)-	No data				1044
4-Vinyl-		120–123/3[a]	n_D^{20} 1.6450 d^{20} 1.0928	188–189 Chloroplatinate, 275+	718, 967, 1960
Dimeric-(4-vinyl)-	148–149	—[a]		242–243 Chloroplatinate, 340+	967
2-*trans*-Prop-1-enyl-		249–253 133–136/13 90/1.8	n_D^{25} 1.6359	182.5–184	201, 720, 925, 926, 1961
2-Allyl-[b] [2-(prop-2-enyl)-]		119–121/4	n_D^{20} 1.5920 d^{20} 1.0385	150–151	126a, 127, 201, 923, 925
2-Isopropenyl- [2-(1-methylethenyl)-]		119–120/3	n_D^{25} 1.6281 d_{25}^{25} 1.0600		712, 1603
6-Isopropenyl-	No data				1515, 1516
2-(But-1-enyl)-		93–94/0.06		149–150	128, 129
2-(But-3-enyl)-		152.5–154/14	n_x^{20} 1.5853 d_4^{20} 1.023	143	124, 212
2-Isobutenyl- [2-(2-methyl-prop-1-enyl)-]		156–158/13 81–83/0.1	n_D^{20} 1.6200	172–173	128, 129, 926, 942
2-(Pent-1-enyl)-		167–168/13		140.5–141.5	65
2-(Pent-3-enyl)-	No data				212

[a] Distils with decomposition.

[b] The product thought to be 2-allylquinoline has subsequently been shown to consist of 2-allyl-1,2-dihydroquinoline.[201] Attempts at purification led to mixtures of 2-allyl- and 2-*cis*- and 2-*trans*-propenylquinolines. 2-Allylquinoline has not been prepared in a pure state.

2-(4-Methylpent-3-enyl)-		112–115/0.2			1649
2-(2-Methylbut-3-enyl)-	No data				212
2-(Oct-1-enyl)-				Hydrochloride, 248–252	711
2-(3-Ethylhept-1-enyl)-				Hydrochloride, 242–244	711
2-(Cyclohexylidenemethyl)-				155–156	128, 129
2-(Buta-1,3-dienyl)-	No data				959a,b
2-(Hepta-1,3,5-trienyl)-	107–114				1962
2-Vinyl-6,7-cyclopenteno-	65				696
4-Methyl-2-vinyl-		129–130/2 98–100/0.3	n_D^{20} 1.635		1044, 1963
6-Methyl-2-vinyl-	—[c]				1044
7-Methyl-2-vinyl-	—[c]				1044
8-Methyl-2-vinyl-		116/1			1044
4-Ethyl-2-vinyl-	No data				1012
4-Benzyl-2-vinyl-	No data				1012
2-Methyl-3-vinyl-	62.5–63			Hydrochloride, 189–189.5	1796
Poly-(6-methyl-2-vinyl)-	No data				1044
Poly-(7-methyl-2-vinyl)-					1044
Poly-(8-methyl-2-vinyl)-					1044
4,6-Dimethyl-2-vinyl-		100/0.2			1044
4,7-Dimethyl-2-vinyl-	—[c]				1044
Poly-(4,6-dimethyl-2-vinyl)-	No data				1044
Poly-(4,7-dimethyl-2-vinyl)-	No data				1044
Poly-(4,8-dimethyl-2-vinyl)-	No data				1044
6,7-Di-*n*-propyl-3-vinyl-	No data				1012
2-Methyl-4-nonyl-6-vinyl-	No data				1012
2-Phenyl-4-(prop-1-enyl)-	54			207	709
4-Allyl-2-methyl-	—[d]				125, 126a

[c] Not isolated in pure state.

[d] In admixture with 1,2-dihydro and 1,4-dihydro derivatives.

TABLE 44 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.), m.p. (°C)	References
4-Allyl-2-(4-chlorophenyl)-6,8-dimethyl-	114–115				1964
4-Isopropenyl-8-dodecyl-	No data				1012
4-Isopropenyl-2-phenyl-		167/0.13		Hydrochloride, 180–182	1964
2-(But-1-enyl)-8-methyl-				Hydrochloride, 198–199 Chloroaurate, 208	755
2-Methyl-3-isobutenyl-		116–118/0.4		200–201	1965
4-Methyl-3-isobutenyl-		115–116/0.3		157–158 Perchlorate, 185–186	958, 1965
2,4-Dimethyl-3-isobutenyl-		99–100/0.15		139–140	1965
4-Methyl-3-(*cis*-pent-1-enyl)-		126–127/0.2			1965
4-Methyl-3-(*trans*-pent-1-enyl)-		129–130/0.2			1965
2,4-Dimethyl-3-(*cis*-pent-1-enyl)-	No data				1965
2,4-Dimethyl-3-(*trans*-pent-1-enyl)-	No data				1965
8-Methyl-2-(4-methylbut-1-enyl)-				164–165	755

TABLE 45. Cycloalkenylquinolines

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
2-(1-Cyclopent-1-enyl)-		*ca.* 180/0.05	Hydrochloride, 160–162	1950
2-(1-Cyclohex-1-enyl)-	No data			939
3-(1-Cyclohex-1-enyl)-	46.5–47.5			1966
4-(1-Cyclohex-1-enyl)-1,2,3,4-tetrahydroacridine	80–82		215–217	158
4-(1-Cyclohex-1-enyl)-9-methyl-1,2,3,4-tetrahydroacridine	94			1876, 1877

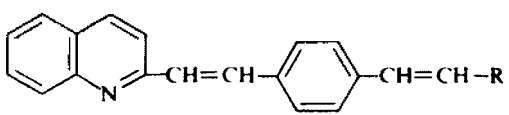
TABLE 46. Aralkenylquinolines

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*	Picrate (and other derivs.), m.p. (°C)	References
2-STYRYLQUINOLINE DERIVATIVES					
2-Styryl-[2-phenylethenyl)quinoline]	99–100			Oxalate, 176–177	100, 128, 129, 698, 707a,b, 723, 742, 745, 753, 761, 763, 764, 814b, 926, 942, 943, 960, 1523, 1547, 1628b, 1967–1970
3-Methyl-2-styryl-	102				702
4-Methyl-2-styryl-	122–123			233–239	543, 693, 698
6-Methyl-2-styryl-	137–138			234	105, 707b, 737
				Chloroplatinate, 279	754
8-Methyl-2-styryl-	72			Chloroplatinate, 229–230	755
4-Benzyl-2-styryl-	99			237	175
4-Phenyl-2-styryl-	114–115				543
2-(2'-Acetamidostyryl)-	181–182				732

TABLE 46 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*	Picrate (and other derivs.), m.p. (°C)	References
2-(3′-Acetamidostyryl)-	152–154			Dipicrate, 225–227	711
2-(2′-Acetoxystyryl)-	92				1096, 1971
2-(4′-Acetoxystyryl)-	133				1096
2-(2′-Aminostyryl)-	158				732
2-(3′-Aminostyryl)-	167–168 (158–159)			Dipicrate, 225–227	711, 726, 1030
2-(4′-Aminostyryl)-	171–173 (154)				722, 761, 1033
2-{4′-[*N*-(3-Aminopropyl)amino]styryl}-	141–142				729
2-[4′-(Bromomethyl)styryl]-				197–198	1972
trans-2-(2′-Chlorostyryl)-	80			236–237	1096, 1971, 1973
2-(3′-Chlorostyryl)-	96				766b
2-(4′-Chlorostyryl)-	143–145			Hydrochloride, 234–236	707a,b, 734, 766b
2-(4′-Cyanostyryl)-	154				1064
2-(4′-Diethylaminostyryl)-	101–103			Methiodide, 224–226	735, 748
2-{4′-[2-(Diethylamino)ethoxy]styryl}-	52–53			Dipicrate, 199–200	699, 1974
2-(4′-Dimethylaminostyryl)-	186–187			167–168	1975
				Oxalate, 108–110	699, 707b, 727, 730,
				Methiodide, 276	739, 740, 744, 761,
					769, 943, 1967, 1974,
					1976
2-{2′-[2-(Dimethylamino)ethoxy]styryl}-				Hydrochloride, 188	1977
2-[3′-(2,5-Dimethyl-1-pyrryl)styryl]-	132–133	200–210/ 0.001			706
2-(2′-Ethoxystyryl)-				Methiodide, 224–226	1974
2-(4′-Fluorostyryl)-				Methiodide, 249	768b
2-(2′-Hydroxystyryl)-	215–217			Methiodide, 236	724, 737, 753, 756,
				Methosulphate, 176–178	1971, 1978–1980
2-(3′-Hydroxystyryl)-				Methiodide, 244	955, 973
2-(4′-Hydroxystyryl)-	264–265			Methiodide, 256	724, 753, 756, 955, 1033, 1096

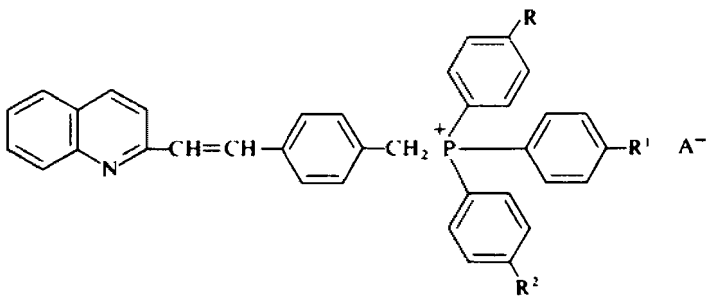
2-(4'-Isopropyl)-	102	212 Chloroplatinate, 229–230	104
2-(4'-Methoxystyryl)-	125–126	Chloroplatinate, 254 Methiodide, 236–237 Oxalate, 205	707a,b, 738, 757, 1967, 1974, 1976
2-(4-Methylstyryl)-	140	Hydrochloride, 218	104, 707b, 1628b
2-{2'-[2-(Methylamino)ethoxy]styryl}-		Hydrochloride, 170	1977
2-(2'-Nitrostyryl)-	102–103	Chloroplatinate, 223	732, 733, 752, 1523
trans-2-(3'-Nitrostyryl)-	157–158	261	40, 698, 707a, 711, 726, 733, 740, 753, 1523, 1628b, 1981
trans-2-(4'-Nitrostyryl)-	173–175		707a, 733, 742, 942, 953, 1523, 1628b, 1982
2-(4'-Phenylstyryl)-	186		1983
{2-[2-(4'-Biphenylyl)ethenyl]quinoline}			
2-{4'-[*N*-(3-phthalimidopropyl)amino]-styryl}-	141–142		729
2-(2'-Trifluoromethylstyryl)-	104–105		706
4-[2-(2-Quinolyl)ethenyl]benzamidine		Hydrochloride, 154	735
2-Methoxyethyl 4-[2-(2-Quinolyl)ethenyl]-benzimidate	72		748
2-{4-[2-(2-Quinolyl)ethenyl]phenyl}-4-quinazolone	255		748
2-(2-{3-[2-(2-Quinolyl)ethenyl]phenyl}ethenyl)-	180		776



R		
4-$(CH_3)_2NC_6H_4$	260–262	1530
4-$CH_3C_6H_4$	263–264	1530
4-$NO_2C_6H_4$	197–199	1972
4-$(C_6H_5)_3P = NC_6H_4$	203–205	1530

TABLE 46 (*Cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*	Picrate (and other derivs.), m.p. (°C)	References
R					
cis-1-Azulenyl	168–170				1530
trans-1-Azulenyl-	200–202				1530
2-Furyl-	104–206				1530
2-Quinolyl-	243				747a,b, 776, 777, 941



A	R	R^1	R^2			
Br	H	H	H	263–265		1972
Br	CH_3	H	H	271–273		1984
Br	CF_3	H	H	269–271		1984
Br	$(CH_3)_2N$	H	H	281–283		1984
ClO_4	$(CH_3)_2N$	$(CH_3)_2N$	H	290–292		1984
Br	CH_3	CH_3	CH_3	282–284		1984
Br	CF_3	CF_3	CF_3	270–271		1984
ClO_4	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	232–234		1984
3,8-Dimethyl-2-styryl-				120		49
4,6-Dimethyl-2-styryl-				106	223	543
2-(2′,3-Dimethoxystyryl)-					Methiodide, 224–225	1974

2-(2',3'-Diethoxystyryl)-	270/15	n_D^{70} 1.5896	1031
2-(2'-Hydroxy-3'-ethoxystyryl)-	90–92		1031
2-(2'-Ethoxy-3'-methoxystyryl)-	60–62		1031
2-(2',4'-Dichlorostyryl)-		Methiodide, 226–227	1974
2-(2',4'-Dinitrostyryl)-	200		702
trans-2-(2'-Chloro-5'nitrostyryl)-	195–197		1973
cis/*trans*-2-(2'-Chloro-5'-nitrostyryl)-	145.5–147		1973
2-(2',6'-Dichlorostyryl)-		Methiodide, 247–248	1974
2-(3',4'-Dichlorostyryl)-		Methiodide, 255–256	1974
2-(3',4'-Dihydroxystyryl)-	249	Methiodide, 266.8	724, 759
2-(3',4'-Dimethoxystyryl)-	112–113	Methiodide, 259–260	725, 1974, 1985
		Hydrochloride, 253–255	
2-(3',4'-Diethoxystyryl)-		Methiodide, 239–240	1974
2-(3',4'-Methylenedioxystyryl)-	156–157	Methiodide, 259–260	740, 750, 760, 1974
2-(4'-Hydroxy-3'-methoxystyryl)-	185	Methosulphate, 213–215	737, 760, 1980
2-(3',5'-Dinitrostyryl)-	270		728
3-Methyl-2-(4'-dimethylaminostyryl)-		Methiodide, 255–255.5	701
3-Methyl-2-(3'-nitrostyryl)-	148–150		835
4-Methyl-2-(4'-dimethylaminostyryl)-	139–141		699
4-Methyl-2-(4'-diethylaminostyryl)-	85–87		699
4-Methyl-2-{4'-[bis-(2-chloroethyl)amino] styryl}-		Hydrochloride, 220–222	700
4-Methyl-2-(2'-nitrostyryl)-	140–141	Hydrochloride, 200	693
4-Methyl-2-(3'-nitrostyryl)-	186		693, 835
6-Methyl-2-(2'-acetamidostyryl)-	188–190		754
6-Methyl-2-(3'-acetamidostyryl)-	167–168		754
6-Methyl-2-(4'-acetamidostyryl)-	247–250		754
6-Methyl-2-(2'-aminostyryl)-	178–179		754

TABLE 46 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*	Picrate (and other derivs.), m.p. (°C)	References
6-Methyl-2-(3'-aminostyryl)-	160.5				722, 754
6-Methyl-2-(4'-aminostyryl)-	190–191 (173)				722, 754
6-Methyl-2-(4'-cyanostyryl)-	215				748
6-Methyl-2-(4'-dimethylaminostyryl)-	201–202				699, 722, 727, 737
6-Methyl-2-(4'-diethylaminostyryl)-	135–136				699
6-Methyl-2-(2'-hydroxystyryl)-	227.5–228.5				737
6-Methyl-2-(4'-hydroxystyryl)-	249			251 Chloroplatinate, 300+	105
6-Methyl-2-(4'-methylstyryl)-	144			Chloroplatinate, 282	105
6-Methyl-2-(2'-nitrostyryl)-	112–112.5				737
6-Methyl-2-(3'-nitrostyryl)-	201			271 Chloroplatinate, 300+	105, 754, 835
6-Methyl-2-(4'-nitrostyryl)-	187–188				722, 754
7-Methyl-2-(3'-nitrostyryl)-	192				835
8-Methyl-2-(4'-cyanostyryl)-	128				748
8-Methyl-2-(2'-nitrostyryl)-	96			Chloroplatinate, 247	755
8-Methyl-2-(3'-nitrostyryl)-	109			Chloroplatinate, 269	755
8-Methyl-2-(4'-nitrostyryl)-	112			Chloroplatinate, 264	755
4-Benzyl-2-(4'-dimethylaminostyryl)-	158			239	175
4-Benzyl-2-(3'-nitrostyryl)-	182			217	175
2-(4'-Acetoxy-3',5'-diiodostyryl)-	187–189				736a,b
2-(4'-Hydroxy-3',5'-diiodostyryl)-	250				736b
3-Methyl-2-(2',4'-dinitrostyryl)-	257				702
4-Methyl-2-(2',4'-dinitrostyryl)-	163.5				703
4-Methyl-2-(4'-hydroxy-3'-methoxystyryl)-	217			Hydrochloride, 256	693
6-Methyl-2-(2',4'-dinitrostyryl)-	213				703

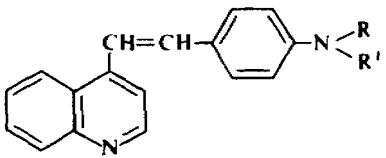
6-Methyl-2-(4′-hydroxy-3′-methoxystyryl)-	211			737
8-Methyl-2-(2′,4′-dinitrostyryl)-	198			702
8-Methyl-2-(3′,4′-methylenedioxystyryl)-	176		239–240	755
4,6-Dimethyl-2-(4′-dimethylaminostyryl)-	162–163			699
4,6-Dimethyl-2-(4′-diethylaminostyryl)-	151–153			699
4,6-Dimethyl-2-(2′-nitrostyryl)-	138			543
4,6-Dimethyl-2-(4′-nitrostyryl)-	179			543
6,8-Dimethyl-2-(4′-cyanostyryl)-	157			748
4,6-Dimethyl-2-(2′,4′-dinitrostyryl)-	195			703
5,6,8-Trimethyl-2-(4′-cyanostyryl)-	135			748
2-Methoxyethyl 4-[2-(5,6,8-trimethyl-2-quinolyl)ethenyl]benzimidate	90			748
2-(1-Methyl-2-phenylethenyl)-[2-(1-methylstyryl)-]	95–97		167–168	128
2-[1-Phenyl-2-(4-methoxyphenyl)ethenyl]-			225	1928
2-(2-Phenylprop-1-enyl)-	102–103	(85–87)		956
[2-(2-methylstyryl)-	103–103.5		215–216	124, 128, 129, 1055, 1986
2-(2,2-Diphenylethenyl)-[2-(2-phenylstyryl)-]				
2-(2-Phenyl-2-(2-aminophenyl)ethenyl)-	164–165			937
2-(2-Phenyl-2-(2-amino-5-chlorophenyl)ethenyl)-	147–148			1055
2-[2-Phenyl-2-(2-methoxyphenyl)ethenyl]-			209–211	1055
2-[2-(2-Aminophenyl)-2-(4-methoxyphenyl)-ethenyl]-	154.5–155.5			937
2-[2-(2-Aminophenyl)-2-(4-methylphenyl)-ethenyl]-	161–162			1055
2-[2,2-Bis(4-dimethylaminophenyl)ethenyl]-	178–179		200	705
2-(2-Benzoyl-2-phenylethenyl)-	191			834, 835, 1765
2-(2-Benzoyl-2-phenylethenyl)-3-methyl-	248			835, 1765
4-STYRYLQUINOLINE DERIVATIVES				
4-Styryl-[4-(2-phenylethenyl)quinoline]	98–99 (88)		Methiodide, 239–241	307, 431, 698, 707b, 742, 773, 774, 943, 960, 1051, 1628b
2-Methyl-4-styryl-	95–96			128, 129
6-Methyl-4-styryl-	115–116			774
8-Methyl-4-styryl-	72–73			774
2-Phenyl-4-styryl-	102.5–103.5		268	709, 766a
4-(4′-Acetamidostyryl)-			Methiodide,	768b
4-(2′-Aminostyryl)-	181–182.5		320	1004

TABLE 46 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*	Picrate (and other derivs.), m.p. (°C)	References
4-(3′-Aminostyryl)-	141				1004, 1941
4-(4′-Aminostyryl)-	152.4–154				768c
4-(4′-Carbamidostyryl)-	262–266				768c
4-(4′-Carbethoxyaminostyryl)-	151.7–152.4				768c
4-(4′-Chlorostyryl)-	128				766a, 774, 1051
					1064
4-(4′-Cyanostyryl)-	169–170				735, 1051
4-(4′-Fluorostyryl)-				Methiodide, 237	768b
4-(4′-Formamidostyryl)-	162.5–164.1				768c
4-(2′-Hydroxystyryl)-	221–222			Methosulphate, 188–190	101, 770, 773, 1941, 1974, 1980
				Methiodide, 272–273	
4-(3′-Hydroxystyryl)-	254–255				1941
4-(4′-Hydroxystyryl)-	253–254			Methiodide, 259–260	101, 717, 955, 1051, 1941
4-(4′-Isopropylstyryl)-	217 (hydrate)			Chloroplatinate, 242	752
4-(2′-Methoxystyryl)-	121				1007
4-(3′-Methoxystyryl)-	95				1007
cis-4-(4′-Methoxystyryl)-	Oil			Methosulphate, 168–169	771
trans-4-(4′-Methoxystyryl)-	89–90			290–292	771, 774, 1007, 1051
				Methosulphate, 172–174	
4-(2′-Nitrostyryl)-	172–173 (162)			Chloroplatinate, 262	752, 767
4-(3′-Nitrostyryl)-	133–134				101, 767, 1941
4-(4′-Nitrostyryl)-	223–224			298–300 (287)	752, 767, 768b, 774, 1051
				Chloroplatinate, 300+	
				Methiodide, 260	

4-[2-(4-Quinolyl)ethenyl]benzamidine			Hydrochloride, 240–241	735
4-(2-{4'-[2-(4-Quinolyl)ethenyl]phenyl}-ethenyl)-		No data		772

Derivatives of 4-(4'-aminostyryl)quinoline:

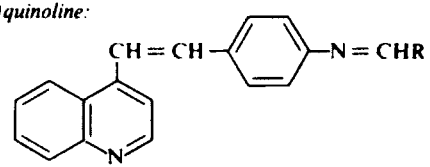


R	R'			
CH_3	H	137–138		1987
n-Butyl	H	128–130		1987
n-Hexyl	H	97–98		1987
n-Heptyl	H	98–99		1987
n-Octyl	H	112–113		1987
C_2H_5	C_2H_5	134–135 (120–122)	Methiodide, 273–275 Dihydrochloride, 220–221	951, 1974, 1999
n-Propyl	*n*-Propyl	76–77		1987
Allyl	Allyl	82–83.5		1987
n-Butyl	*n*-Butyl	81–83		1987
Isobutyl	Isobutyl	94–95		1987
sec-Butyl	*sec*-Butyl	96–96.5	231–232	1987
n-Pentyl	*n*-Pentyl	88–89	186	1987
n-Hexyl	*n*-Hexyl	23–23.5	185–186 Maleate, 133	1987
n-Heptyl	*n*-Heptyl	Oil	181 Maleate, 115	1987
n-Octyl	*n*-Octyl	Oil	159–160	1987
n-Nonyl	*n*-Nonyl	Oil	Maleate, 103	1987
n-Decyl	*n*-Decyl	Oil	Maleate, 106–107	1987
n-Octadecyl	*n*-Octadecyl	52–53		1987
Benzyl	Benzyl	99–100		1987
CH_2CH_2Cl	CH_2CH_2Cl	115–116	241	1987
C_2H_5	CH_3	123.7–124.8		768c

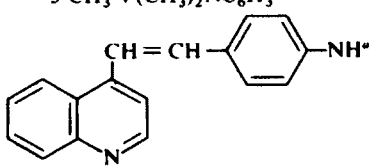
TABLE 46 (*cont.*)

Compound		M.p. (°C)	B.p. (°C/mmHg)	*n*	Picrate (and other derivs.), m.p. (°C)	References
R	R^1					
Benzyl	CH_3	118–118.5				1987
Benzyl	C_2H_5	110.9–111.4			Methiodide, 189–190	768c
CH_3	$CH_2CH_2N(CH_2CH_3)_2$	54–55			225–226	1987
CH_3	CH_2COOH	236–237				1987
C_2H_5	$CH_2CH_2N(CH_2CH_3)_2$	72–73				1987
C_2H_5	$CH_2CH_2CH_2N(CH_3)_2$				239–240	1987
n-Butyl	CH_2CH_2CN	115–116				1987
n-Butyl	CH_2CH_2COOH	181–182				1987
CH_3	NO	120.5–122				1988
C_2H_5	NO	157–158				1988

Schiff base derivatives of 4-(4'-aminostyryl)quinoline:



R			
4-$(CH_3)_2NC_6H_4$	194–195.5		768c
4-$(ClCH_2CH_2)_2NC_6H_4$	160–161		1987
3,4-$(C_2H_5O)_2C_6H_3$	147		1987
3-CH_3-4-$(CH_3)_2NC_6H_3$	114		1987

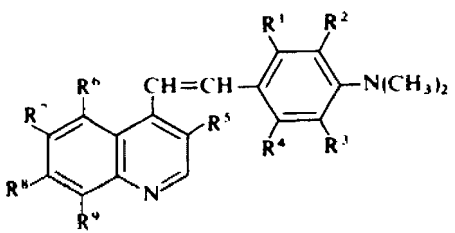


	224–225		768c
2-Furyl-	125		1987
2-Thienyl-	132		1987

[a] Alternative name: *NN'*-bis{4-[2-(4-quinolyl)ethenyl]phenyl}-formamidine

4-(2',4'-Diaminostyryl)-	196.5–197		1004
4-(3'-Amino-4'-methylaminostyryl)-	194–195		717
4-(3',4'-Diethoxystyryl)-	105		1007
4-(3',4'-Dihydroxystyryl)-		Chloroplatinate, 215	759
4-(4'-Hydroxy-3'-methoxystyryl)-	214–215	Methosulphate. 227	773, 1980
4-(3'-Hydroxy-4'-methylaminostyryl)-	51–53		717
4-(2',3'-Dimethoxystyryl)-	116		1007
4-(2',4'-Dimethoxystyryl)-	130		1007
4-(2',5'-Dimethoxystyryl)-	85		1007
4-(3',4'-Dimethoxystyryl)-	157		1007
4-(4'-Methylamino-3'-nitrostyryl)-	194–195		717
4-(3',4'-Methylenedioxystyryl)-	129		1007
3-Methyl-4-(4'-diethylaminostyryl)-	104.6–107.1	270–270.8	768c
4-(4'-Amino-3',5'-dibromostyryl)-	222.5–224		1989
4-(2',4',5'-Trimethoxystyryl)-	133		1007
4-(3',4',5'-Trimethoxystyryl)-	167–168 (134)[b]		1007
3-Methyl-4-(2',6'-dimethyl-4'-dimethylaminostyryl)-	130		952

Derivatives of 4-(4'-dimethylaminostyryl)quinoline:



(i) Quinoline ring-substituted derivatives ($R^1 = R^2 = R^3 = R^4 = H$)

R^5	R^6	R^7	R^8	R^9			
H	H	H	H	H	144–145	Methiodide, 302	706, 744, 769, 943, 1051, 1974, 1990
CH_3	H	H	H	H	166	Methiodide, 284–285	768a,b

[b] This derivative is tabulated twice in ref. 1007 with m.p. 134 and 167–168 °C; presumably one entry is in error.

TABLE 46 (*cont.*)

Compound					M.p. (°C)	B.p. (°C/mmHg)	*n*	Picrate (and other derivs.), m.p. (°C)	References
R^5	R^6	R^7	R^8	R^9					
H	H	CH_3	H	H	157				768a
H	H	H	CH_3	H	153				768a
H	H	H	H	CH_3	154			Methiodide, 272	768a,b
H	H	H	H	C_6H_5				Methiodide, 231–232	768b
CH_3	H	CH_3	H	H	98				768a
CH_3	H	H	H	CH_3	146				768a
H	CH_3	H	CH_3	H	172				768a
H	CH_3	H	H	CH_3	159				768a
H	H	CH_3	CH_3	H	226				768a
H	H	CH_3	H	CH_3	145				768a
H	H	H	CH_3	CH_3	153				768a

(ii) Styryl ring-substituted derivatives ($R^5 = R^6 = R^7 = R^8 = R^9 = H$)

Isomer	R^1	R^2	R^3	R^4					
	H	NH_2	H	H	129–130				717
	H	Br	H	H	117.4–119.1				1989
	Cl	H	H	H	159.4–160.6				1989
	H	Cl	H	H	103.5–104.6				1989
	H	C_2H_5	H	H	124–125				717
	F	H	H	H	126.3–127.5				1989
	H	F	H	H	92.1–93.1				1989
	OH	H	H	H	219–220				717
	H	OH	H	H	139–140				717
	OCH_3	H	H	H	137–140				717
cis-	H	OCH_3	H	H	120				717
trans-	H	OCH_3	H	H	170–171				717
	CH_3	H	H	H	163.5–164.5				952
	H	CH_3	H	H	191–193				952
	H	NO_2	H	H	128–130				717
	F	H	F	H	107.8–108.5				1989
	OCH_3	H	OCH_3	H	114–116				717
cis (?)	CH_3	CH_3	H	H	155–156				717
trans (?)	CH_3	CH_3	H	H	216–217				717
	CH_3	H	H	CH_3	140.6–141.9				952

Other styrylquinoline derivatives			
cis-3-Styryl-	No data		1527a
trans-3-Styryl-	98–99		1527a
3-(4′-Nitrostyryl)-	174		947
2-Methyl-5-styryl-	96–97		617
5-(2-Phenylprop-1-enyl)-	No data		957
6-Styryl-	119		948
2-Methyl-6-styryl-	156–157	205–206	617
6-(4′-Aminostyryl)-	214–215		948, 1004
6-(4′-Nitrostyryl)-	199–200		948
7-(4′-Aminostyryl)-	208–209.5		1004
8-(4′-Aminostyryl)-	156		948, 1004
8-(4′-Nitrostyryl)-	171		948
2,4-Distyryl-	119.5–120	260–263	224, 543
6-Methyl-2,4-distyryl-	127	*ca.* 280	543
2,4-Bis(4′-dimethylaminostyryl)-	168–169		1991
2,4-Bis(4′-nitrostyryl)-	230		543
2,4-Bis(2′,4′-dinitrostyryl)-	270		703
PHENYLBUTADIENYLQUINOLINES			
2-(4-Phenylbuta-1,3-dienyl)- (cinnamylidenequinaldine)	118–119	244 Methiodide, 214.5–215.5	103, 307, 759, 803, 934, 942, 963
2-[4-(2-Acetamidophenyl)buta-1,3-dienyl]-	179		801
2-[4-(2-Aminophenyl)buta-1,3-dienyl]-	135.5		801
2-[4-(3-Aminophenyl)buta-1,3-dienyl]-	147		729
2-[4-(4-Dimethylaminophenyl)buta-1,3-dienyl]-	182–184		800, 982
2-[4-(2-Formamidophenyl)buta-1,3-dienyl]-	185.5		801
2-[4-(2-Hydroxyphenyl)buta-1,3-dienyl]-		Ethiodide, 259	955
2-[4-(2-Methoxycarbonylaminophenyl)buta-1,3-dienyl]-	175.5		801
2-[4-(2-Nitrophenyl)buta-1,3-dienyl]-	149		801
2-[4-(3-Nitrophenyl)buta-1,3-dienyl]-	158–159	Methiodide, 229–230	729
2-[4-(4-Nitrophenyl)buta-1,3-dienyl]-	185.5		801
4-[4-(4-Dimethylaminophenyl)buta-1,3-dienyl]-	165–166	Methiodide, 256 ($+1H_2O$)	802, 982
2-Methyl-5-(4-phenylbuta-1,3-dienyl)-	129–130		617
2-Methyl-6-(4-phenylbuta-1,3-dienyl)-	200–201		617

TABLE 46 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*	Picrate (and other derivs.), m.p. (°C)	References
OTHER ARALKENYLQUINOLINES					
2-[2-(1-Naphthyl)ethenyl]-	101				1983
2-[2-(2-Hydroxy-1-naphthyl)ethenyl]-	219–221			Methosulphate, 215–216 (204)	1978–1980
4-[2-(2-Hydroxy-1-naphthyl)ethenyl]-	218–220			Methosulphate, 188–190 Perchlorate, 262	1978, 1980
2-[2-(9-Anthryl)ethenyl]-	181–182				1983
2-[2-(2-Anthraquinonyl)ethenyl]-	174				933
2-[2-(1-Pyrenyl)ethenyl]-	136				1983
2-(2-Quinolyl)ethenylferrocene	187–188			Methiodide, 180–181	1639
2-(2-Phenylbut-3-enyl)-	No data				212
2-(6-Phenylhexa-1,3,5-trienyl)-	161–162				1992, 1993
3-(6-Phenylhexa-1,3,5-trienyl)-	No data				1994
2-[4-(4-Dimethylaminophenyl)hexa-1,3,5-trienyl]-	No data				982
2-(2,3-Dimethyl-6-phenylhexa-1,3,5-trienyl)-	141–142				963
2-(8-Phenylocta-1,3,5,7-tetraenyl)-	194.8–195.6				1992
2-(12-Phenyldodeca-1,3,5,7,9,11-hexaenyl)-	232.4–232.8				1992
2-(2,3,4,5-Tetraphenyl-2,4-cyclopentadien-1-ylidenemethyl)-	242–243				1943
4-(2,3,4,5-Tetraphenyl-2,4-cyclopentadien-1-ylidenemethyl)-	226.5–227.5				1943
6-(2,3,4,5-Tetraphenyl-2,4-cyclopentadien-1-ylidenemethyl)-	210–210.5				1943
4-[3-(2,3,4,5-Tetraphenyl-2,4-cyclopentadien-1-ylidene)propenyl]-	217–218				961a

TABLE 47. Heteroaralkenylquinolines

Compound	M.p. (°C)	Picrate (and other derivs.), m.p. (°C)	References
QUINOLINE DERIVATIVES			
(α)-*cis*-1,2-di(2-quinolyl)-ethylene	245	Dipicrate, 147–151	1078a
(β)-*trans*-1,2-di(2-quinolyl)-ethylene			
Two compounds have been described:			
Low-melting form	192–194	Dipicrate, 286–288 Methiodide, 212–213	1073, 1078a, b, 1079, 1092, 1093, 1097
High-melting form (?)	326–327		1091, 1995
1-(2-Quinolyl)-2-(4-quinolyl)-ethylene	116		1097
1-(2-Quinolyl)-2-(6-quinolyl)-ethylene	148		1033, 1546
1-(2-Quinolyl)-2-(7-quinolyl)-ethylene	Oil		1030
1,2-Di(4-quinolyl)ethylene ethylene	207		469, 480, 1091, 1097
1-(4-Quinolyl)-2-(6-quinolyl)-ethylene	135	Dimethiodide, 299–301	944b, 1529
1,2-Di(7-quinolyl)ethylene	No data		1529
1-(2-Quinolyl)-2-(2-methyl-5-quinolyl)ethylene[a]		Nitrate, 135–136	1030
1-(2-Quinolyl)2-(2-methyl-6-quinolyl)ethylene			
Two compounds have been described:			
Low-melting form	157.5		1033
High-melting form	300+		1996
1-(2-Quinolyl)-2-(2-methyl-7-quinolyl)ethylene[a]		Nitrate, 135–136	1030
1-(6-Methyl-2-quinolyl)-2-(6-quinolyl)ethylene	177–178	Dimethiodide, 277–278	781
Tetra(2-quinolyl)ethylene	284–285		1076, 1997
1,3-Di(2-quinolyl)propene	220	194–195	1094, 1998
1,4-Di(2-quinolyl)buta-1,3-diene	197–199		1095
1,4-Di(4-quinolyl)buta-1,3-diene	255–257		1095
2,3-Diphenyl-1,4-di(2-quinolyl)-buta-1,3-diene (?)	245–246		1765
OTHER MONOHETEROCYCLIC DERIVATIVES			
2-[2-(2-Furyl)ethenyl]quinoline	60	Methiodide, 226	724, 793
2-[-(2-Thienyl)ethenyl]quinoline	97 (84–86)		128, 129, 777, 2000
4-[2-(2-Thienyl)ethenyl]quinoline	86		784
2-[2-(2-Pyridyl)ethenyl]quinoline	95–96	Dimethiodide, 234–235 Dihydrochloride, 210–212	746, 946, 960

[a] Sample considered as a mixture of 5- and 7-isomers; exact identity not established.

TABLE 47 (*cont.*)

Compound	M.p. (°C)	Picrate (and other derivs.), m.p. (°C)	References
2-[2-(3-Pyridyl)ethenyl]quinoline	96	Dihydrochloride, 270–273	746, 784
2-[2-(4-Pyridyl)ethenyl]quinoline	125–126	Dihydrochloride, 257–261	746, 1097
4-[2-(2-Pyridyl)ethenyl]quinoline	65–66	Dimethiodide, 237 Dihydrochloride, 228–231	799, 946
4-[2-(3-Pyridyl)ethenyl]quinoline	109–110 72–73 ($+\frac{1}{2}H_2O$)	Dihydrochloride, 295–297.5	784, 799
4-[2-(4-Pyridyl)ethenyl]quinoline	115–116	Dihydrochloride, 308–310	799
6-[2-(2-Pyridyl)ethenyl]quinoline		Dimethiodide, 283–284	944b
6-[2-(4-Pyridyl)ethenyl]quinoline	140–141	Dimethiodide, 295	944b
7-[2-(3-Pyridyl)ethenyl]quinoline	No data		1529
2-[2-(2-Benzofuryl)ethenyl]-quinoline	140–141		789
4-[2-(2-Benzofuryl)ethenyl]-quinoline	115–116		789
2-[2-(3-Indolyl)ethenyl]quinoline	212–213		784
4-[2-(3-Indolyl)ethenyl]quinoline	241–243		784
6-[2-(2-Benzothiazolyl)ethenyl]-quinoline	169–170	Methiodide, 273–276	1546
6-[2-(2-Benzoselenazolyl)ethenyl]-quinoline	193–194	Methiodide, 269–270	944a
2-{2-[2-Naphtho(2,1-*b*)furan-2-yl]-ethenyl}quinoline	191–192		789
4-{2-[2-Naphtho(2,1-*b*)furan-2-yl]-ethenyl}quinoline	No data		789
6-{2-[2-Naphtho(1,2-*d*)thiazol-2-yl]ethenyl}quinoline	203		1546
6-[2-(9-Acridyl)ethenyl]quinoline	127–128	Dihydrochloride, 296–298	944b
4-{2-[2,3,6,7-Tetrahydro-(1*H*,5*H*)-benzo(*ij*)quinolizin-9-yl]-ethenyl}quinoline	153–154		1999
2-[2-(5-Methylsulphonyl-2-furyl)-ethenyl]quinoline	130–132		996
2-[2-(5-Nitro-2-furyl)ethenyl]-quinoline	180–182	Hydrochloride, 209–210	778–780, 949, 988, 992, 1525, 2001, 2002
4-[2-(5-Nitro-2-furyl)ethenyl] quinoline	154–155		778, 779, 949, 2002
4-Methyl-2-[2-(5-nitro-2-furyl)-ethenyl]quinoline	179		779
2,4-Bis[2-(5-nitro-2-furyl)-ethenyl[quinoline	242		779
2,5-Bis[2-(2-quinolyl)ethenyl] furan	187		2000
2-[1-Methyl-2-(5-nitro-2-furyl)-ethenyl]quinoline	137–138		782, 1009

TABLE 47 (*cont.*)

Compound	M.p. (°C)	Picrate (and other derivs.), m.p. (°C)	References
2-[2-(5-Nitro-2-thienyl)ethenyl]-quinoline	199–200		783
4-[2-(5-Nitro-2-thienyl)ethenyl]-quinoline	181–182		783
2,5-Bis[2-(2-quinolyl)ethenyl]-thiophen	172		2000
3,4-Dibromo-2,5-bis[2-(2-quinolyl)ethenyl]thiophen	247–248		776
3,4,3',4'-Tetrachloro-5,5'-bis-[2-(2-quinolyl)ethenyl]2,2'-bithienyl	284		776
4-[2-(1-Methyl-5-nitro-2-pyrryl)-ethenyl]quinoline	240–242		798
2-[2-(5-Nitro-5-thiazolyl)-ethenyl]quinoline	208–209		751, 788, 2003
2-[2-(2-Acetamido-5-thiazolyl)-ethenyl]quinoline	273–274		2003
2-[2-(2-Amino-5-thiazolyl)-ethenyl]quinoline	244–246		2003
2-[2-(5-Acetamido-1,3,4-thia-diazol-2-yl)ethenyl]quinoline	No data		787, 2004
2-[2-(5-Amino-1,3,4-thiadiazol-2-yl)ethenyl]quinoline	No data		787, 2004
2-[2-(5-Nitro-1,3,4-thiadiazol-2-yl)ethenyl]quinoline	No data		787, 2004
2-[2-(6-Aminosulphonyl-2-benzo-furyl)ethenyl]quinoline	No data		789
2-[2-(5-*t*-butyl-2-benzofuryl)-ethenyl]quinoline	No data		789
2-[2-(6-Cyano-2-benzofuryl)-ethenyl]quinoline	No data		789
2-[2-(6-Methoxy-2-benzofuryl)-ethenyl]quinoline	135–136		789
4-[2-(1-Methyl-3-indolyl)ethenyl]-quinoline	172–173		784
4-[2-(1,2-Dimethyl-3-indolyl)-ethyl]quinoline	192–193		795
2-{2-[2-(4-Methoxyphenyl)-3-indolyl]ethenyl}quinoline		Hydrochloride, 167	1543
6-[2-(5-Phenyl-2-benzoxazolyl)-ethenyl]quinoline	172	Methiodide, 263–264	1546
6-[2-(5-Methoxy-2-benzothiazolyl)-ethenyl]quinoline	195–196	Methiodide, 269–270	944a
6-[2-(5-Methoxy-2-benzoselenazo-lyl)ethenyl]quinoline	219–220	Methiodide, 275–277	944a
2-[2-(1-Methyl-2-benzimidazolyl)-ethenyl]quinoline	204		2005
1-Methyl-4-[2-(2-quinolyl)-ethenyl]-2-quinolone	185–186		796
1-Methyl-4-[2-(4-quinolyl)-ethenyl]-2-quinolone	224–245		796

TABLE 47 (*cont.*)

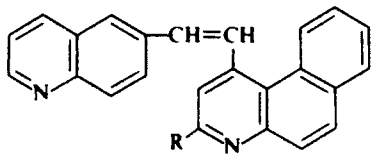
Compound	M.p. (°C)	Picrate (and other derivs.), m.p. (°C)	References
4-[2-(1-Methyl-1,2,3,4-tetrahydro-6-quinolyl)ethenyl]-quinoline	137		784
2-{2-[3-Phenylbenzo(*f*)quinolin-1-yl]ethenyl}quinoline	172–173		2210, 2211
4-{2-[3-Phenylbenzo(*f*)quinolin-1-yl]ethenyl}quinoline	189–190		2210, 2211
Substituted 6-{2-[3-R-benzo(f)quinolin-1-yl]ethenyl}quinolines:			
			
R			
C_6H_5	222		2006
m-$NO_2C_6H_4$	245–246		2006
p-$NO_2C_6H_4$	235–236		2006
2-Quinolyl	230		2006
4-Quinolyl	209–210		2006
6-Quinolyl	215–216		2006
2-[4-(5-Nitro-2-furyl)buta-1,3-dienyl]quinoline	179–180		786, 2007
4-[4-(5-Nitro-2-furyl)buta-1,3-dienyl]quinoline	179–180		797, 2007
2-[3-Methyl-4-(5-nitro-2-furyl)-buta-1,3-dienyl]quinoline	170–171		2007
4-[3-Methyl-4-(5-nitro-2-furyl)-buta-1,3-dienyl]quinoline	191–192		2007

TABLE 48. Alkynyl-, Aralkynyl- and Heteroaralkynylquinolines

Compound	M.p. (°C)	B.p. (°C/mmHg)	n	Picrate (and other derivs.), m.p. (°C)	References
2-Ethynyl-	Oil				1522
3-Ethynyl-	80–80.5				1060
4-Ethynyl-	95				1522
5-Ethynyl-	109–111				1060
6-Ethynyl-	48.5–49.5				1060
7-Ethynyl-	66–67.5				1060
8-Ethynyl-	62.5–63.5				1060
2-(But-3-ynyl)-		116–118/0.4 100–102/0.08	n_D^{25} 1.6042	128	1067, 1071a,c
2-(Pent-4-ynyl)-		136–137/0.2		122.5	1071a,c
2-(Hex-5-ynyl)-		140–142/0.3		109	1071a,c
2-(Hept-6-ynyl)-		148–150/0.4		114.5	1071a,c
2-(Oct-3-ynyl)-[a]		148–153/0.4			1071b
2-(Dec-5-ynyl)-		172–173/0.4		108.5	1071b
2-(Undec-6-ynyl)-		177–179/0.2		93	1071b
2-(Dodec-11-ynyl)-	30	195–197/0.4		78.5	1071a,c
2-(Hexadec-11-ynyl)-		215–217/0.2		69	1071b
2-(1-Butylbut-3-ynyl)-[a]		148–153/0.4			1071b
2-(1-Butylundec-6-ynyl)-		179–181/0.5		76	1071b
2-[1-(Prop-2-ynyl)but-3-ynyl]-	69	136–137/0.2			1071a
2-Phenylethynyl-	63 (101)[b]			Methosulphate, 123 Methoperchlorate, 224	1063, 2008
4-Phenylethynyl-	93–96	205–210/3			1059–1061, 1064
2-(4-Chlorophenylethynyl)-	137–137.5				734, 1064
2-Methyl-6-phenylethynyl-	98–99			182–183	1065
1,2-Di(2-quinolyl)acetylene	179–180			Dipicrate, 286–288	1073, 1078a,b, 1079
2-[4-(2-Quinolyl)buta-1,3-dinynyl]-quinoline	200+				1068

[a] A mixture of 2-(oct-3-ynyl)quinoline (85%) and 2-(1-butylbut-3-ynyl)quinoline (15%) was prepared.

[b] The m.p. of 101 °C is considered to be in error.[1063]

TABLE 49. Arylquinolines

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.), m.p. (°C)	References
MONOPHENYLQUINOLINES					
(i) Unsubstituted					
2-Phenyl-	86	363 310/187 194–198/6 140–142/2		193–194 Chloroplatinate, *ca.* 210	138, 187, 656, 939, 1150, 1166, 1168a, 1189, 1190, 1191, 1226, 1252, 1554, 1673, 1682, 1764, 1782, 1867, 2009–2019
3-Phenyl-	52	205–207/12 165–168/1.5–2 134/0.1		206–207	514, 618, 1171, 1189, 1190, 1195, 1198, 1252, 1672, 1725, 1726, 1966, 2020
4-Phenyl-	61–62	156/0.3		228–230 Chloroplatinate, 244	817, 1158, 1173, 1189, 1190, 1226, 1252, 1307, 1569, 1782, 2021–2026
5-Phenyl-	82–83			210–211	1189, 1190, 1201, 2027
6-Phenyl-	110–111	260/77	d^{20} 1.1945	205	1189, 1190, 1252, 1309, 1318, 2028–2030
7-Phenyl-	59–60	158–161/3		212.3–213	1189, 1190, 1252, 1336, 2028, 2031, 2032
8-Phenyl-[a]	48	185–186/5.5 163/0.3		154 Methiodide, 174	1189, 1190, 1252, 1309, 1314, 1318, 1929, 2033, 2034
2-(Phenyl-d_5)-	83.6–84.2			189	1265, 2035

[a] A number of earlier preparations of 8-phenylquinoline resulted in a product which consisted of a mixture of 8-phenylquinoline and 8-hydroxyquinoline. The physical properties listed are those of the *pure* compound; for further details see ref. 2033.

(ii) Monosubstituted[b]			
2-(2-Acetamidophenyl)-	133		1863
2-(3-Acetamidophenyl)-	135		1863
2-(3-Acetoxyphenyl)-	92		2036
2-(4-Acetoxyphenyl)-	123		1302
2-(4-Acetylphenyl)-	137–138	Phenylhydrazone, 174–175 Semicarbazone, 281–282	2037
2-(4-Acetylsulphanilamidophenyl)-	225–226		2056
2-(2-Aminophenyl)-	161		1863
2-(3-Aminophenyl)-	122		1162, 1863
2-(4-Aminophenyl)-	138	194–195	1138, 1204, 1302, 1374, 2038–2044
2-(3-Benzalaminophenyl)-	68–70		1181
2-(4-Benzalaminophenyl)-	156		1354, 2040
2-(2-Benzamidophenyl)-	124		2045
2-(4-Benzamidophenyl)-	234		2040
2-(4-Benzoylphenyl)-	126	164 Oxime, 185	2046
2-[4-(2-Benzoylethenyl)phenyl]-	163		2037
2-(4-Benzylaminophenyl)-	136		2040
2-(2-Bromophenyl)-	72–73		2047, 2048
2-(3-Bromophenyl)-	74.5–76		1135
2-(4-Bromophenyl)-	123–124 (105)	181–182	1135, 1755, 1867, 2037
2-(2-Chlorophenyl)-	79.5–80		2047, 2048
2-(3-Chlorophenyl)-	64–65	184–185	2049
2-(4-Chlorophenyl)-	112	192–193	1755, 1867
2-(4-Cinnamoylphenyl)-	148		2037
2-(4-Cyclohexylphenyl)-	135		2050
2-(4-Cyclopentylphenyl)-	110		2051
2-(2-Diacetamidophenyl)-	120		1863
2-(3-Diacetamidophenyl)-	130		1181
2-(4-Diacetamidophenyl)-	153.5		2040
2-[4-(Dibutylamino)phenyl]-	63–64	200–201	2052

[b] Compounds substituted on the aryl ring are listed first, followed by compounds substituted on the quinoline ring.

TABLE 49 (*cont.*)

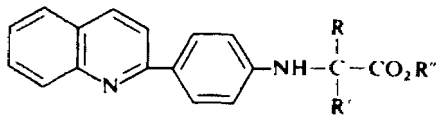
Compound	M.p. (°C)	B.p. (°C/mmHg)	*n, d*	Picrate (and other derivs.), m.p. (°C)	References
2-[2-(Diethylamino)phenyl]-		216–218/3		181	1137
2-[3-(Diethylamino)phenyl]-	103–104			170–171	1137
2-[4-(Diethylamino)phenyl]-	85–87 (99–99.5)			203–205 (210)	1137, 1202, 1204, 2052
2-[4-(2-Diethylaminoethoxy)phenyl]-	Oil			Hydrochloride, 209–210	2053
2-[4-(Dimethylamino)phenyl]-	179–180			219–220	1125, 1183, 1227, 1248, 2038, 2043, 2052, 2054–2056
2-(4-Dipropylarsinophenyl)-		218–219/0.08			1127
2-(4-*n*-Dodecylphenyl)-	36–37				2057
2-(4-Ethoxyphenyl)-	127			218	1755
2-(4-Ethylphenyl)-	50			196–197	1755
2-[4-(Ethylamino)phenyl]-	110				2041
2-(2-Fluorophenyl)-		173/1 127–129/0.02	n_D^{21} 1.6614		2047, 2048, 2058
2-(3-Fluorophenyl)-	132–133				2059
2-(4-Fluorophenyl)-	94 (113–115)			167	2058–2060
2-(4-Formamidophenyl)-	160				2040
2-(4-*n*-Heptylphenyl)-	43–44				2057
2-(4-Hydrazinophenyl)-	125				2037
2-(2-Hydroxyphenyl)-	117–119	300 + 150–170/3		184–185 Methic dide, 180	140, 1133, 1174, 1200, 1261, 2061–2064
2-3(-Hydroxyphenyl)-	158–159			Chloroplatinate, 225 Methiodide, 194–195	1162, 2036, 2064, 2065
2-(4-Hydroxyphenyl)-	237–238			196–197 Methiodide, 209	140, 955, 1200, 1202, 1302, 2036, 2043, 2063, 2064
2-[4-(2-Hydroxybenzal)aminophenyl]-	188–188.5				1138

2-(4-Iodophenyl)-	146			2037
2-(4-Isopropylphenyl)-	60 (50)		195	1174, 1755
2(2-Methoxyphenyl)-		203.5/2	177–178	1134
2-(3-Methoxyphenyl)-	110			1867
2-(4-Methoxyphenyl)-	125–126 (111–112)		201–202 Chloroplatinate, 214	1179, 1764, 1867, 1967, 2066, 2067
2-[4-((4-Methoxybenzal)aminophenyl]-	190			2040
2-(4'-Methoxy-4-phenoxyphenyl)-	165		190	2068
2-(2-Methylphenyl)-	76–76.2	197/4	176	123, 1261
2-(3-Methylphenyl)-	77 (92)			1301, 1867
2-(4-Methylphenyl)-	84–85 (91)	240/15 150–190/2.5	197–198	1178, 1791, 1867, 2069, 2070
2-[4-(Methylamino)phenyl]-	82		186	2041
2-[4-(4-Methylbenzal)aminophenyl]-	171			2040
2-[4-(2-Naphthylamino)phenyl]-	152–153			2056
2-(2-Nitrophenyl)-	121–123	187–190/0.2	176–178	656, 2071
2-(3-Nitrophenyl)-	123–124		182	656, 1162, 2066, 2072–2074
2-(4-Nitrophenyl)-	129–131			656
2-[4-(4-Nitrocinnamylidene)amino-phenyl]-	211–214			1354
2-(4-*n*-Nonylphenyl)-	32–33			2057
2-(4-*n*-Octylphenyl)-	31–32			2057
2-(4-Phenoxyphenyl)-	121			1755
2-[4-(Phenylamino)phenyl]-	138–139			2056
2-{4-[4-(Phenylamino)phenylamino] phenyl}-	155–156			2056
2-[4-(2-Phenylethyl)phenyl]-	122			2075
2-(4-Phenylthiophenyl)-	119			1755
2-(4-Phthalimidophenyl)-	266–268			2037
2-(4-Selenoureidophenyl)-	217			2040
2-(4-Sulphanilamidophenyl)-	255–256			2056
2-(4-Thioureidophenyl)-	206			2040
2-(3-Trifluoromethylphenyl)-	74 (51–52)	142–144/1–2	160	1139, 2076
2-(4-Trimethylsilylphenyl)-	69–70	165–166/0.005		1136
2-(2-Ureidophenyl)-	210			1863
2-(4-Ureidophenyl)-	300 +			2040

TABLE 49 (*cont.*)

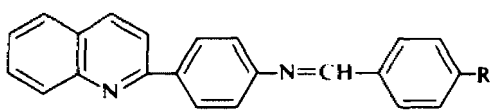
Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.), m.p. (°C)	References
4-(2-Quinolyl)benzamide	234				2042
N-(2-Hydroxyethyl)-4-(2-quinolyl)-benzamide	182				2042
NN-Diethyl-4-(2-quinolyl)benzamide	112				2042
3-(2-Quinolyl)benzoic acid	215–215.5				1135
4-(4-Quinolyl)benzoic acid	252–253			Methyl ester, 154 Ethyl ester, 87 β-Chloroethyl ester, 98 *n*-Propyl ester, 72 Isopropyl ester, 75	1135, 1178, 1287, 2037, 2042
4-(2-Quinolyl)benzoic acid, hydrazide	300+				2042
4-(2-Quinolyl)benzaldehyde	89.5				2037
4-(2-Quinolyl)benzoyl chloride	No data				2037
3-(2-Quinolyl)benzenesulphonic acid	300+				2036
4-(2-Quinolyl)benzenesulphonic acid	No data				2036
4-(2-Quinolyl)benzoylmalonic acid				Diethyl ester, 112–113	2037
4-(2-Quinolyl)phenylmethanediol				Diacetate, 128	2037
2-[3-(2,5-Dimethyl-1-pyrryl)phenyl]-	107–108				1918
2-[4-(2,5-Dimethyl-1-pyrryl)phenyl]-	149–150			176–177	1148
2-[4-(3,5-Diphenyl-2-pyrazolin-1-yl)-phenyl]-	196–197				2037
2-[4-(1,5-Diphenyl-2-pyrazolin-3-yl)-phenyl]-	206–208			212–214	2037
2-[4-(1,3-Diphenyl-2-pyrazolin-5-yl)-phenyl]-	187–188				2037
2-[3-(4-Pyrimidinyl)phenyl]-	129				1142
2-(3-{6-[5-(2-pyridyl)-2-thienyl]-4-pyrimidinyl}-phenyl)-	217–219				1142

Derivatives of N-phenylglycine:



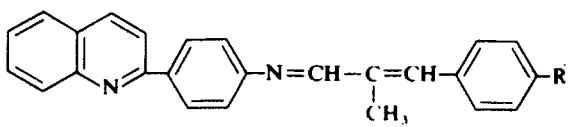
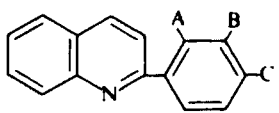
R	R′	R″		
H	H	H	218	2041
H	H	CH_3	152	2041
H	H	C_2H_5	144	2041
CH_3	H	H	215–217	2041
CH_3	H	C_2H_5	86	2041
C_2H_5	H	H	187	2041
CH_3	CH_3	H	192–195	2041
n-C_3H_7	H	H	163–165	2041
n-C_3H_7	H	C_2H_5	108	2041
iso-C_3H_7	H	H	180–182	2041
n-$C_{15}H_{31}$	H	H	127–128	2041
n-$C_{15}H_{31}$	H	C_2H_5	65	2041
C_6H_5	H	H	178–180	2077
C_6H_5	H	C_2H_5	173	2077
4-$CH_3C_6H_4$	H	H	158–162	2077
4-$CH_3C_6H_4$	H	C_2H_5	95	2077
4-$(CH_3)_2CHC_6H_4$	H	H	102–105	2077
$C_6H_5CH_2$	H	H	120	2077
$C_6H_5CH_2CH_2$	H	H	170–190	2077

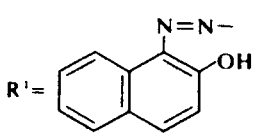
Further derivatives of 2-(4-aminophenyl)quinoline:

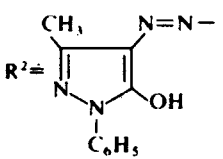


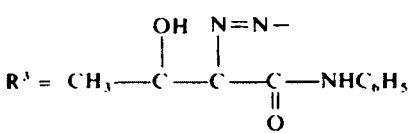
R		
R^1	203–204	1278
R^2	269–270	1278
R^3	226–227	1278

TABLE 49 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.), m.p. (°C)	References
					
R					
R^1	213–214				1278
R^2	259–260				1278
R^3	228–229				1278
Substituted azophenylquinoline derivatives:					
					
A	B	C			
R^1	H	H	183–184		1277b
H	R^1	H	194–195		1277b
H	H	R^1	215–216		1277b
R^2	H	H	184–185		1277b
H	R^2	H	186–187		1277b
H	H	R^2	223–224		1277b







3-(4-Acetamidophenyl)-	188–189		618
3-(4-Aminophenyl)-	175.5–177		618
3-(4-Benzamidophenyl)-	203–204		618
3-(2-*t*-Butylphenyl)-	No data		1199b
3-(3-*t*-Butylphenyl)-	No data		1199b
3-(4-*t*-Butylphenyl)-	No data		1199b
3-(2-Chlorophenyl)-	No data		1199b
3-(3-Chlorophenyl)-	No data		1199b
3-(4-Chlorophenyl)-	133–144		1199b, 2078, 2079
3-(2-Cyanophenyl)-	No data		1199b
3-(3-Cyanophenyl)-	No data		1199b
3-(4-Cyanophenyl)-	No data		1199b
3-(4-Hydroxyphenyl)-	224.5–226		618
3-(2-Methoxyphenyl)-	No data		1199b
3-(3-Methoxyphenyl)-	No data		1199b
3-(4-Methoxyphenyl)-		Hydrochloride, 207	1199b, 2080
3-(2-Methylphenyl)-	No data		1199b
3-(3-Methylphenyl)-	No data		1199b
3-(4-Methylphenyl)-	77–79		1199b, 2020
3-(4-Nitrophenyl)-	178–179	230.5–231.5	618
4-(3-Aminophenyl)-	198		930, 1173
4-(4-Aminophenyl)-	156–157		1173, 2038, 2039, 2081
4-(4-Chlorophenyl)-		233–234	2021
4-[4-(Diethylamino)phenyl]-	182–184	207–209	1202, 1204a
4-[4-(Dimethylamino)phenyl]-	179–179.5		2038
4-(2-Ethoxyphenyl)-	80–81	201–202	930, 2082, 2083
4-(2-Hydroxyphenyl)-	208	Chloroplatinate, 274	930, 931, 2082, 2083

TABLE 49 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n. d*	Picrate (and other derivs.), m.p. (°C)	References
4-(3-Hydroxyphenyl)-	235				930, 931, 1173
4-(4-Hydroxyphenyl)-	243			234–235	931, 1173, 2081
4-(4-Methoxyphenyl)-	82–83			234–235	2021, 2025, 2026
4-(4-Methylphenyl)-				206	1697, 2026
4-(3-Nitrophenyl)-	117–118				930, 1173, 2021
4-(4-Nitrophenyl)-	187				1173, 2081
5-[*x*-(1-Methylethenyl)phenyl]-	No data				957
6-(*x*-Aminophenyl)-	182				1163
4-(6-Quinolyl)benzenesulphonic acid	300+				1309
7-(2-Aminophenyl)-	125–127				1336
7-(4-Aminophenyl)-	122–123				2032
7-(4-Bromophenyl)-	107–109				1389, 2028, 2031
7-(2-Chlorophenyl)-	Oil				2028, 2031
7-(4-Chlorophenyl)-	99–100				2028, 2031
7-(2-Nitrophenyl)-	77–78				1336
7-(4-Nitrophenyl)-	183–184				2032
8-(2-*t*-Butylphenyl)-	No data				1199b
8-(3-*t*-Butylphenyl)-	No data				1199b
8-(4-*t*-Butylphenyl)-	No data				1199b
8-(2-Chlorophenyl)-	No data				1199b
8-(3-Chlorophenyl)-	No data				1199b
8-(4-Chlorophenyl)-	No data				1199b
8-(2-Cyanophenyl)-	No data				1199b
8-(3-Cyanophenyl)-	No data				1199b
8-(4-Cyanophenyl)-	No data				1199b
8-(2-Methoxyphenyl)-	No data				1199b
8-(3-Methoxyphenyl)-	No data				1199b
8-(4-Methoxyphenyl)-	No data				1199b
8-(2-Methylphenyl)-	No data				1199b
8-(3-Methylphenyl)-	No data				1199b

8-(4-Methylphenyl)-	No data			1199b
Methyl *x*-(*x*-quinolyl)benzoate	No data			1206
Dimethyl *x*-(*x*-quinolyl)isophthalate	No data			1206
3-Methyl-2-phenyl-	52–53	300+ 144–145/1.5	208	1178, 1258b, 1760, 1762, 1823, 2011, 2070, 2071, 2084–2086
4-Methyl-2-phenyl-	64–65	373–375 161–164/1.3	212–213.5	1132, 1311, 1457, 1735, 1817, 1884, 2071, 2087, 2088
5-Methyl-2-phenyl-		185–190/6	219–220	450
6-Methyl-2-phenyl-	69	270/12	208	1152, 1166, 1178, 1782, 1791, 2010, 2015, 2086, 2089, 2090
7-Methyl-2-phenyl-	99–100		192 Chloroplatinate, 243–244	1179, 1791, 2010, 2091
8-Methyl-2-phenyl-	49–50	165–170/3	126–128	1166, 1782, 2071, 2091
3-Ethyl-2-phenyl-	63	190/2	168	2086, 2092
4-Ethyl-2-phenyl-	50		189–190	2093
3-Butyl-2-phenyl-			Methiodide, 204	2094
2-Phenyl-4-propenyl-	54		207	709
3-Benzyl-2-phenyl-	96–97			1176
4-Benzyl-2-phenyl-			192	2046
3-(2-Aminobenzyl)-2-phenyl-	177–178			1939
3-(4-Chlorobenzyl)-2-phenyl-			226	2095
2-Phenyl-4-styryl-	102		268	709
2-Methyl-3-phenyl-		207–209/12 164/1.7	170	924, 1760, 1761, 1928, 2070, 2096
4-Methyl-3-phenyl-	No data			1726
6-Methyl-3-phenyl-	63–64	226/17	256–257	1930
8-Methyl-3-phenyl-			Hydrobromide, 237–238	2097, 2098
2-Ethyl-3-phenyl-		200–203/17	177	1928

TABLE 49 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.), m.p. (°C)	References
3-Phenyl-2-*n*-propyl-				191–192	2099, 2100
2-Isopropyl-3-phenyl-				194–195	2100
2-*n*-Butyl-3-phenyl-				186–187	2099, 2100
2-Isobutyl-3-phenyl-				185–186	2099, 2100
2-*sec*-Butyl-3-phenyl-				180–181	2099, 2100
2-*n*-Pentyl-3-phenyl-				150–151	2099, 2100
2-Isopentyl-3-phenyl-				200–201	2099, 2100
2-*n*-Hexyl-3-phenyl-				170–171	2099, 2100
2-Benzyl-3-phenyl-	60	260–265/2		190 Chloroplatinate, 208 Methosulphate, 193–195	168, 1873, 1928, 2101, 2102
3-Phenyl-2-styryl-	103				1928
2-(4′-Methoxystyryl)-3-phenyl-	120				1928
2-(2′-Nitrostyryl)-3-phenyl-	120				1928
2-Methyl-4-phenyl-	100			206–207 Chloroplatinate, 235	197a,b, 429, 447, 543, 721, 819, 1187, 1735, 1761, 1817, 2103–2108
3-Methyl-4-phenyl-	98–99			229–230	1158, 1569
6-Methyl-4-phenyl-		300–340		214	1782, 2109
7-Methyl-4-phenyl-				207	1782
8-Methyl-4-phenyl-				217	1782
2-Ethyl-4-phenyl-		161–162/2		179–180	1879
3-Ethyl-4-phenyl-	95–97				1158
2-Benzyl-4-phenyl-	77–78.5			178–179	1879, 2110
4-Phenyl-2-styryl-	114–115				543
4-Phenyl-2-(4′-dimethylaminostyryl)-	167–168				699
4-Phenyl-2-(4′-diethylaminostyryl)-	135–136				699
2-Methyl-6-phenyl-	94–95			200	617
3-Benzyl-6-phenyl-	134			257–259	1929

3-Benzyl-8-phenyl-	120–122		173–175	1929
(iii) Disubstituted[b,c]				
2-(4-Acetamido-3-methylphenyl)-	176–177			1301
2-(4-Acetamido-3-nitrophenyl)-	185–186			2056
2-(4-Acetoxy-3-methylphenyl)-	106			1301
2-(4-Amino-3-methylphenyl)-	112			1301
2-(4-Amino-3-nitrophenyl)-	196–197			2056
2-(4-Benzyloxy-2-hydroxyphenyl)-	72			1867
2-(2-Bromo-4-Chlorophenyl)-	164			2111
2-(2-Bromo-5-chlorophenyl)-	141			2111
2-(2-Bromo-4-fluorophenyl)-	108			2112
2-(2-Bromo-5-fluorophenyl)-	126			2112
2-(3-Bromo-4-fluorophenyl)-	99			2112
2-(3-Bromo-4-methoxyphenyl)-	114		215	2113
2-(4-Butoxy-3-methylphenyl)-	113			2114
2-(5-*t*-Butyl-2-hydroxyphenyl)-	No data			2061
2-(5-*t*-Butyl-2-methoxyphenyl)-	84	240–245/2	150	2115
2-(3-Chloro-4-ethoxyphenyl)-	106		186	2113
2-(2-Chloro-4-fluorophenyl)-	99			2117
2-(3-Chloro-4-fluorophenyl)-	108			2117
2-(5-Chloro-2-hydroxyphenyl)-	30			1867
2-(3-Chloro-4-methoxyphenyl)-	128		200	2113
2-[3-Chloro-4-(methylthio)phenyl]-	102			2118
2-(3-Chloro-2-nitrophenyl)-	129–130		144–145	2049
2-(5-Chloro-2-nitrophenyl)-	156		166–167	2049
2-(3,4-Diaminophenyl)-	131–132			2056
2-(3,4-Dichlorophenyl)-	112			1755
2-(2,3-Dihydroxyphenyl)-	192–193			2063
2-(2,4-Dihydroxyphenyl)-	197–198			1219, 1867, 2063
2-(3,4-Dihydroxyphenyl)-	209–210			2063
2-(2,4-Dimethoxyphenyl)-	132	240–250/2	200–201	2115
2-(2,5-Dimethoxyphenyl)-	142	240–250/2	150	2115
2-(3,4-Dimethoxyphenyl)-	116–117	240–250/2	187	2115
2-(2,4-Dimethylphenyl)-	71	195/3	189–190	2119

[b] Compounds substituted on the aryl ring are listed first, followed by compounds substituted on the quinoline ring.

[c] Compounds with substituents on both aryl and quinoline rings are listed last.

TABLE 49 (*cont.*)

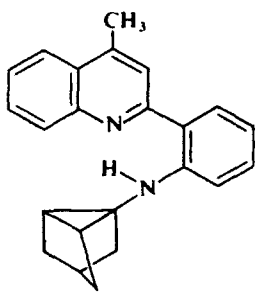
Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.), m.p. (°C)	References
2-(2,5-Dimethylphenyl)-	60			179	1755
2-(3,4-Dimethylphenyl)-	90–91				1755
2-(2-Dimethylamino-5-methylphenyl)-		212–217/0.1		178	1137
2-(2,6-Dinitrophenyl)-	140–142			183–184	2049
2-(4-Ethoxy-3-methylphenyl)-	126				2114
2-(3-Fluoro-4-methoxyphenyl)-	105			190	2120
2-(2-Fluoro-5-methylphenyl)-				198	2121
2-(4-Fluoro-2-methylphenyl)-				190	2121
2-(2-Hydroxy-5-methylphenyl)-	148			211–212	2054, 2122
2-(4-Hydroxy-3-methylphenyl)-	195–196				1301
2-(4-Hydroxy-3-nitrophenyl)-	151				1302
2-(2-Hydroxy-4-octyloxyphenyl)-	No data				2061
2-(4-Isoamyloxy-3-methylphenyl)-	139				2114
2-[3,4-(Methylenedioxy)phenyl]-	96–97			216	541, 1542, 2123–2127
2-(4-Methoxy-2-methylphenyl)-	110				1867
2-(4-Methoxy-3-methylphenyl)-	113				2114
3-[3,4-(Methylenedioxy)phenyl]-	106				2080
4-(4-Acetyl-2-hydroxyphenyl)- *or* 4-(5-Acetyl-2-hydroxyphenyl)-	107–109				2082
4-(2-Ethoxy-4-ethylphenyl)- *or* 4-(2-Ethoxy-5-ethylphenyl)-	No data				2082, 2116
4-(4-Ethyl-2-hydroxyphenyl)- *or* 4-(5-Ethyl-2-hydroxyphenyl)-	184–185				2082, 2116, 2128
4-(2-Methoxy-5-methylphenyl)-				213	1697, 2026
4-(3,4-Dimethylphenyl)-				250–253	2026
3-Ethoxy-4-(4-quinolyl)benzoic acid *or* 4-Ethoxy-3-(4-quinolyl)benzoic acid	253–254				2082
3-Hydroxy-4-(4-quinolyl)benzoic acid *or* 3-Hydroxy-3-(4-quinolyl)benzoic acid	290+				2082
3,4-Dimethyl-2-phenyl-	80				1823
3-Benzyl-7-methyl-2-phenyl-	99				1176
4,6-Dimethyl-2-phenyl-	93–93.5				2087

6-Ethyl-4-methyl-2-phenyl-	74				2129
4-Ethyl-6-methyl-2-phenyl-	109			183	2093
4,6-Diethyl-2-phenyl-				158	2093
4,8-Dimethyl-2-phenyl-	91.5				2129
5,6-Dimethyl-2-phenyl-	110				1786
6,7-Dimethyl-2-phenyl-	147				1786
6,8-Dimethyl-2-phenyl-	38.5	330–350		186–187 Chloroplatinate, 204–205	1179, 1782
4,5-Dimethyl-2-phenyl- *or* 4,7-Dimethyl-2-phenyl-	Oil				2087
4-Ethyl-5-methyl-2-phenyl- *or* 4-Ethyl-7-methyl-2-phenyl-	112			185–188	2093
2,4-Dimethyl-3-phenyl-		164/0.3	n_D^{20} 1.6433		1823
2-Benzyl-4-methyl-3-phenyl-	84.5–85				1823
2,6-Dimethyl-3-phenyl-	85			181	2130
2-Benzyl-6-methyl-3-phenyl-	72–73			189–191	2102
2,3-Dimethyl-4-phenyl-	119–120			183–184	1879, 2110
6,7-Dimethyl-4-phenyl-	113–114				2131
6,8-Dimethyl-4-phenyl-				215	1782
7,8-Dimethyl-4-phenyl-	113.5–114				2131
2-Ethyl-3-methyl-6-phenyl-		380–385		205	2132
3-Ethyl-2-*n*-propyl-6-phenyl-		370–373		184	2132
2-*n*-Butyl-3-*n*-propyl-6-phenyl-		360–365		156	2132
3-*n*-Butyl-2-*n*-pentyl-6-phenyl-	46			150	2132
2,4-Dimethyl-7-phenyl-	87			237	1866, 2133
2-(3-Aminophenyl)-3-methyl-	115				2085
2-(2-Bromophenyl)-3-methyl-	83.5–84.5				2047, 2048
2-(4-Bromophenyl)-3-methyl-	108			195–196	1755
2-(4-*t*-Butylphenyl)-3-methyl-	66	250–260/15			1755
2-(2-Chlorophenyl)-3-methyl-	89–90				2047, 2048
2-(4-Chlorophenyl)-3-methyl-	92				1755
2-(4-Ethoxyphenyl)-3-methyl-	92			177	1755
2-(4-Ethylphenyl)-3-methyl-		220–225/15		191–192	1755
2-[4-(Ethylthio)phenyl]-3-methyl-	70			186	1755
2-(4-Fluorophenyl)-3-methyl-	67			162	2060
2-(4-Hexadecyloxyphenyl)-3-methyl-	50			126–127	2134
2-(2-Hydroxyphenyl)-3-methyl-	119				2135

TABLE 49 (*cont.*)

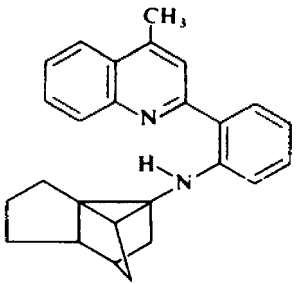
Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.), m.p. (°C)	References
2-(4-Hydroxyphenyl)-3-methyl-	235				2135, 2136
2-(2-Methoxyphenyl)-3-methyl-				188	2135
2-(4-Methoxyphenyl)-3-methyl-	83				2135
2-(4′-Methoxy-4-phenoxyphenyl)-3-methyl-	118			198	2068
2-(4-Methylphenyl)-3-methyl-	59			220	1755
2-[4-(Methylthio)phenyl]-3-methyl-	86			180	1755
2-(3-Nitrophenyl)-3-methyl-	145				2085
2-(4-Phenoxyphenyl)-3-methyl-	91				1755
2-[4-(2-Phenylethyl)phenyl]-3-methyl-	Oil			220–222	2075
2-[4-(Phenylthio)phenyl]-3-methyl-	76			175	1755
2-(4-Isopropylphenyl)-3-methyl-	61			193	1755
2-(4-Tetradecyloxyphenyl)-3-methyl-		300+/20		123–124	2134
2-(3-Trifluoromethylphenyl)-3-methyl-	84			177	2076
2-[4-(2,5-Dimethyl-1-pyrryl)phenyl]-3-methyl-	152				1918
2-(4-Bromophenyl)-3-ethyl-	62			192	1755
2-(4-Chlorophenyl)-3-ethyl-	42			181	1755
2-(4-Ethoxyphenyl)-3-ethyl-	Oil			190	1755
2-(4-Ethylphenyl)-3-ethyl-		228–230/15		182–183	1755
2-[4-(Ethylthio)phenyl]-3-ethyl-	Oil			184	1755
2-(2-Hydroxyphenyl)-3-ethyl-				188	2135
2-(4-Hydroxyphenyl)-3-ethyl-				198	2135
2-(4′-Methoxy-4-phenoxyphenyl)-3-ethyl-	107			189	2068
2-[4-(Methylthio)phenyl]-3-ethyl-	81	220/6		191	2137
2-(4-Phenoxyphenyl)-3-ethyl-	75			188	1755
2-(3-Trifluoromethylphenyl)-3-ethyl-	94			203	2076
2-(3-Trifluoromethylphenyl)-3-*n*-propyl-	38			145	2076
2-(4-Ethylphenyl)-3-benzyl-				217	2095
2-(4-Methoxyphenyl)-3-benzyl-				203	2095

2-(4-Ethylphenyl)-3-(4-chlorobenzyl)-			197	2095
2-(4-Methoxyphenyl)-3-(2-phenylethyl)-			206	2095
2-(2-Acetamidophenyl)-4-methyl-	138			1164, 2138, 2139
2-(4-Acetamidophenyl)-4-methyl-	162–163			2140, 2141
2-(4-Acetoxyphenyl)-4-methyl-	128–129			1304
2-(2-Aminophenyl)-4-methyl-	83–84			1164, 1823, 2138, 2142, 2143
2-(4-Aminophenyl)-4-methyl-	97	133–141/15		1304, 1311, 1457, 2141, 2144–2147
2-(2-Benzalaminophenyl)-4-methyl-	125–130			2148
2-(2-Benzamidophenyl)-4-methyl-	152			2139, 2149
2-(4-Bromophenyl)-4-methyl-	66–68			1823
2-(2-Butyramidophenyl)-4-methyl-	104			1164
2-(2-Isobutyramidophenyl)-4-methyl-	117			2149
2-(4-Chlorophenyl)-4-methyl-	71–72			1823
2-[4-(Ethylamino)phenyl]-4-methyl-	No data			1311
2-(2-Formamidophenyl)-4-methyl-	107			1164, 2138
2-(2-Hydroxyphenyl)-4-methyl-	91–92			1823
2-(4-Hydroxyphenyl)-4-methyl-	244–245			1304, 1311, 1457, 1823
2-(2-Methoxyphenyl)-4-methyl-	83.5–84.5	214–215/1		1823
2-(4-Methoxyphenyl)-4-methyl-	67–68	224–225/1		1823
2-(4-Nitrophenyl)-4-methyl-	128.5–129.5			1304, 1311, 1823
2-(4-Propionamidophenyl)-4-methyl-	137			1164



214.5–216 — 2150

TABLE 49 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.), m.p. (°C)	References
	232.5–234.5				2150
2-(3-Chlorophenyl)-6-methyl-	104–105				1124
2-(4-Chlorophenyl)-6-methyl-	167–167.5 (154–155)			214–215 (185–186)	1124, 1755, 2089
2-(4-Cyclopentylphenyl)-6-methyl-	142				2051
2-[4-(Diethylamino)phenyl]-6-methyl-	142–143			Methiodide, 210–211	2151
2-[4-(Dimethylamino)phenyl]-6-methyl-	185–186			219 (178–179)	1125, 2054, 2152
2-(4-Fluorophenyl)-6-methyl-	117–118				2058, 2089
2-(2-Hydroxyphenyl)-6-methyl-	144–145	200–235/3		216–217	2062
2-(4-Hydroxyphenyl)-6-methyl-	286				1179b
2-(4-Methoxyphenyl)-6-methyl-	136			213 Chloroplatinate, 242–243	1125, 1179, 2067
2-(4-Methylphenyl)-	137–138	150–200/2.5		200–201	2069
2-(3-Nitrophenyl)-6-methyl-	142–142.5			190–190.5	2073, 2074
2-[4-(Dimethylamino)phenyl]-6-isopropyl-	125–126			190–191	2152
2-(4-Chlorophenyl)-7-methyl-	143–144			202–203	1124, 1715

2-[4-(Dimethylamino)phenyl]-7-methyl-	190–191			231–232	1125, 2054, 2152
2-(2-Hydroxyphenyl)-7-methyl-	126–127	160–190/4		197	2062
2-(4-Hydroxyphenyl)-7-methyl-	240–241				1179b
2-(4-Methoxyphenyl)-7-methyl-	141–142			209 Chloroplatinate, 219	1125, 1179, 2067
2-(3-Nitrophenyl)-7-methyl-	158			185–186	2073, 2074
2-(4-Chlorophenyl)-8-methyl-	79–80				1124
2-[2-(Diethylamino)phenyl]-8-methyl-		153–159/0.1		171.5–172	1137
2-[3-(Diethylamino)phenyl]-8-methyl-		168–171/0.1		189	1137
2-[4-(Diethylamino)phenyl]-8-methyl-	110			187	1137
2-[4-(Dimethylamino)phenyl]-8-methyl-	155			195–196	1125, 2152
2-(4-Dipropylarsinophenyl)-8-methyl-	84–85				1127
2-(2-Hydroxyphenyl)-8-methyl-	101–102	160–200/3		194–195	2062
2-(4-Hydroxyphenyl)-8-methyl-	108–109				1179b
2-(4-Methoxyphenyl)-8-methyl-	85.5–87	160–200/3		187 Chloroplatinate, 202–204	1125, 1179, 2067
2-(3-Trifluoromethylphenyl)-8-methyl-		145–147/1–2	n_D^{20} 1.5406 d_4^{20} 1.1475		1139
2-[4-(2,5-Dimethyl-1-pyrryl)phenyl]-8-methyl-	124–125				1148
3-(2-Hydroxyphenyl)-2-ethyl-	200–202				1938
3-(2-Nitrophenyl)-4-methyl-	No data				2153
4-(4-Aminophenyl)-2-methyl-	159–160				2039
4-(2-Hydroxyphenyl)-2-methyl-	187–188				930, 2154
4-(3-Hydroxyphenyl)-2-methyl-	259–260				930, 2154
4-(4-Hydroxyphenyl)-2-methyl-	255				2081, 2154
(iv) Trisubstituted[b,c]					
2-(2,5-Dibromo-4-fluorophenyl)-	118				2112
2-(2,6-Dibromo-3-fluorophenyl)-	140				2112
2-(2,6-Dibromo-4-fluorophenyl)-	133				2112
2-(4-*t*-Butyl-2,6-dimethylphenyl)-	No data				2119

[b] Compounds substituted on the aryl ring are listed first, followed by compounds substituted on the quinoline ring.

[c] Compounds with substituents on both aryl and quinoline rings are listed last.

TABLE 49 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.), m.p. (°C)	References
2-(6-*t*-Butyl-4-methoxy-2-methylphenyl)-	69–70			177–178	2119
2-(5-Chloro-2,4-dihydroxyphenyl)-	213.5–214.5				1219
2-(4-Hydroxy-3-methyl-5-nitrophenyl)-	160				1301
2-(4-Hydroxy-2-methyl-5-isopropylphenyl)-	121				2155
2-(4-Hydroxy-5-methyl-2-isopropylphenyl)-	125				2156
2-(2-Methoxy-4,5-dimethylphenyl)-	164				2157
2-(4-Methoxy-2,6-dimethylphenyl)-	70				2157
2-(2,5-Dimethyl-4-propoxyphenyl)-	107				2157
2-(2,3,4-Trihydroxyphenyl)-	241–242				2063
2-(2,3,4-Trimethoxyphenyl)-	146 (105)	240–250/2		152	2115, 2158
2-(2,4,5-Trimethylphenyl)-		200/3		179–180	2119
2-(2,4,6-Trimethylphenyl)-	69–69.5	200/4		216.5	123, 1258b
2-(3,4,5-Trimethylphenyl)-	106			237	1842
4-(2-Acetoxy-4,5-diethylphenyl)-	118–119				2116
4-(4,5-Diethyl-2-ethoxyphenyl)-	70–71			180–181	2026, 2082, 2116, 2128
4-(4,5-Diethyl-2-hydroxyphenyl)-	210–211			179–180 Chloroplatinate, 235	2026, 2062, 2116, 2128, 2159
4-(4,5-Diethyl-2-methoxyphenyl)-				200 Hydrochloride, *ca.* 198	2026, 2128
4-(2-Methoxy-4,5-dimethylphenyl)-				215	2026
4-Ethoxy-5-(4-quinolyl)phthalic-anhydride	210–211				2082
4-Ethoxy-5-(4-quinolyl)phthalic acid	236				2082

4-(4-Acetyl-5-ethyl-2-hydroxyphenyl)- *or* 4-(5-Acetyl-4-ethyl-2-hydroxyphenyl)-	104–106			2082
5-Ethoxy-2-ethyl-4-(4-quinolyl)-benzoic acid *or* 4-ethoxy-2-ethyl-5-(4-quinolyl)benzoic acid	163–164			2082, 2128
2-Ethyl-5-methoxy-4-(4-quinolyl)-benzoic acid *or* 2-ethyl-4-methoxy-5-(4-quinolyl)benzoic acid		233–234		2128
4,5,8-Trimethyl-2-phenyl-	111.5			2129
4-Ethyl-6,8-dimethyl-2-phenyl-	88		158	2093
2-(3-Bromo-4-hydroxyphenyl)-3-methyl-	218		223–224	2135
2-(3-Chloro-4-hydroxyphenyl)-3-methyl-	206		213	2135
2-(3-Chloro-4-methoxyphenyl)-3-methyl-	116 (106)			2065, 2113
2-(3-Chloro-4-(methylthio)phenyl)-3-methyl-	84			2118
2-(3-Fluoro-4-hydroxyphenyl)-3-methyl-	199			2065
2-(5-Fluoro-2-methoxyphenyl)-3-methyl-	89		185	2160
2-(2-Fluoro-5-methylphenyl)-3-methyl-	80		192	2121
2-(4-Hydroxy-2-methylphenyl)-3-methyl-	203			2122
2-(3-Hydroxy-5-methylphenyl)-3-methyl-	188			2122
2-(4-Methoxy-2-methylphenyl)-3-methyl-	76			2122
2-(4-Methoxy-3-methylphenyl)-3-methyl-	117			2114
2-(3-Chloro-4-methoxyphenyl)-3-ethyl-	80		188	2113
2-(4-Methoxy-3-methylphenyl)-3-ethyl-	88			2114
2-(3-Chloro-4-(methylthio)phenyl)-6-methyl-	116			2118

TABLE 49 (*cont.*)

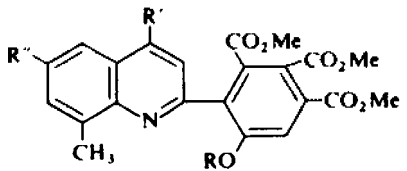
Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.), m.p. (°C)	References
2-(2-Fluoro-5-methylphenyl)-6-methyl-				210	2121
2-(2-Hydroxy-3-methylphenyl)-6-methyl-	169–170			162–163	2054
2-(2-Hydroxy-5-methylphenyl)-6-methyl-	143			210–211	2054
2-(2-Hydroxy-3-methylphenyl)-7-methyl-	102–103			203	2054
2-(2-Hydroxy-5-methylphenyl)-7-methyl-	174–175			231–232	2054
2-(3,4-Methylenedioxyphenyl)-7-methyl-	138			221–222	2127
2-(2-Diethylamino-5-methylphenyl)-8-methyl-		200–202/0.1		176–177	1137
2-[4-(Methylthio)phenyl]-3-ethyl-6-methyl-	98	225/2			2137
2-(4-Dimethylaminophenyl)-4,6-dimethyl-	156–158			Methiodide, 280–281	2151
2-(2-Hydroxyphenyl)-6,8-dimethyl-	124–125	185–200/3		204–205	2062
2-(4-Hydroxyphenyl)-6,8-dimethyl-	151				1179b
2-(4-Methoxyphenyl)-6,8-dimethyl-	94			171–172 Chloroplatinate, 202–204	1179
4-(2-Ethoxy-*x*-sulphophenyl)-2-methyl-	No data				930, 931
4-(3-Methoxy-*x*-sulphophenyl)-2-methyl-	No data				930, 931
4-(4-Methoxy-*x*-sulphophenyl)-2-methyl-	No data				931, 2081
4-(2-Ethoxy-*x*-sulphophenyl)-2-styryl-	No data				930, 931
4-(3-Methoxy-*x*-sulphophenyl)-2-styryl-	No data				930, 931

4-(4-Methoxy-*x*-sulphophenyl)-2-styryl-	No data			931, 2081
(v) Tetrasubstituted[b,c]				
2-(2,3,4,5-Tetramethylphenyl)-		205/3	222–223	2161
4-(3-Amino-4,5-diethyl-2-hydroxyphenyl)- (?)	220			2082
4-(3-Bromo-4,5-diethyl-2-hydroxyphenyl)- (?)	186–188			2116
4-(2-Ethoxy-4,5-diethyl-3-nitrophenyl)- (?)	*ca.* 124			2082
4-(4,5-Diethyl-2-hydroxy-3-nitrophenyl)- (?)	228			2082
4,5,6,8-Tetramethyl-2-phenyl-	128			2129
2-(2-Methoxy-4,5-dimethyl)-3-methyl-	120–121			2157
2-(2,5-dimethyl-4-propoxyphenyl)-3-methyl-	101			2157
2-(2,4,5-Trimethylphenyl)-3-methyl-		230/13	212–213	1755
2-(4-Hydroxy-5-methyl-2-isopropylphenyl)-4-methyl-	81			2156
2-(4-Hydroxy-2-methyl-5-isopropylphenyl)-4-methyl-	121			2155
2-(2-Fluoro-5-methylphenyl)-3,6-dimethyl-			171	2121
2-(2-Acetamido-5-methylphenyl)-4,6-dimethyl-	286			2162
2-(2-Amino-5-methylphenyl)-4,6-dimethyl-	252–253			2162
2-(2-Hydroxy-5-methylphenyl)-6,8-dimethyl-	140–141		209–210	2054

[b] Compounds substituted on the aryl ring are listed first, followed by compounds substituted on the quinoline ring.
[c] Compounds with substituents on both aryl and quinoline rings are listed last.

TABLE 49 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.), m.p. (°C)	References
(vi) Higher substituted[b,c]					
Derivatives of 2-(2,3,4-trismethoxycarbonylphenyl)quinoline:					



R	R'	R''				
H	H	H	173–175			2163
CH_3	H	H	168–171			2163
H	CH_3	CH_3	152–156			2163
cis-$C(CO_2CH_3)$=$CHCO_2CH_3$	CH_3	CH_3	194.5–196.5			2163
$CH(CO_2CH_3)CH_2CO_2CH_3$	CH_3	CH_3	160–162			2163
DIPHENYLQUINOLINES						
(i) Unsubstituted						
2,3-Diphenyl-			95–96	*ca.* 420 *ca.* 310/80	224–225	517a,b, 1169, 1249, 1350a, 1867 2164–2166
2,4-Diphenyl-			114		198 Chloroplatinate, *ca.* 200	721, 1284, 1350a, 2108, 2110, 2165, 2167–2169
2,6-Diphenyl-			204–205		235.5	1252
2,7-Diphenyl-			105		206	2133
3,4-Diphenyl-			140–141		195–196	2110
4,6-Diphenyl-			144–145			2027
(ii) Monosubstituted[b]						
2-(4-Benzylphenyl)-3-phenyl-			75	300/14	188	2170

[b] Compounds substituted on the aryl ring are listed first, followed by compounds substituted on the quinoline ring.
[c] Compounds with substituents on both aryl and quinoline rings are listed last.

2-(4-Chlorophenyl)-3-phenyl-	94–95 (45)			1249, 1867
2-(4-Ethoxyphenyl)-3-phenyl-	100		192	1755
2-(4-Ethylphenyl)-3-phenyl-	60	290–291/18	207	2170
2-(4-Fluorophenyl)-3-phenyl-	86–87		204–205	2060
2-(4-Methoxyphenyl)-3-phenyl-	85			1867
2-(4-Methylphenyl)-3-phenyl-	105		200	1867, 2170
2-(4-Phenoxyphenyl)-3-phenyl-	109		201	1755
2-[4-(Phenylthio)phenyl]-3-phenyl-	62		192	1755
2-(3-Trifluoromethylphenyl)-3-phenyl-	90		186	2076
2-Phenyl-3-(4-chlorophenyl)-	38			1867
2-Phenyl-3-(4-methoxyphenyl)-	118			1867
2-Phenyl-3-(4-methylphenyl)-			208–209	2094
2-(4-Chlorophenyl)-4-phenyl-	104			2168
2-(4-Methylphenyl-4-phenyl-	106			2168
2-(4-Nitrophenyl)-4-phenyl-	160			2168
4-Methyl-2,3-diphenyl-	126.5			1823
3-Methyl-2,4-diphenyl-	145–146		176–177	1879, 2110
2-Methyl-3,4-diphenyl-	174–175		234–235	1879
2-Benzyl-3,4-diphenyl-	136–137		181–182	1879
2-Methyl-4,7-diphenyl-	92		218	2133
(ii) Disubstituted				
2-(3-Bromo-4-methoxyphenyl)-3-phenyl-	114		212	2170
2-(2-Chloro4-methylphenyl)-3-phenyl-	139	270/14	230	2171
2-(3-Fluoro-4-hydroxyphenyl)-3-phenyl-	200			2065
2-(5-Fluoro-2-methoxyphenyl)-3-phenyl-	139			2160
2-(3-Fluoro-4-methoxyphenyl)-3-phenyl)-	104			2065
2-(2-Fluoro-5-methylphenyl)-3-phenyl-	130		216	2121
2-(4-Hydroxy-2-methylphenyl)-3-phenyl-	241			2122
2-(4-Methoxy-2-methylphenyl)-3-phenyl-	106			2122

TABLE 49 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n, d*	Picrate (and other derivs.), m.p. (°C)	References
2-(4-Methoxy-3-methylphenyl)-3-phenyl-	113				2114
2-Phenyl-3-(2,4-dimethylphenyl)-				203–204	2094
2-(4-Methoxyphenyl)-3-(2-methoxyphenyl)-	145–146				1938
2,3-Bis(4-hydroxyphenyl)-	265–266				2065
2,3-Bis(4-methoxyphenyl)-	110 (98–100)				2065, 2122
2,3-Bis(4-methylphenyl)-	126				2173
(iv) Trisubstituted					
2-(2-Methoxy-4,5-dimethylphenyl)-3-phenyl-	122				2157
2-(2-Chloro-4-methylphenyl)-6-methyl-3-phenyl-		310/17			2170
POLYPHENYLQUINOLINES					
2,3,4-Triphenyl-	198–202			Dipicrate, 154–155	1350a, 1879, 2164, 2165, 2174
2,4,7-Triphenyl-	130			220	2133
2-(2-Methylphenyl)-3,4-diphenyl-	No data				2174
5,6,7,8-Tetraphenyl-	228–230				2175
BIPHENYLYLQUINOLINES					
(i) Unsubstituted					
2-(2-Biphenylyl)-	102–103	162–166/0.007			1138
2-(3-Biphenylyl)-	77–78			184–185	1138
2-(4-Biphenylyl)-	178–179				1138, 2176
6-(4-Biphenylyl)-	190–191				2177
(ii) Monosubstituted[b]					
2-(4'-Ethyl-4-biphenylyl)-	179				2178
2-(4'-Hydroxy-4-biphenylyl)-	223				2179

[b] Compounds substituted on the aryl ring are listed first, followed by compounds substituted on the quinoline ring.

2-(6-Hydroxy-3-biphenylyl)-	205		2180
2-(4'-Methoxy-4-biphenylyl)-	219	202	1755, 2179
2-(6-Methoxy-3-biphenylyl)-	100	190	2180
2-(4'-Methyl-4-biphenylyl)-	197		2178
2-(4'-Propyl-4-biphenylyl)-	172		2181
2-(4-Biphenylyl)-3-methyl-	121	230	1755
2-(4-Biphenylyl-3-ethyl-	100	211	1755
2-(4-Biphenylyl)-3-(4-chlorobenzyl)-		204	2095
(iii) Di- and tri-substituted[b,c]			
2-(3'-Bromo-4'-methoxy-4-biphenylyl)-	205		2182
2-(3'-Chloro-2'-methoxy-4-biphenylyl)-	199	188	2183
2-(3'-Chloro-4'-methoxy-4-biphenylyl)-	221		2184
2-(5-Chloro-6-methoxy-3-biphenylyl)-	201	192	2183
2-(2',6-Dimethoxy-3-biphenylyl)-	112		2185
2-(6-Hydroxy-3-biphenylyl)-3-methyl-	196		2180
2-(4'-Methoxy-4-biphenylyl)-3-methyl-	153–154	180	1755, 2179
2-(6-Methoxy-3-biphenylyl)-3-methyl-	100	179	2180
2-(6-Hydroxy-3-biphenylyl)-3-ethyl-	184		2180
2-(4'-Ethyl-4-biphenylyl)-3-phenyl-	125	226	2181
2-(6-Hydroxy-3-biphenylyl)-3-phenyl-	204		2180
2-(6-Methoxy-3-biphenylyl)-3-phenyl-	118		2180
2-(3'-Chloro-4'-methoxy-4-biphenylyl)-3-methyl-	183		2184

[b] Compounds substituted on the aryl ring are listed first, followed by compounds substituted on the quinoline ring.
[c] Compounds with substituents on both aryl and quinoline rings are listed last.

TABLE 49 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n, d*	Picrate (and other derivs.), m.p. (°C)	References
2-(2',6-Dimethoxy-3-biphenylyl)-3-methyl-	136				2185
2-(3'-Chloro-4'-methoxy-4-biphenylyl)-3-ethyl-	136				2184
2-(3'-Chloro-4'-hydroxy-4-biphenylyl)-3-phenyl-	220				2184
2-(3'-Chloro-4'-methoxy-4-biphenylyl)-3-phenyl-	172				2184
POLYPHENYLYLQUINOLINES					
2-(4-Terphenyl-4-yl)-	274–275				1136, 1185
NAPHTHYLQUINOLINES					
(i) Unsubstituted					
2-(1-Naphthyl)-	96	210/0.1		187	1867, 2050
2-(2-Naphthyl)-	164			176–177 (161–162) Methiodide, 188	1077, 1180, 1793, 2050, 2180
4-(2-Naphthyl)-	No data				1697
2-(5,6,7,8-Tetrahydro-2-naphthyl)-	75	286–288/20		191	1180
x-(*x*-Naphthyl)-	No data				1206, 2187
(ii) Monosubstituted[b]					
2-(4-Fluoro-1-naphthyl)-	79			234	2188
2-(1-Hydroxy-2-naphthyl)-	162–163 (150)				2063, 2189
2-(3-Hydroxy-2-naphthyl)-	214–215				1230
2-(2-Methoxy-1-naphthyl)-		250–260/2		187–188	2119
2-(4-Methoxy-1-naphthyl)-	105–106	260–270/2		236–237	2115
2-(1-Methoxy-2-naphthyl)-	110				2189, 2190
2-(3-Methoxy-2-naphthyl)-	87.5–89			229–230	1230
2-(6-Methoxy-2-naphthyl)-	103				2134
2-(2-Methyl-1-naphthyl)-	160			202–203	2119

[b] Compounds substituted on the aryl ring are listed first, followed by compounds substituted on the quinoline ring.

2-(4-Methyl-1-naphthyl)-	76		234–235	2119
2-(6-Methylthio-2-naphthyl)-	182		208	2191
x-(1-Hydroxy-*x*-naphthyl)-	262			141
2-(2-Naphthyl)-3-methyl-	99		203–204	2119
2-(2-Naphthyl)-3-ethyl-			198–199	2119
2-(2-Naphthyl)-3-*n*-propyl-			195–196	2186, 2192
2-(2-Naphthyl)-3-*n*-butyl-			203–204	2186, 2192
2-(2-Naphthyl)-3-isobutyl-			197–198	2186, 2192
2-(2-Naphthyl)-3-*n*-pentyl-			190–191	2186, 2192
2-(2-Naphthyl)-3-*n*-hexyl-			172–173	2186, 2192
2-(2-Naphthyl)-3-*n*-heptyl-			153–154	2186, 2192
2-(2-Naphthyl)-3-*n*-nonyl-			127–128	2186, 2192
2-(2-Naphthyl)-3-*n*-undecyl-			107–108	2186, 2192
2-(5,6,7,8-Tetrahydro-2-naphthyl)-3-methyl-	70			1755
2-(5,6,7,8-Tetrahydro-2-naphthyl)-3-ethyl-		275–280/16	196–197	1755
2-(5,6,7,8-Tetrahydro-2-naphthyl)-3-phenyl-			240–241	2170
(iii) Disubstituted[b,c]				
2-(6,7-Dihydroxy-2-naphthyl)-	281			2193
2-(4,6-Dimethoxy-1-naphthyl)-			218	2194
2-(4,7-Dimethoxy-1-naphthyl)-	121			2195
2-(6,7-Dimethoxy-2-naphthyl)-	164		203	2193
2-(2,7-Dimethyl-1-naphthyl)-			245–247	2196
2-(5-Ethyl-6-methoxy-2-naphthyl)-	148		235	2197
2-(2-Methoxy-6-methyl-1-naphthyl)-		*ca.* 300/10	175	2198
2-(2-Methoxy-6-*n*-propyl-1-naphthyl)-			214	2199
2-(6-Methoxy-2-naphthyl)-3-methyl-	151			2134
2-(4-Methyl-1-naphthyl)-3-methyl-		270–272/13	224	1755
2-(6-Methylthio-2-naphthyl)-3-methyl-	138		198	2191
2-(3-Methylthio-2-naphthyl)-4-methyl-	127.5–128			2212

[b] Compounds substituted on the aryl ring are listed first, followed by compounds substituted on the quinoline ring.
[c] Compounds with substituents on both aryl and quinoline rings are listed last.

TABLE 49 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.), m.p. (°C)	References
3-(1-Nitro-2-naphthyl)-4-methyl-	186–187				2200
2-(6-Methylthio-2-naphthyl)-6-methyl-	183			203	2191
2-(6-Methoxy-2-naphthyl)-3-ethyl-	118			184	2134
2-(4-Chloro-1-naphthyl)-3-phenyl-	152	320–330/25		214	2170
2-(6-Methoxy-2-naphthyl)-3-phenyl-	152				2134
2-(6-Methyl-1-naphthyl)-3-phenyl-	165			235	2170
2-(7-Methyl-1-naphthyl)-3-phenyl-	158	310–315/25		219	2170
2-(3-Methylthio-2-naphthyl)-4-phenyl-	133–134				2212
(iv) Trisubstituted[b,c]					
2-(6,7-Dihydroxy-2-naphthyl)-3-methyl-	220				2193
2-(6,7-Dimethoxy-2-naphthyl)-3-methyl-				155	2193
2-(6,7-Dimethyl-2-naphthyl)-3-phenyl-	158			248–249	2201
2-(3-Methylthio-2-naphthyl)-3,4-dimethyl-	177.5–178.5				2212
2-(6-Methylthio-2-naphthyl)-3,6-dimethyl	143				2191
2-(3-Methylthio-2-naphthyl)-3-methyl-4-phenyl-	154.5–155.5				2212
(v) Dinaphthyl derivatives					
x,*x*-Di-(*x*-naphthyl)-	No data				2187
OTHER ARYLQUINOLINES					
2-[2,3-Dihydro-(1*H*)-inden-5-yl)-	81–82				2057
2-[6,7,8,9-Tetrahydro-(5*H*)-benzocyclohepten-2-yl)-6-methyl-	134			199	2202

[b] Compounds substituted on the aryl ring are listed first, followed by compounds substituted on the quinoline ring.
[c] Compounds with substituents on both aryl and quinoline rings are listed last.

2-(5-Acenaphthenyl)-	122		231–232	2050
2-(5-Acenaphthenyl)-3-methyl-	163		206–210	2119
2-(5-Acenaphthenyl)-3-ethyl-			217–219	2119
2-(5-Acenaphthenyl)-3-phenyl-	160		228	2170
2-(2-Fluorenyl)-	228 (209–210)		215–216	2057, 2119
2-[7-(11-Cyclopentylundecyl)-3-fluorenyl]-	Cryst.			2213
2-(2-Fluorenyl)-3-methyl-	147		215–216	2119
2-(2-Fluorenyl)-3-ethyl-	105–106		190–191	2119
2-(2-Fluorenyl)-3-phenyl-	148		232	2203
2-(2-Anthryl)-	180			2050
2-(9-Anthryl)-	165–167			1246
2-(2-Phenanthryl)-	196		*ca.* 210	2204
2-(3-Phenanthryl)-	138		*ca.* 200	2204
2-(9-Phenanthryl)-	130		229	2205
2-(1,2,3,4-Tetrahydro-9-phenanthryl)-	113			2205
2-(3-Phenanthryl)-3-ethyl-	79–80	280–290/2	178	2119
2-(3-Fluoranthenyl)-	235		245	2206
2-(8-Fluoranthenyl)-	136		242	2207
2-(6-Chrysenyl)-	185		225	2050
2-(1-Pyrenyl)-	145		*ca.* 260	2050
POLYQUINOLYLARENES				
1,4-Di(2-quinolyl)benzene	251		Monopicrate, 261 Dipicrate, 262	784, 2037
1,4-Bis(6-phenyl-2-quinolyl)benzene	368			1185
1,4-Bis(3,4-diphenyl-2-quinolyl)-benzene	No data			1350b
1,2-Bis(2-biphenylenyl-4-phenyl-6-quinolyl)benzene	294–297			2208
1,3,5-Tri(2-quinolyl)benzene	202		277	784
1,3,5-Tris(6-methyl-2-quinolyl)-benzene	253		275	784
4,4'-Di(2-quinolyl)bibenzyl	221			2075
4,4'-Bis(3-methyl-2-quinolyl)-bibenzyl	211–212			2075
4,4'-Di(2-quinolyl)biphenyl	323			1185, 1389, 2176

TABLE 49 (*cont.*)

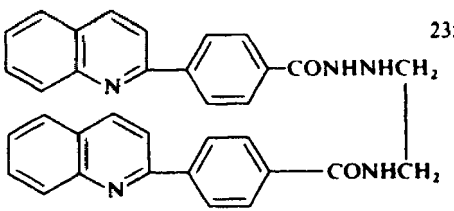
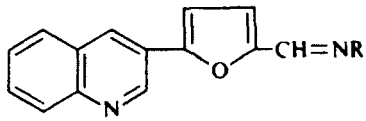
Compound	M.p. (°C)	B.p. (°C/mmHg)	*n*, *d*	Picrate (and other derivs.), m.p. (°C)	References
2,6'-Bis(4-phenyl-2-quinolyl)-biphenylene	333–335				2208
1,5-Di(2-quinolyl)naphthalene	252			Dipicrate, 262	1185
3,6-Di(2-quinolyl)acenaphthene	234			198	1185
2,7-Di(2-quinolyl)fluorene	173			234	1185
4,4'-Bis(2-phenyl-4-quinolyl) diphenyl ether	193–197				1284
NN'-Bis[4-(2-quinolyl)phenyl]urea	233				2042
	235–237				2209
QUINOLYLFERROCENES					
(2-Quinolyl)ferrocene	139–141				1140, 1141
(4-Butyl-2-quinolyl)ferrocene	No data				1333
1,1'-Di(2-quinolyl)ferrocene	209–211				1140, 1141
2,2"-Bis(2-quinolyl)biferrocene	208–211				885
2,5"-Bis(2-quinolyl)biferrocene	247–248				885
2,2"-(4-Butyl-1,4-dihydroquinolyl)-(4-butylquinolyl)biferrocene	110+ (decomp.)				885
2,5"-(4-Butyl-1,4-dihydroquinolyl)-(4-butylquinolyl)biferrocene	187–189				885

TABLE 50. Heteroarylquinolines (5-Membered Rings)

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
ONE HETEROATOM[a,b,c]				
2-[(1*H*)-Pyrrol-2-yl]-	129			1154, 1358
2-[(1*H*)-Pyrrol-2-yl]-4-methyl-	124–125			2214
2-[(1*H*)-Pyrrol-2-yl]-4-phenyl-	111–112			2214
2-[1-Methyl-2,5-diphenyl-(1*H*)-pyrrol-3-yl]-	153–155			2215
2-(2-Furyl)-	92		186	1177, 2216
4-(2-Furyl)-			202–203	2217
2-(5-Nitro-2-furyl)-	196–198			1276, 2218
3-{5-[2-(5-Nitro-2-furyl)-ethenyl]-2-furyl}-	206			1250b, 2219
3-{5-[2-(5-Carbethoxy-2-furyl)ethenyl]-2-furyl}-	158–159			1250b, 2219
3-[5-(2-Benzoxazolyl)-2-furyl]-	217–218			2219
3-(5-Formyl-2-furyl)-	146–148			1250a
Derivatives of 3(5-iminomethyl-2-furyl)quinoline:				
				
R				
$NHCONH_2$	254–255			1250a
$NHCSNH_2$	182–184			1250a
$4\text{-}C_6H_4N(CH_3)_2$	152–153			1250a
$4\text{-}C_6H_4CO_2H$	279			1250a
$4\text{-}C_6H_4CO_2C_2H_5$	124			1250a
$4\text{-}C_6H_4OH$	113–114			1250a
$3,4\text{-}C_6H_3(OH)CO_2H$	209			1250a
$2,5\text{-}C_6H_3(OH)Cl$	215–216			1250a
4-(5-Nitro-2-furyl)-	No data			1276
2-(2-Furyl)-4-methyl-		131/0.05		2212
2-(2-Furyl)-4-phenyl-	103–103.5			2212
2-(5-Nitro-2-furyl)-4-methyl-	167–168			2218
4-(5-Nitro-2-furyl)-2-methyl-	138–139		Hydrochloride, 138–139	462, 1276, 2218
4-(5-Nitro-2-furyl)-3-methyl-	175–196			2218
4-(5-Nitro-2-furyl)-2-ethyl-	127–128			462, 2218
2-(2-Furyl)-3,4-dimethyl-	87.5–88.5			2212
2-(2-Furyl)-3-methyl-4-phenyl-	124.5–125.5			2212
2-(2-Furyl)-4-methyl-3-phenyl-	138–138.5			2212
2-(2-Furyl)-3,4-diphenyl-	220.5–221			2212

[a] Heteroatoms present are generally listed in the order N, O, S. Within each series, compounds are grouped in increasing order of number of substituents present and listed in order of position of substituents.

[b] Compounds substituted on the heteroaryl ring are listed first, followed by compounds substituted on the quinoline ring.

[c] Compounds with substituents on both heteroaryl and quinoline rings are listed last.

TABLE 50 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
4-(5-Nitro-2-furyl-2,6-dimethyl	151			1276, 2218
4-(5-Nitro-2-furyl)-2,7-dimethyl	145–146			2218
4-(5-Nitro-2-furyl)-2,8-dimethyl-	157–158.5			2218
4-(5-Nitro-2-furyl)-6-ethyl-2-methyl-	114–115			2218
4-(5-Nitro-2-furyl)-8-ethyl-2-methyl-	No data			1276
4-(5-Nitro-2-furyl)-2-ethyl-6-methyl-	112.5–113.5			2218
4-(5-Nitro-2-furyl)-2,6-diethyl-	117.5–118.5			1276, 2218
4-(5-Nitro-2-furyl)-2,5,8-trimethyl-	133–134			2218
4-(5-Nitro-2-furyl)-2,6,8-trimethyl-	143–143.5			2218
2-(2-Thienyl)-	132–133		194–195	1128, 1260, 1312a, 2220
3-(2-Thienyl)-	214–215			1199a, 2176, 2221
3-(3-Thienyl)-	No data			1199a
4-(2-Thienyl)-		120–122/0.25	204–206	2023, 2222, 2223
8-(2-Thienyl)-	No data			1199a
8-(3-Thienyl)-	No data			1199a
2-(5-*t*-Butyl-2-thienyl)-	65		202	2224
2-(5-Carboxy-2-thienyl)-	206–207			1128
2-[5-(4-Chlorophenyl)-2-thienyl]-	154		227	2225
2-(5-Ethyl-2-thienyl)-	59		178	2226
2-(5-Formyl-2-thienyl)-	150–152			1260
2-(3-Methyl-2-thienyl)-	51		179	2227
2-(4-Methyl-2-thienyl)-	159		224–225	2228
2-(5-Methyl-2-thienyl)-	122–123			2220
2-[5-(4-Methylphenyl)-2-thienyl]-	168		239	2225
2-(5-Phenyl-2-thienyl)-	144–145.5			1182
2-(5-Nitro-2-thienyl)-	202–203			1312a, b
2-{5-[2-(2-Thienyl)ethyl]-2-thienyl}-	87			1144
2-(3-Trimethylsilyl-2-thienyl)-	85–87			2229
2-(5-Trimethylsilyl-2-thienyl)-	68–69			2229
2-(5-Triphenylsilyl-2-thienyl)-	168–170			1147
2-[5-(2-Benzothiazolyl)-2-thienyl]-	173–174			1260
2-[3-(4-Pyrimidinyl)-2-thienyl]-	No data			2230
2-[5-(4-Pyrimidinyl)-2-thienyl]-	No data			2230

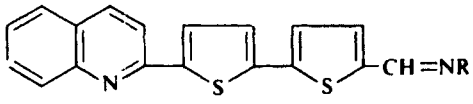
TABLE 50 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
2-[2-(2-Pyridyl)-3-thienyl]-	No data			2230
2-[2-(4-Pyrimidinyl)-3-thienyl]-	No data			2230
2-(2-Thienyl)-3-methyl-	66		165–167 (202)	1992, 2231
2-(2-Thienyl)-4-methyl-	120–121 (83)			1143, 2212
2-(2-Thienyl)-6-methyl-	120		208	1992, 2089
2-(2-Thienyl)-3-ethyl-	63		149–151	1992
2-(2-Thienyl)-3-*n*-propyl-	59		143–145	1992
2-(2-Thienyl)-4-*n*-nonyl-	43			1143
2-(2-Thienyl)-3-phenyl-	84		177–178	1992
2-(2-Thienyl)-4-phenyl-	85–86			2212
2-(2-Thienyl)-3-phenylethyl-	82			2095
3-(2-Thienyl)-2-methyl-		225/14	178	2130, 2232
3-(2-Thienyl)-2-ethyl-	No data			2232
3-(2-Thienyl)-2-*n*-propyl-	No data			2232
3-(2-Thienyl)-2-isopropyl-	No data			2232
3-(2-Thienyl)-2-*n*-butyl-	No data			2232
3-(2-Thienyl)-2-*n*-pentyl-	No data			2232
3-(2-Thienyl)-2-benzyl-	No data			2232
2-(2,5-Dimethyl-2-thienyl)-		220–225/15		2220
2-(2,5-Diethyl-2-thienyl)-			185	2233
2-(3-Methyl-2-thienyl)-3-methyl-	67–68			2228
2-(4-Methyl-2-thienyl)-6-methyl-	115		198–199	2228
2-(5-Ethyl-2-thienyl)-3-methyl-			141	2226
2-(5-Ethyl-2-thienyl)-6-methyl-	83.5		185	2226
2-(5-Ethyl-2-thienyl)-3-ethyl-	48		186	2226
2-(5-*n*-Hexadecyl-2-thienyl)-4-*n*-nonyl-	34			1143
2-[5-(4-Chlorophenyl)-2-thienyl]-3-methyl-	167			2223
2-[5-(4-Chlorophenyl)-2-thienyl]-3-phenyl-	219		ca. 218	2223
2-(2-Thienyl)-3,4-dimethyl-	140.5–141			2212
2-(2-Thienyl)-3,6-dimethyl-	107		207–208	1992
3-(2-Thienyl)-2,6-dimethyl-	101	230/16	186	2130
2-(2-Thienyl)-3-ethyl-6-methyl-	96		210	1992
2-(2-Thienyl)-6-methyl-3-*n*-propyl-	80.5		167–169	1992
2-(2-Thienyl)-3-*n*-butyl-6-methyl-	81		186	2234
2-(2-Thienyl)-6-methyl-3-*n*-pentyl	65		163	2234
2-(2-Thienyl)-3-*n*-hexyl-6-methyl-	34		161	2234
2-(2-Thienyl)-3-*n*-heptyl-6-methyl-	52		192	2234
2-(2-Thienyl)-6-methyl-3-*n*-octyl-	50		162	2234
2-(2-Thienyl)-6-methyl-3-*n*-nonyl-	67		127	2234

TABLE 50 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
2-(2-Thienyl)-3-*n*-decyl-6-methyl-	68			2234
2-(2-Thienyl)-3-methyl-4-phenyl-	101.5–102			2212
2-(2-Thienyl)-4-methyl-3-phenyl-	121.5–122			2212
2-(2-Thienyl)-6-methyl-3-phenyl-	133–135		188–189	1992
2-(2-Thienyl)-3,4-diphenyl-	232.5–233.5			2212
2-(2,5-Dimethyl-3-thienyl)-3-methyl-		230–235/14	182	2235
2-(2,5-Diethyl-3-thienyl)-6-methyl-	60		194	2233
2-(5-Ethyl-2-thienyl)-3,6-dimethyl-	51.5			2226
2-[(2,2′-Bithiophen)-5-yl]-	142–143			1144, 1260, 1312a,b, 2176, 2236
2-[(5′-Cyano-2,2′-bithiophen)-5-yl]-	167			2236
2-[(5′-Ethyl-2,2′-bithiophen)-5-yl]-	69–70			2236
2-[(5′-Formyl-2,2′-bithiophen)-5-yl]-	135–136			1260, 2236
2-[(5′-Methyl-2,2′-bithiophen)-5-yl]-	128–130			2236
2-[(3′-Nitro-2,2′-bithiophen)-5-yl]-	170–171			1312a,b
2-[5′-Nitro-2,2′-bithiophen-5-yl]-	225–226			1312a,b, 2236

Derivatives of 2-[(5′-iminomethyl-2,2′-bithiophen)-5-yl]quinoline:



R			
C_6H_5	143		2237
2-HOC_6H_4	146		2237
4-HOC_6H_4	270		2237
2-$CH_3OC_6H_4$	142		2237
4-$CH_3OC_6H_4$	205		2237
2-$CH_3C_6H_4$	144		2237
4-$CH_3C_6H_4$	215		2237
1-Naphthyl	220.5		2237
2-Naphthyl	220		2237
2-[(2,2′-Bithiophen)-5-yl]-4-methyl-	145–148		2236
2-[(2,2′-Bithiophen)-5-yl]-6-methyl-	173		2236
2-[(2,2′-Bithiophen)-5-yl]-7-methyl-	112–114		2236

TABLE 50 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
2-[(2,2'-Bithiophen)-5-yl]-8-methyl-	115			2236
2-[(5'-Methyl-2,2'-Bithiophen)-5-yl]-6-methyl-	161			2236
ONE HETEROATOM—Benzo derivatives, etc.[a,b,c]				
2-[(1*H*)-Indol-2-yl]-	190–191.5			1400, 2238
2-[(1*H*)-Indol-3-yl]-	194–195 (180)		245 (260–262) Hydrochloride, 194	1072, 1202, 1203a, 1229, 1237, 1239, 2238–2242
2-[1-Methyl-(1*H*)-indol-2-yl]-	174–175			1129, 1202, 2240
2-[3-Methoxy-(1*H*)-indol-2-yl]-	138–139			2238
2-[1-Acetyl-(1*H*)-indol-3-yl]-	194–194.5			2240
2-[2-Chloro-(1*H*)-indol-3-yl]-	196–200			2242
2-[2-Ethoxy-(1*H*)-indol-3-yl]-	178–180			2238
2-[1-Methyl-(1*H*)-indol-3-yl]-	182–183			1202, 2238, 2240–2242
2-[2-Methyl(1*H*)-indol-3-yl]-	No data			2243
2-[2-Phenyl-(1*H*)-indol-3-yl]-	273–274		Hydrochloride, 284–286	1229, 2239–2241
4-[1-Methyl-(1*H*)-indol-3-yl]-	147–148			1202, 2238, 2240–2242
2-[(1*H*)-Indol-3-yl]-4-methyl-			Hydrochloride, 179–180	1229, 2239
2-[(1*H*)-Indol-3-yl]-8-methyl-	218–219		205–207	1202
2-[2,3-Dihydro-1-methyl-(1*H*)-indol-5-yl]-			147–148	2152
2-[2,3-Dihydro-1-ethyl-(1*H*)-indol-5-yl]-	122–123		193–194	1238, 2152
2-[2-Chloro-1-methyl-(1*H*)-indol-3-yl]-	137			2242
2-[2-Ethoxy-1-methyl-(1*H*)-indol-3-yl]-	104–105			2238
2-[1-Methyl-2-phenyl-(1*H*)-indol-3-yl]-	145			1229, 2239
4-[2-Chloro-1-methyl-(1*H*)-indol-3-yl]-	134–136			2242
2-[2-Phenyl-(1*H*)-indol-3-yl]-4-methyl-			Hydrochloride, 190	2239
2-(2-Benzofuryl)-	129		227	2244, 2245
2-(2,3-Dihydro-5-benzofuryl)-	126–127	224–228/17	187	2246, 2247
2-(5-Chloro-2-benzofuryl)-	189		218–219	2245
2-(7-Methoxy-2-benzofuryl)-	148		220	2245

[a] Heteroatoms present are generally listed in the order N, O, S. Within each series, compounds are grouped in increasing order of number of substituents present and listed in order of position of substituents.

[b] Compounds substituted on the heteroaryl ring are listed first, followed by compounds substituted on the quinoline ring.

[c] Compounds with substituents on both heteroaryl and quinoline rings are listed last.

TABLE 50 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
2-(2-Benzofuryl)-3-ethyl-	99			2248
2-(2-Benzofuryl)-3-methyl-	133		227	2248
2-(2-Benzofuryl)-4-methyl-	152.5			2212
2-(2-Benzofuryl)-6-methyl-	151		232	2248
2-(2-Benzofuryl)-4-phenyl-	202.5			2212
2-(2,3-Dihydro-5-benzofuryl)-3-methyl-	113		218	2246, 2247
2-(2,3-Dimethyl-6-benzofuryl)-	129			2249
2-(6-Benzyloxy-3-methyl-2-benzofuryl)-	85			1867
2-(2-Benzofuryl)-3,6-dimethyl-	101		239	2248
2-(2,3-Dihydro-5-methyl-7-benzofuryl)-6-methyl-	144		219	2250
2-[benzo(*b*)thien-2-yl]-	189.8–189.9		221.5–222	1146
2-[4,5,6,7-Tetrahydrobenzo-(*b*)thien-2-yl]-	138		225	2251
2-[Benzo(*b*)thien-3-yl]-	186		201	2207
2-[4,5,6,7-Tetrahydrobenzo-(*b*)thien-2-yl]-3-methyl-	138.5–139		194	2252
2-[4,5,6,7-Tetrahydrobenzo-(*b*)thien-2-yl]-6-methyl-	168		230	2251
2-[Benzo(*b*)thien-3-yl]-3-methyl-	119		171–172	2119
2-[Benzo(*b*)thien-3-yl]-3-ethyl-	98		175–176	2119
2-[2,3-Dimethylbenzo(*b*)thien-5-yl]-6-methyl-	166		226	2252
2-[2,3-Dimethylbenzo(*b*)thien-6-yl]-6-methyl-	140–141		235	1184
2-[2,3,5-Trimethylbenzo(*b*)-thien-6-yl]-6-methyl-	Oil		245	1184
2-[5,6,7,8-Tetrahydro(4*H*)-cyclohepta(*b*)thien-2-yl]-	112		213	2253
2-[(9*H*)-Carbazol-2-yl]-	254–255			2057
2-[(9*H*)-Carbazol-3-yl]-	222–223			2056
2-[9-Acetyl-(9*H*)-carbazol-3-yl]-	162–163			2056
2-[3-Chloro-9-ethyl-(9*H*)-carbazol-3-yl]-	161			2254
2-[9-Ethyl-(9*H*)-carbazol-3-yl]-	116			2255
2-(2-Dibenzofuryl)-	139		220–221	2185, 2256
2-(8-Bromo-2-dibenzofuryl)-	172		235–240	2256
2-(8-Ethyl-2-dibenzofuryl)-	113		*ca.* 210	2213
2-(8-Propyl-2-dibenzofuryl)-	116		196–200	2213
2-(2-Methoxy-3-dibenzofuryl)-	175			2257
2-(2-Dibenzofuryl)-3-ethyl-	141		215	2256
2-(2-Dibenzofuryl)-3-methyl-	110		230	2185, 2256
2-(2-Dibenzofuryl)-3-phenyl-	194		262–264	2256
2-(8-Ethyl-2-dibenzofuryl-2-methyl	Resinous mass			2213
2-(8-Bromo-2-dibenzofuryl-3-phenyl-	196		235	2256
2-[Naphtho(2,1-*b*)furan-2-yl]-	159		210+	2245
2-[1,2-Dihydronaphtho(2,1-*b*)-furan-4-yl]-	186		215	2258

TABLE 50 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
2-(2-Dibenzothienyl)-	144–145			2259
2-(2-Dibenzothienyl)-3-methyl-	149		235–236	2119
2-(6,7,8,9-Tetrahydro-2-dibenzothienyl)-6-methyl-	157.5		212	2369
2-(2-Dibenzothienyl)-3-phenyl-	206		247–249	2256
2-(Dibenzoselenophene-*x*-yl)-3-methyl-	134		233–234	2260
2-(Dibenzoselenophene-*x*-yl)-3-phenyl-			252	2260
TWO HETEROATOMS[a,b,c]				
4-(5-Methylpyrazol-3-yl)-	123–126		211–213	1224
2-[4,5-Dihydro-1,5-diphenyl-(1*H*)-pyrazol-3-yl]-	175			2261
4-[5-Amino-1-*sec*-butyl-(1*H*)-pyrazol-3-yl]-	130–132		Hydrochloride, 182	2262
4-[1-Phenyl-3-methyl-(1*H*)-pyrazol-5-yl]- *or* 4-[1-phenyl-5-methyl-(1*H*)-pyrazol-3-yl]-	120			1234
2-[(1*H*)-Imidazol-2-yl]-	119		201 Chloroplatinate, 330+	1358
2-[(1*H*)-Imidazol-4-yl]- (normacrorine)	156–157		211–212	1122
5-[(1*H*)-Imidazol-2-yl]-	No data			2263
2-[1-Benzyl-(1*H*)-imidazol-2-yl]-	114.5–115.5		200–201	1145
2-[4-Trifluoromethyl-(1*H*)-imidazol-2-yl]-	156.5–158.5			2264–2267
2-[1-Methyl-(1*H*)-imidazol-4-yl]- (macrorine)	160		180 Dipicrate, 202	1121, 1123
2-[1-Methyl-(1*H*)-imidazol-5-yl]- (isomacrorine)	110		Mono-perchlorate, 204–205.5 Diperchlorate, 294–307	1121, 1123, 1157a, b
2-[1-Methyl-(1*H*)-imidazolyl-4-yl-1-d_3]-	160			1123
2-[1-Methyl-(1*H*)-imidazol-5-yl-1-d_3]-	110			1123
4-[4-Trifluoromethyl-(1*H*)-imidazol-2-yl]-	206–207			2266, 2267
5-[4-Nitro-(1*H*)-imidazol-2-yl]-	No data			2263
6-[4-Trifluoromethyl-(1*H*)-imidazol-2-yl]-	254.5–255			2264–2267

[a] Heteroatoms present are generally listed in the order N, O, S. Within each series, compounds are grouped in increasing order of number of substituents present and listed in order of position of substituents.

[b] Compounds substituted on the heteroaryl ring are listed first, followed by compounds substituted on the quinoline ring.

[c] Compounds with substituents on both heteroaryl and quinoline rings are listed last.

TABLE 50 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
7-[4-Trifluoromethyl-(1*H*)-imidazol-2-yl]-	268–270			2266
2-[4,5-Diphenyl-(1*H*)-imidazol-2-yl]-	189–191			1281, 2268
2-[4,5-Bis(4-methylphenyl)-(1*H*)-imidazol-2-yl]-	193–194			2268
3-[4,5-Diphenyl-(1*H*)-imidazol-2-yl]-	273–274			1281, 2268
3-[4,5-Bis(4-methoxyphenyl)-(1*H*)-imidazol-2-yl]-	264–265			2269
3[4,5-Bis(4-methylphenyl)-(1*H*)-imidazol-2-yl]-	275–277			2268
4-[4,5-Diphenyl-(1*H*)-imidazol-2-yl]-	304–305			1281, 2268
4-[4,5-Bis(4-bromophenyl)-(1*H*)-imidazol-2-yl]-	269–271			2269
4-[4,5-Bis(4-methoxyphenyl)-(1*H*)-imidazol-2-yl]-	227–228			2269
4-[4,5-Bis(4-methylphenyl)-(1*H*)-imidazol-2-yl]-	256–257			2268
4-[4-(4-Nitrophenyl)-5-phenyl-(1*H*)-imidazol-2-yl]-	213–214			2269
5-[1-Methyl-5-nitro-(1*H*)-imidazol-2-yl]-	No data			2263
5-[4,5-Diphenyl-(1*H*)-imidazol-2-yl]-	298–299			1281, 2268
5-[4,5-Bis(4-methylphenyl)-(1*H*)-imidazol-2-yl]-	270–272			2268
6-[5-Methyl-4-phenyl-(1*H*)-imidazol-2-yl]-	254–255 98 (hydrate)			2270
6-[4,5-Diphenyl-(1*H*)-imidazol-2-yl]-	235–237			1281, 2268
6-[4,5-Bis(4-bromophenyl)-(1*H*)-imidazol-2-yl]-	283–284			2269
6-[4,5-Bis(4-methoxyphenyl)-(1*H*)-imidazol-2-yl]-	132–133			2269
6-[4,5-Bis(4-methylphenyl)-(1*H*)-imidazol-2-yl]-	248–250			2268
6-[4-(4-Nitrophenyl)-5-phenyl-(1*H*)-imidazol-2-yl]-	218–219			2269
7-[4,5-Diphenyl-(1*H*)-imidazol-2-yl]-	241–242			1281, 2268
7-[4,5-Bis(4-bromophenyl)-(1*H*)-imidazol-2-yl]-	290–292			2269
7-[4,5-Bis(4-methoxyphenyl)-(1*H*)-imidazol-2-yl]-	191–192			2269
7-[4,5-Bis(4-methylphenyl)-(1*H*)-imidazol-2-yl]-	273–274			2268
7-[4-(4-Nitrophenyl)-5-phenyl-(1*H*)-imidazol-2-yl]-	271–272			2269
8-[4,5-Diphenyl-(1*H*)-imidazol-2-yl]-	155–156			1281, 2268

TABLE 50 (*cont.*)

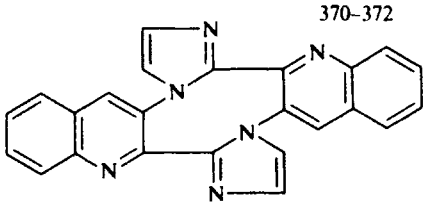
Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
8-[4,5-Bis(4-bromophenyl)-(1*H*)-imidazol-2-yl]-	188–190			2269
8-[4,5-Bis(4-methoxyphenyl)-(1*H*)-imidazol-2-yl]-	183–184			2269
8-[4,5-Bis(4-methylphenyl)-(1*H*)-imidazol-2-yl]-	145–147			2268
8-[4-(4-Nitrophenyl)-5-phenyl-(1*H*)-imidazol-2-yl]-	194–195			2269
2-[1-Hydroxy-4,5-dimethyl-(1*H*)-imidazol-2-yl]-	230–231			2271
	370–372			2272
2-(2-Oxazolyl)-	112–114		204–207	2273
2-(4-Methyl-2-oxazolyl)-	108–110		191–194	2273
2-(5-Phenyl-2-oxazolyl)-	137–138			2274
6-(5-Phenyl-2-oxazolyl)-	147–148			2274
2-(5-Methyl-4-phenyl-2-oxazolyl)-	163–163.5			1223
2-(4,5-Diphenyl-2-oxazolyl)-	140.5–141			1244
6-(5-Methyl-4-phenyl-2-oxazolyl)-	150–151			1223, 2270
4-(5-Phenyl-2-oxazolyl)-2-phenyl-	157–158			2274
8-(2-Thiazolyl)-	69–70			2275
2-(5-Methyl-2-thiazolyl)-	121.5–122.5			2275
2-(2-Amino-4-thiazolyl)-	218.5–219			2276
3-(5-Methyl-2-thiazolyl)-	118–118.5			2275
4-(5-Methyl-2-thiazolyl)-	82.5–83.5			2275
4-(2-Amino-4-thiazolyl)-	268–269			2276
5-(5-Methyl-2-thiazolyl)-	97–98			2275
6-(5-Methyl-2-thiazolyl)-	90.5–91.5			2275
2-(2-Methyl-4-thiazolyl)-4-methyl-	105–106			2214
2-(2-Methyl-4-thiazolyl)-4-phenyl-	158–159			2214
2-(2-Phenyl-4-thiazolyl)-4-methyl-	149–150			2214
2-(2-Phenyl-4-thiazolyl)-4-phenyl-	202–203			2214
2-(2-Amino-4-methyl-5-thiazolyl)-4-methyl-	210–211			2214
2-(2-Amino-4-methyl-5-thiazolyl)-4-phenyl-	211–212			2214
2-(2,4-Dimethyl-5-thiazolyl)-4-methyl-	69–70			2214

TABLE 50 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
2-(2,4-Dimethyl-5-thiazolyl)-4-phenyl-	100–101			2214
2-(4-Methyl-2-phenyl-5-thiazolyl)-4-methyl-	100–101			2214
2-(4-Methyl-2-phenyl-5-thiazolyl)-4-phenyl	150–151			2214
TWO HETEROATOMS—Benzo derivatives, etc.[a,b,c]				
2-[(1*H*)-Benzimidazol-2-yl]-	221–222		276	1207, 1208, 1209a, 1212, 1213a, 1214, 1270, 1548, 2277
3-[(1*H*)-Benzimidazol-2-yl]-			255	1207
4-[(1*H*)-Benzimidazol-2-yl]-	219.5–220		236	1207, 1548
5-[(1*H*)-Benzimidazol-2-yl]-	255 (135–136)		228	1207, 2278
6-[(1*H*)-Benzimidazol-2-yl]-	221		262	1207, 2278, 2279
7-[(1*H*)-Benzimidazol-2-yl]-	273 (135–136)		293	1207, 2278, 2279
8-1(2*H*)-Benzimidazol-2-yl]-	118 (108, 124)		273	1207, 2278, 2280, 2281
2-[5-Acetamido-(1*H*)-benzimidazol-2-yl]-	273			1325
2-[5-Amino(1*H*)-benzimidazol-2-yl]-	254			1325
2-[5-Carboxy-(1*H*)-benzimidazol-2-yl]-	308–309			1325
2-[5-Chloro-(1*H*)-benzimidazol-2-yl]-	192–193			1325
2-[5-(2-Hydroxybenzalamino)-(1*H*)-benzimidazol-2-yl]-	212–213			1325
2-[1-Methyl-(1*H*)-benzimidazol-2-yl]-	123–124			1323
2-[5-Methyl-(1*H*)-benzimidazol-2-yl]-	195			1325
2-[5-Nitro-(1*H*)-benzimidazol-2-yl]-	248			1325
2-[5-Phenyl-(1*H*)-benzimidazol-2-yl]-	110			1325
2-[(1*H*)-Benzimidazol-2-yl]-4-methyl-	227–228			1210
2-[(1*H*)-Benzimidazol-2-yl]-8-methyl-	165			1323
2-[(1*H*)-Benzimidazol-2-yl]-4-phenyl-	220–221			1213a
4-[(1*H*)-Benzimidazol-2-yl]-2-methyl-	239–240			1210

[a] Heteroatoms present are generally listed in the order N, O, S. Within each series, compounds are grouped in increasing order of number of substituents present and listed in order of position of substituents.

[b] Compounds substituted on the heteroaryl ring are listed first, followed by compounds substituted on the quinoline ring.

[c] Compounds with substituents on both heteroaryl and quinoline rings are listed last.

TABLE 50 (*cont.*)

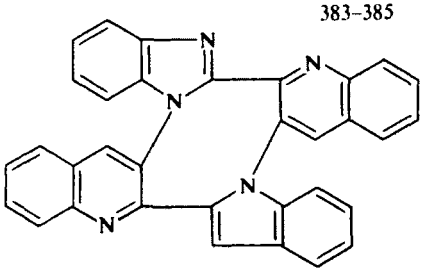
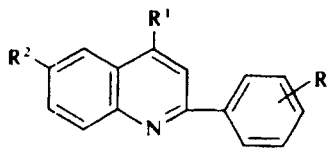
Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
4-[(1*H*)-Benzimidazol-2-yl]-2-phenyl-	212–215			1209b
4-[(1*H*)-Benzimidazol-2-yl]-2-[2-(2-hydroxy-1-naphthylazo)phenyl]-	276–278			1211
4-[(1*H*)-Benzimidazol-2-yl]-2-[3-(2-hydroxy-1-naphthylazo)phenyl]-	301–302			1211
4-[(1*H*)-Benzimidazol-2-yl]-2-[4-(2-hydroxy-1-naphthylazo)phenyl]-	323–324			1211
6-[(1*H*)-Benzimidazol-2-yl]-2-methyl-	254–255			1210
6-[(1*H*)-Benzimidazol-2-yl]-4-methyl-	270–272			1210
2-[1-Methyl-(1*H*)-benzimidazol-2-yl]-8-methyl-	138			1323
3-[(1*H*)-Benzimidazol-2-yl]-2,4-dimethyl-	328–330		250	2282
	383–385			2272
2-(2-Benzoxazolyl)-	179–180			1209a, 1213a,b 1548
3-(2-Benzoxazolyl)-	178–179		203	2283
3-(6-Chloro-2-benzoxazolyl)-	199			2284
2-(2-Benzoxazolyl)-4-methyl-	137–138			1210
2-(2-Benzoxazolyl)-4-phenyl-	189–190			1213a,b
4-(2-Benzoxazolyl)-2-methyl-	144–145			1210
4-(2-Benzoxazolyl)-2-phenyl-	158–160			1209b
6-(2-Benzoxazolyl)-2-methyl-	172–173			1210
6-(2-Benzoxazolyl)-4-methyl-	176–177			1210
2-(2-Benzothiazolyl)-	199–201			831, 1209a, 1213a,c, 1548, 2285
3-(2-Benzothiazolyl)-	198–199		223–224	2283
4-(2-Benzothiazolyl)-	88			2286
2-(6-Butoxy-2-benzothiazolyl)-	158–159.5			831
2-(5-Chloro-2-benzothiazolyl)-	271–272			2287
2-(7-Chloro-2-benzothiazolyl)-	213–215			2287
2-(6-Ethoxy-2-benzothiazolyl)-	172–173			831
2-(6-Isopropoxy-2-benzothiazolyl)-	135.5–136.5			831

TABLE 50 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
2-(6-Methoxy-2-benzothiazolyl)-	194–195.5			831
2-(5-Methyl-2-benzothiazolyl)-	236–237			2287
2-(6-Methyl-2-benzothiazolyl)-	220–221.5			831, 1548
2-(7-Methyl-2-benzothiazolyl)-	171–172			2287
2-(6-Propoxy-2-benzothiazolyl)-	191–192			831
6-(6-Methyl-2-benzothiazolyl)-	147	250/45		2288–2291
2-(2-Benzothiazolyl)-4-methyl	173–174			1210
2-(2-Benzothiazolyl)-4-phenyl-	240–241			1213a,c
4-(2-Benzothiazolyl)-2-(2-aminophenyl)-	160–161			1277b
4-(2-Benzothiazolyl)-2-(3-aminophenyl)-	138–140			1277b
4-(2-Benzothiazolyl)-2-(4-aminophenyl)-	181–182			1277b
4-(2-Benzothiazolyl)-2-methyl-	90–91			1210
4-(2-Benzothiazolyl)-2-phenyl-	110			1209b
6-(2-Benzothiazolyl)-2-(2-aminophenyl)-	283–284			1277b
6-(2-Benzothiazolyl)-1-(3-aminophenyl)-	256–257			1277b
6-(2-Benzothiazolyl)-2-(4-aminophenyl)-	276–277			1277b
6-(2-Benzothiazolyl)-2-methyl-	165–166			1210
6-(2-Benzothiazolyl)-4-methyl-	173–174			1210
6-(2-Benzothiazolyl)-2-(2-nitrophenyl)-	231–232			2292
6-(2-Benzothiazolyl-2-(3-nitrophenyl)-	294–295			2292
6-(2-Benzothiazolyl)-2-(4-nitrophenyl)-	335–336			2292

Derivatives of 4- and 6-(2-benzothiazolyl)-2-phenylquinoline:

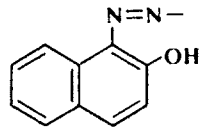


R	R¹	R²	M.p. (°C)	
2'-X	H	2-BT	282–283	1277b
3'-X	H	2-BT	264–265	1277b
4'-X	H	2-BT	284–285	1277b
2'-X	2-BT	H	275–276	1277b

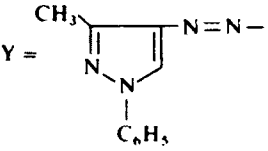
TABLE 50 (*cont.*)

Compound			M.p. (°C)	Picrate (and other derivs.) m.p. (°C)	References
R	R^1	R^2			
3'-X	2-BT	H	227–228		1277b
4'-X	2-BT	H	254–255		1277b
2'-Y	H	2-BT	278–279		1277b
3'-Y	H	2-BT	251–253		1277b
4'-Y	H	2-BT	282–284		1277b
2'-Y	2-BT	H	225–226		1277b
3'-Y	2-BT	H	218–219		1277b
4'-Y	2-BT	H	261–262		1277b

X =



Y =



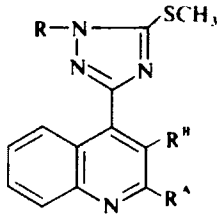
2-BT = 2-benzothiazolyl

Compound	M.p. (°C)	B.p. (°C/mm Hg)	Picrate (and other derivs.) m.p. (°C)	References
6-(6-Methyl-2-benzothiazolyl)-6-methyl-			Hydrochloride, no data	2293
6-(4,6-Dimethyl-2-benzothiazolyl)-2,8-dimethyl-	No data			2293
2-[(1*H*)-Perimidin-2-yl]-	290–300			1209a
2[(1*H*)-Naphth(1,2-*d*)imidazol-2-yl]-	203–205			1209a
4-[(1*H*)-Naphth(1,2-*d*)imidazol-2-yl]-2-phenyl-	196			1209b
2-[Naphtho(2,1-*d*)thiazol-2-yl]-	220			1241
6-[1-Phenyl-(1*H*)-pyrazolo(3,4-*b*)pyridin-3-yl]-	147.5–148	282–6/3	Dipicrate, 252–253	2294
2-[(1*H*)-Imidazo(4,5-*b*)pyridin-2-yl]-	276–277			2295, 2296
2-[(1*H*)-Imidazo(4,5-*c*)pyridin-2-yl]-	227–230			1209a
2-[1-Methyl-(1*H*)-imidazo(4,5-*c*)-pyridin-2-yl]-	178–179			2295, 2296
2-[1-Isopropyl-(1*H*)-imidazo-(4,5-*c*)pyridin-2-yl]-	119–120			2295
4-[(1*H*)-Imidazo(4,5-*c*)pyridin-2-yl]-2-phenyl-	290–294			1209b

TABLE 50 (*cont.*)

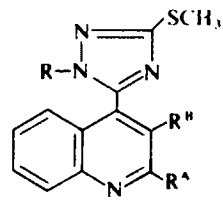
Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
THREE HETEROATOMS[a,b,c,d]				
2-[1,5-Diphenyl-(1*H*)-1,2,3-triazol-4-yl]-	156			2297
6-[5-(4-Pyridyl)-(1*H*)-1,2,4-triazol-3-yl]-	316–317			2266, 2298–2300
8-[5-Benzyl-(1*H*)-1,2,4-triazol-3-yl]-	122–123		153–154	2301

Derivatives of 4-[5-methylthio-(1H)-1,2,4-triazol-3-yl]quinoline:



R	R^A	R^B	M.p. (°C)	
H	CH_3	H	214–215	2302
H	C_2H_5	H	203–204	2302
H	CH_3	CH_3	207–208	2302
H	$(CH_2)_3$		225	2302
H	$(CH_2)_4$		213–214	2302
H	CH_3	C_6H_5	199–200	2302
CH_3CO	CH_3	H	159–160	2302
CH_3CO	C_2H_5	H	102	2302
CH_3CO	$(CH_2)_3$		144–145	2302
$CH_2CO_2CH_3$	CH_3	H	132–133	2302
CH_3	CH_3	H	101	2302
CH_3	C_2H_5	H	184	2302

Derivatives of 4-[3-methylthio-(1H)-1,2,4-triazol-5-yl]quinoline:



[a] Heteroatoms present are generally listed in the order N, O, S. Within each series, compounds are grouped in increasing order of number of substituents present and listed in order of position of substituents.

[b] Compounds substituted on the heteroaryl ring are listed first, followed by compounds substituted on the quinoline ring.

[c] Compounds with substituents on both heteroaryl and quinoline rings are listed last.

[d] Compounds have generally been arranged in ascending order of position numbers of heteroatoms.

TABLE 50 (*cont.*)

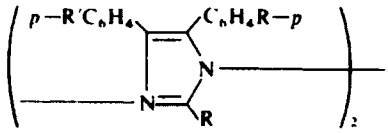
R	R^A	R^B	M.p. (°C)	Reference
$CH_2CO_2CH_3$	CH_3	H	No data	2302
CH_3	CH_3	H	No data	2302
CH_3	C_2H_5	H	No data	2302
CH_3	CH_3	CH_3	160–161	2302

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
4-[1(?)-Acetyl-3-methylthio-(1*H*)-1,2,4-triazol-5-yl]-2,3-cyclohexeno-[e]	173			2302
4-[1(?)-Acetyl-3-methylthio-(1*H*)-1,2,4-triazol-5-yl]-2-methyl-3-phenyl-	182			2302
4-[4-Methyl-5-methylthio-(4*H*)-1,2,4-triazol-3-yl]-2-methyl-	127			2302
6-(5-Methyl-1,2,4-oxadiazol-3-yl)-	175			1236
6-[5-(2-Carboxyphenyl)-1,2,4-oxadiazol-3-yl]-	203			1236
2-(4,5-Dihydro-4-methyl-3-phenyl-1,2,4-oxadiazol-5-yl)-	97–99			2303
4-(4,5-Dihydro-4-butyl-3-phenyl-1,2,4-oxadiazol-5-yl)-			187–188	2303
4-[4,5-Dihydro-4-(4-methylphenyl)-3-phenyl-1,2,4-oxadiazol-5-yl]-			190–191	2303
2-(1,3,4-Oxadiazol-2-yl)-	174–175			2304
2-(5-Phenyl-1,3,4-oxadiazol-2-yl)-	171–173			1510
2-[5-(2-Methoxyphenyl)-1,3,4-oxadiazol-2-yl]-	129–131			1510
2-[5-(3-Nitrophenyl)-1,3,4-oxadiazol-2-yl]-	250–252			1510
3-(5-{4-[2-(5-Methyl-2-benzoxazolyl)-ethenyl]phenyl}-1,3,4-oxadiazol-2-yl)-	No data			2305
2-[4,5-Dihydro-3-phenyl-4-(2-naphthyl)-1,2,4-oxathiazol-5-yl]-	129–131			2303
2-[5-(2-Benzoxazolyl)-1,3,4-thiadiazol-2-yl]-	288–290			2306
FOUR HETEROATOMS				
3-[(1*H*)-Tetrazol-5-yl]-	249–251			1225
POLYQUINOLYLHETEROARENES				
2,5-Di(2-quinolyl)thiophen	187–189			1144, 1260
2,5-Bis(4-nonyl-2-quinolyl)-thiophen	70			1143
5,5'-Di(2-quinolyl)-2,2'-bithienyl	250–251			1144, 2176, 2230

[e] 1,2,3,4-Tetrahydroacridine derivative.

TABLE 50 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	Picrate (and other derivs.), m.p. (°C)	References
5,5'-Bis(4-nonyl-2-quinolyl)-2,2'-bithienyl-	84-85			1143
1,2-Bis[5-(2-quinolyl)-2-thienyl]ethane-	189			1144
3-Methoxy-1,2-di(2-quinolyl)-indole	116-117.5			2238
1,3-Di(2-quinolyl)-(2*H*)-isoindole	180			2307
2,2'-Di(2-quinolyl)-3,3'-bibenzo(*b*)thiophen	No data			2230
9-Ethyl-3,6-di(2-quinolyl)-(9*H*)-carbazole	203-204			2255
2,8-Di(2-quinolyl)dibenzothiophen	206-207			2259
x,*x*-Di(2-quinolyl)dibenzoselenophene	201			2260
Derivatives of 1,1'-biimidazolyl:				



R	R'			
3-Quinolyl	H	118-120		2269
4-Quinolyl	H	197-203		1281, 2269
5-Quinolyl	H	177-179		2269
6-Quinolyl	H	179-181		2269
7-Quinolyl	H	179-182		2269
3-Quinolyl	CH_3	175-178		2269
4-Quinolyl	CH_3	162-165		2269
6-Quinolyl	CH_3	167-170		2269
7-Quinolyl	CH_3	168-170		2269
3-Quinolyl	OCH_3	152-156		2269
6-Quinolyl	OCH_3	135-137		2269
7-Quinolyl	OCH_3	137-140		2269

TABLE 51. Heteroarylquinolines (6-Membered and 7-Membered Rings, Including Biquinolyls)

Compound	M.p. (°C)	B.p. (°C/mmHg)	[η] (intrinsic viscosity)	Picrate (and other derivs.), m.p. (°C)	References
(1) SIX-MEMBERED RINGS					
(A) ONE HETEROATOM[a,b]					
2-(2-Pyridyl)-	99			182–183 Chloroplatinate, 197	1358, 1413, 2308–2310
2-(3-Pyridyl)-	68	135–140/0.1		199	2308, 2311, 2312
2-(4-Pyridyl)-	96			207	2308
3-(2-Pyridyl)-	101.5			227–228	938, 1196, 2308, 2313
3-(3-Pyridyl)-	124			Dipicrate—two forms: (i) *210* (ii) 224–225	1196, 2308, 2313
3-(4-Pyridyl)-	124–125			Dipicrate, 213–214	1196
4-(2-Pyridyl)-				199–200	2025
4-(3-Pyridyl)-	74	156–157/1		Dipicrate, 210–212	2308
4-(4-Pyridyl)-	83	152/0.1		Dipicrate, 225	2308
5-(2-Pyridyl)-	89–90			212	1242, 2313, 2314
6-(2-Pyridyl)-	82–83	246–248/23			2313, 2314
6-(3-Pyridyl)-	45 (32–33)	170–173/0.1		Dipicrate, 249–250	2313, 2314
6-(4-Pyridyl)-	105				1240, 2313, 2314
6-(*x*-Pyridyl)-(mixed isomers)	50–58				2314
7-(2-Pyridyl)-	87–88			221	1242, 2313, 2314
7-(3-Pyridyl)- *or* 7-(4-Pyridyl)-	104				1421b
8-(2-Pyridyl)-	76			209–210	2313, 2314
8-(3-Pyridyl)-	111–112			226	1243, 2313, 2314
8-(4-Pyridyl)-	127			238–240	2313
2-(6-Acetyl-2-pyridyl)-	141–142				2315
2-(4-Methyl-2-pyridyl)-	95–96				2310

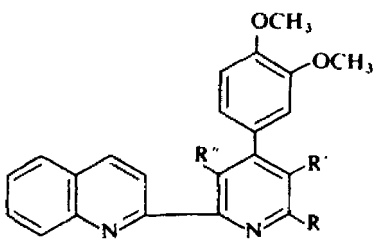
[a] Compounds substituted on the heteroaryl ring are listed first, followed by compounds substituted on the quinoline ring.
[b] Compounds with substituents on both heteroaryl and quinoline rings are listed last.

TABLE 51 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	[η] (intrinsic viscosity)	Picrate (and other derivs.) m.p. (°C)	References
2-(5-Methyl-2-pyridyl)-	112–114				2310
2-(6-Methyl-2-pyridyl)-	97–98				2310
2-(2-Pyridyl)-3-methyl-	76				1324a,b
2-(2-Pyridyl)-4-methyl-	69–70	156/0.5		160	2212, 2308, 2310
2-(2-Pyridyl)-4-phenyl-	153.5–154				2212
2-(3-Pyridyl)-4-methyl-	66.5	176–180/0.7		219–220	2308
2-(4-Pyridyl)-4-methyl-	101–102	178/0.7		250–252	2308, 2317
3-(2-Pyridyl)-2-methyl-	Oil			227–229	938
3-(*x*-Pyridyl)-4-methyl-(mixed isomers)				Dipicrate, 267–268 Isomeric dipicrate, 194–195	2025
3-(*x*-Pyridyl)-4-phenyl-(mixed isomers)				169–172 Dipicrate, 177–181	1315
3-(*x*-Pyridyl)-4-(4-methylphenyl)-(mixed isomers)				230–232	1315
4-(2-Pyridyl)-2-methyl-	84–85			186–187	2308, 2316
4-(3-Pyridyl)-2-methyl-	107	150–152/0.5		Dipicrate, 202–203	2308
4-(3-Pyridyl)-2-styryl-	164				2308
4-(4-Pyridyl)-2-methyl-	103	162–164/0.5		Dipicrate, 186–187	2308, 2317
6-(2-Pyridyl)-2-methyl-	106–107				2318
6-(3-Pyridyl)-2-methyl-	65–66				2318
6-(4-Pyridyl)-2-methyl-	180				2318
5-(*x*-Pyridyl)-8-methyl-(mixed isomers)		180–190/0.1			2314
8-(*x*-Pyridyl)-5-*t*-butyl-		120/0.0002			2318–2320
2-(2,6-Dimethyl-3-pyridyl)-	93–95				1232
2-(2,6-Dimethyl-4-pyridyl)-	135			230	2321
2-(4-Phenyl-6-methyl-2-pyridyl)-	146				2322
2-[4-(4-Chlorophenyl)-6-methyl-2-pyridyl]-	131				2322
2-[4-(4-Methoxyphenyl)-6-methyl-2-pyridyl]-	116				2322
2-[4-(2,3,4-Trimethoxyphenyl)-6-methyl-2-pyridyl]-	148				2322
3-(2,6-Dimethyl-4-pyridyl)-	100				2321

4-(2,6-Dimethyl-4-pyridyl)-	122			1257, 2321
5-(2,6-Dimethyl-4-pyridyl)-	151		231–234 (107–109)	2321, 2323
6-(2,6-Dimethyl-3-pyridyl)-	68		*ca.* 243	2321
6-(2,6-Dimethyl-4-pyridyl)-	84	220–230/15	224–225	2321, 2324
7-(2,6-Dimethyl-4-pyridyl)-	125		223 (107–109)	2321, 2323
8-(2,6-Dimethyl-4-pyridyl)-	132			2321
5-(2-Pyridyl)-6,7-diphenyl-	193–194			2325
6-(2-Pyridyl)-5,7-diphenyl-	156–157			1118, 2325
6-(2-Pyridyl)-5,7-bis(*x*-methoxyphenyl)-	192–194			1120
2-(6-Methyl-2-pyridyl)-4-methyl-	114–115			2310
2-(5,6-Dimethyl-4-phenyl-2-pyridyl)-	176–178			1245, 2322
2-(4-Chloro-2,6-dimethyl-3-pyridyl)-[c]	119–120			1232
6-(3-Methoxy-2-pyridyl)-5,7-bis-(*x*-methoxyphenyl)-	No data			1120

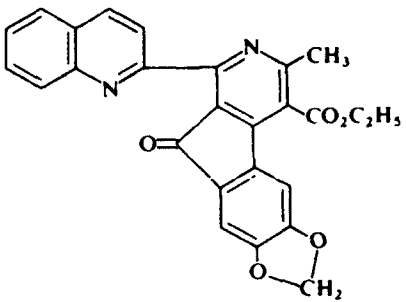
Derivatives of 2-[4-(3,4-dimethoxyphenyl)-2-pyridyl]quinoline:



R	R′	R″		
CH_3	CH_3	H	195–197	2326
CH_3	$CO_2C_2H_5$	H	160–161	2326
CH_3	$CO_2C_2H_5$	NH_2	217–218	2326
CH_3	$CO_2C_2H_5$	$CONH_2$	178–179	2326
CH_3	$CO_2C_2H_5$	$NHCO_2CH_3$	167–168	2326
CH_3	$CH_2O_2CCH_3$	H	214–216	2326
CH_3	$CH_2O_2CCH_3$	NH_2	211–212	2326
CH_3	$CH_2O_2CNHC_6H_5$	NH_2	232–233	2326
CH_3	$CH_2O_2CNHC_6H_5$	$NHCONHC_6H_5$	226.5	2326
CH_2Br	$CO_2C_2H_5$	$NHCOCH_3$	178–179	2326

[c] This compound was previously thought to be 2-[(4-chloro-6-methyl-2-pyridyl)methyl]quinoline.

TABLE 51 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	[n] (intrinsic viscosity)	Picrate (and other derivs.), m.p. (°C)	References
	255–256				2326
5,8-Di(*x*-pyridyl)- (mixed isomers)	2 fractions: (i) 167 (140–154) (ii) 138–149				2327, 2328
6,8-Di(*x*-pyridyl)- (mixed isomers)	152–156				2327, 2328
6-(2-Pyridyl)-8-(*x*-pyridyl)- (mixed isomers)	118–121				2327
2,3-Di(2-pyridyl)-4-methyl-	153.5–154				2212
2,3-Di(2-Pyridyl)-4-phenyl-	186.5–187				2212

(B) ONE HETEROATOM—Benzo derivatives, etc.[a,b,d,e]

(1) Quinoline derivatives (biquinolyls)

Note on extent of coverage:

This section includes biquinolyl (biquinoline) derivatives which are substituted on one or both rings by alkyl, aryl and substituted aryl groups, etc. Also included are substituted biquinolyls in which the substituent is *not* alkyl or aryl, e.g. 2'-chloro-2,3'-biquinolyl. Such compounds have been regarded as (substituted quinolyl)quinoline derivatives [i.e. 2-(3-chloroquinolin-2-yl)quinoline] and are therefore considered within the scope of this section. For those biquinolyl derivatives which bear substituents on each ring, but neither of which are alkyl or aryl (e.g. 4,4'-dichloro2,2'-biquinolyl) the appropriate chapter devoted to the functional group(s) should be consulted e.g. Part 1, Chapter 3, Table 46 in the case of the compound indicated).

(i) Unsubstituted				
2,2'-Biquinolyl		196	211–212 Chloroplatinate, 300+	140, 141, 1072, 1203b, 1352, 1358, 1364a,b, 1365, 1366, 1368, 1387a, 1396, 1400, 1401, 1403, 1405, 1407, 1409, 1411–1413, 2049
2,3'-Biquinolyl	176–177	400+	194 Chloroplatinate, 278 2,4-Dinitrophenol addn. compd. 127–128	642, 643, 1072, 1347, 1348, 1360, 1370, 1375, 1379, 1380, 1397, 1487, 2329
2,4'-Biquinolyl	177–179 (153–154)		261–262	1345, 1411
2,5'-Biquinolyl	115			1162
2,6'-Biquinolyl	144	210–250/3		514, 1815, 2330
2,7'-Biquinolyl	159–160		240	1162, 1390b
3,3'-Biquinolyl	271 (258)		Dipicrate, 300+	1390c, 1395, 1419
3,4'-Biquinolyl	83–84		243	1348
4,4'-Biquinolyl	174.5		262–263 (192) Monomethiodide, 146–152 Dimethiodide, 328–332 (+)-Tartrate, 167–169	1410, 1411, 1439, 1441, 2331, 2332
4,6'-Biquinolyl	122		264	1173
5,5'-Biquinolyl	(±) 175 (+) 164–166		300+ (+)-Tartrate, 204	1390a, 1439
5,7'-Biquinolyl	128–129			1336

[a] Compounds substituted on the heteroaryl ring are listed first, followed by compounds substituted on the quinoline ring.

[b] Compounds with substituents on both heteroaryl and quinoline rings are listed last.

[d] Heteroatoms present are generally listed in the order N, O, S. Within each series compounds are grouped in increasing order of number of substituents present and listed in order of position of substituents.

[e] Compounds have generally been arranged in ascending order of position numbers of heteroatoms.

TABLE 51 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	[*n*] (intrinsic viscosity)	Picrate (and other derivs.), m.p. (°C)	References
5,8'-Biquinolyl	107–108				1336
6,6'-Biquinolyl	181			260+ 2,4-Dinitrophenol addn. compound, 184–186	1383, 1456, 1489, 2333–2335
6,7'-Biquinolyl	132–133				2032
6,8'-Biquinolyl	148			268	1485, 1489
7,7'-Biquinolyl	171–172			300	
7,8'-Biquinolyl	193–194				1336
8,8'-Biquinolyl	214–216				1363, 1384, 1389, 2336
3,7'- *or* 4,7'-biquinolyl[f]	192–193				454, 1368, 1370, 1390c, 1419, 1421a,b, 2337–2339
4,5'- *or* 4,7'-biquinolyl	116–117			248	1173
(*ii*) *Monosubstituted* (see note at beginning of section)					
3-Methyl-2,2'-biquinolyl	136				1324a,b
4-Methyl-2,2'-biquinolyl	171–172				1349, 2310
3-Ethyl-2,2'-biquinolyl	96–97				1349
2-*n*-propyl-2,2'-biquinolyl	49–50				1349
3-Phenyl-2,2'-biquinolyl	147–148				1349
4-Phenyl-2,2'-biquinolyl	203				1186, 1349
4-Benzylamino-2,2'-biquinolyl	176–178				1476
4-Phenylamino-2,2'-biquinolyl	254–255				1476
4-(4-Bromophenylamino)-2,2'-biquinolyl	227–228				1476
4-(4-Methoxyphenylamino)-2,2'-biquinolyl	184–185				1476
4-(4-Methylphenylamino)-2,2'-biquinolyl	188–190				1476
4[(1-Naphthyl)amino]-2,2'-biquinolyl	199–200				1476
2,2'-Biquinolyl-4-carbonyl chloride	230–235				1366

[f] The substance referred to as 3,7'- or 4,7'-biquinolyl has also been considered as 3,3'-biquinolyl. It has also been found[2049] that the product obtained from certain reactions is in fact 2,2'-biquinolyl. Hence the reported identity of the substances obtained should be treated with caution.

2,2′-Biquinolyl-3-carboxylic acid, ethyl ester	109–110			1349
2,2′-Biquinolyl-4-carboxylic acid	265–267			1366
2,2′-Biquinolyl-4-carboxylic acid, 3-methylbutyl ester	69			1366
NN-Diethyl-2,2′-biquinolyl-4-carboxamide	192			1366, 2340
N-(2-Hydroxyethyl)-2,2′-biquinolyl-4-carboxamide	234			2340
2′-Chloro-2,3′-biquinolyl	170–171			1487, 1535, 2341, 2342
4′-Chloro-2,3′-biquinolyl	179–180			1535, 2341
2′-Cyano-2,3′-biquinolyl	208–209			1535
2′-Ethoxy-2,3′-biquinolyl	204–205			1535
2′-Hydroxy-2,3′-biquinolyl	328–330			2341, 2342
4′-Hydroxy-2,3′-biquinolyl	300			2341
2′-Methyl-2,3′-biquinolyl	191–193			1346
2,3′-Biquinolyl-2′-(α-cyanoacetic acid), ethyl ester	214–215			1535
2,3′-Biquinolyl-2′-carboxamide	215–217			1535
2,3′-Biquinolyl-2′-carboxylic acid	192 (175)			1346, 1348, 1535
2,3′-Biquinolyl-2′-carboxylic acid, ethyl ester	140			950
2-(2,3′-Biquinolin-2′-yl)cyclohexanone oxime	164–165			1535
4′-Methyl-2,6′-biquinolyl	138			1457
2′-{4-[3-(6-Quinolyl)allylideneamino]-phenyl}-2,6′-biquinolyl	248–249			1354
2′-(4-Aminophenyl)-2,6′-biquinolyl	234			1354
2′-(4-Nitrophenyl)-2,6′-biquinolyl	266–268			1354
2,6′-Biquinolyl-4-carboxylic acid	334			1354
1′-Methyl-1′,2′,3′,4′-tetrahydro-2,6′-biquinolyl	113–114		204–205	2152
1′-Ethyl-1′,2′,3′,4′-Tetrahydro-2,6′-biquinolyl	73–74		209–210	2152
1′-*n*-Propyl-1′,2′,3′,4′-Tetrahydro-2,6′-biquinolyl		230–235/20	192–193	2152
1′-*n*-Butyl-1′,2′,3′,4′-Tetrahydro-2,6-biquinolyl		275–280/20	218–220	2152
1′-Benzyl-1′,2′,3′,4′-Tetrahydro-2,6′-biquinolyl	78–80		228–230	2152

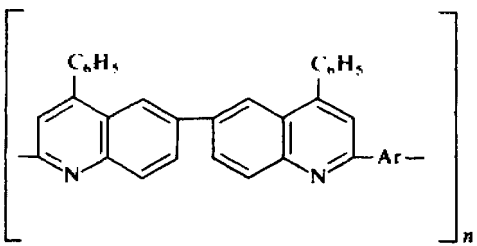
TABLE 51 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	[*n*] (intrinsic viscosity)	Picrate (and other derivs.), m.p. (°C)	References
3,4′-Biquinolyl-2-carboxylic acid	204 ($+1\frac{1}{2}$ H_2O)				1348
5-Methyl-8,8′-biquinolyl	211.5–212				1363
8,8′-Biquinolyl-5-carboxylic acid	310–312				1363
(iii) Disubstituted—similarly substituted					
3,3′-Dimethyl-2,2′-biquinolyl (?)	143–144				1400
4,4′-Dimethyl-2,2′-biquinolyl	280–281			236 (350)	1387a, 1393, 1398, 1400, 1411, 1413, 1422, 2310
6,6′-Dimethyl-2,2′-biquinolyl	267			232	1072, 1393, 1401, 1422
7,7′-Dimethyl-2,2′-biquinolyl	288				1072, 1351, 1400
8,8′-Dimethyl-2,2′-biquinolyl	210–211				1072, 1351, 1394, 1403, 1404
4,4′-Diethyl-2,2′-biquinolyl	182–183				1387c
8,8′-Diethyl-2,2′-biquinolyl	122–123				1394
4,4′-Diphenyl-2,2′-biquinolyl	362				1349, 1387b, 1403, 1404, 1469
8,8′-Diphenyl-2,2′-biquinolyl	247–248				1394
4,4′-Dimethyl-2,3′-biquinolyl	265–267			342	1411
6,6′-Dimethyl-2,3′-biquinolyl[a]	207.5–208.5			282–283	1072, 1376, 2343
7,7′-Dimethyl-2,3′-biquinolyl[a]	208–209			285–286	1376, 1411
8,8′-Dimethyl-2,3′-biquinolyl[a]	147–147.5			264–265	1376, 1411
2,2′-Dimethyl-3,3′-biquinolyl	144 104–105 ($+2H_2O$)				1793
2,2′-Dimethyl-4,4′biquinolyl	245–247 (263–265)				1389, 1411
2,2′-Diphenyl-4,4′-biquinolyl (?)	303			234	1168a,b

[a] These compounds were originally regarded[1376,1411] as 2,2′-biquinolyl derivatives, but have subsequently been shown by unambiguous synthesis[1394] and by spectral data[1072,2343] to be 2,3′-biquinolyl derivatives.

2,2'-Dimethyl-6,6'-biquinolyl	208–209	360+	*ca.* 230	1340, 1342, 1408, 1428, 2154
3,8'-Dimethyl-6,6'-biquinolyl	192			2344, 2345
5,5'-Dimethyl-8,8'-biquinolyl	215			2346
7,7'-Dimethyl-8,8'-biquinolyl	213–215			1338
(iv) Disubstituted—dissimilarly substituted (see also notes at beginning of section)				
4'-Methyl-2,2'-biquinolyl-4-carboxylic acid	286			1486
4'-Methyl-2,2'-biquinolyl-4-carboxylic acid, methyl ester	170–171			1486
4'-Methyl-2,2'-biquinolyl-4-carboxylic acid, ethyl ester	125–126			1486
4'-Phenyl-2,2'-biquinolyl-4-carbonyl chloride	275–277			1186
4'-Phenyl-2,2'-biquinolyl-4-carboxylic acid	295–296			1186
4'-Phenyl-2,2'-biquinolyl-4-carboxylic acid, 3-methylbutyl ester	136–138			1186
NN-Diethyl-4'-phenyl-2,2'-biquinolyl-4-carboxamide	232–233			1186
N,4'-Diphenyl-2,2'-biquinolyl-4-carboxamide	328–330			1186
2,3'-Biquinolyl-2',4'-dicarboxylic acid, 2'-ethyl ester	183–188			1355
1'-Ethyl-2'-methyl-1',2',3',4'-tetrahydro-2,6'-biquinolyl	70–71		227–228	2152
5-Methyl-8,8'-biquinolyl-5'-carboxylic acid	331–332			1363
(v) Polysubstituted				
4,4',6,6'-Tetramethyl-2,2'-biquinolyl	258–259			1387a
4,4',7,7'-Tetramethyl-2,2'-biquinolyl	275–276			1387a
4,4',8,8'-Tetramethyl-2,2'-biquinolyl	246–247			1387a
4,4'-Diethyl-6,6'-dimethyl-2,2'-biquinolyl	225			1387c
4,4'-Diethyl-7,7'-dimethyl-2,2'-biquinolyl	175			1387c
4,4'-Diethyl-8,8'-dimethyl-2,2'-biquinolyl	189–190			1387c
4,4'-Dimethyl-6,6'-diphenyl-2,2'-biquinolyl	289–289.5			1387c
6,6'-Dimethyl-4,4'-diphenyl-2,2'-biquinolyl	341–342			1387b, 1468, 1469
7,7'-Dimethyl-4,4'-diphenyl-2,2'-biquinolyl	348–349			1387b, 1469

TABLE 51 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	[n] (intrinsic viscosity)	Picrate (and other derivs.), m.p. (°C)	References
8,8'-Dimethyl-4,4'-diphenyl-2,2'-biquinolyl	279–280				1387b, 1469
2,2',4,4'-Tetramethyl-6,6'-biquinolyl	235				1341, 1343, 2347, 2348
2,2',8,8'-Tetramethyl-6,6'-biquinolyl	189–190 (160–165)				1342, 2344
2,2',4,4'-Tetramethyl-7,7'-biquinolyl	No data				1389
4,4',5,5'-Tetramethyl-8,8'-biquinolyl	292–295				2349, 2350
5,5',7,7'-Tetramethyl-8,8'-biquinolyl	No data				1338
2,2',4,4',8,8'-Hexamethyl-6,6'-biquinolyl	252.5 (225, 242)				1341, 1343, 1344
(vi) Ter- and Quaterquinolyls					
2,6':2',6"-Terquinolyl	267–269				1354
2,3':3',4"-Terquinolyl	150–151			Chloroplatinate, 200+	1234
2"-(3,4,5-Trihydroxyphenyl)-2,8':2',8"-Terquinolyl	No data				2143
2,6':2',6":2",6"'-Quaterquinolyl	348–350				1354
(vii) Polyquinolyls					
Poly[2,6-(4-phenylquinoline)]			[n] 2.2		1282, 1283, 1443
	No data				1350a

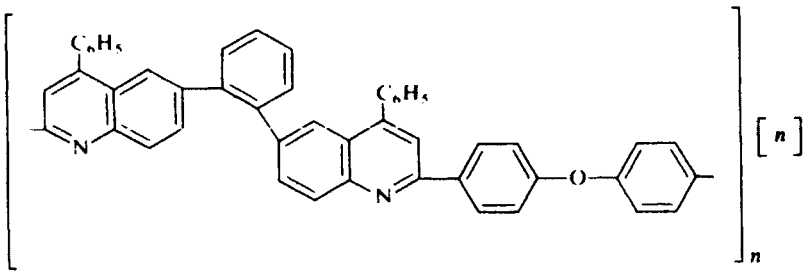
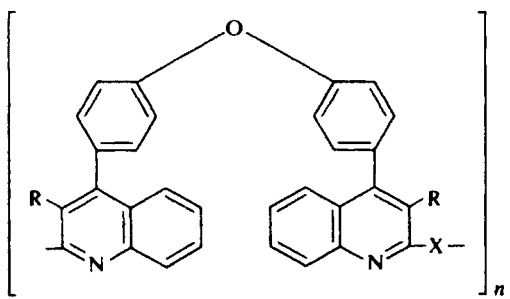
1350b

No data

2208

[η] 0.43

TABLE 51 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	[*n*] (intrinsic viscosity)	Picrate (and other derivs.), m.p. (°C)	References
			[*n*] 0.04		2208
					

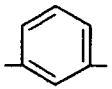
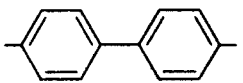
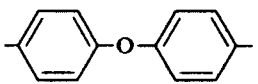
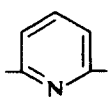
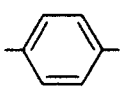
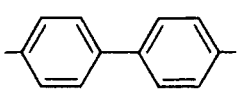
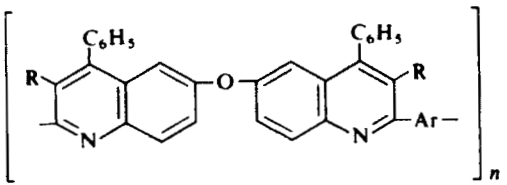
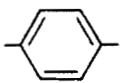
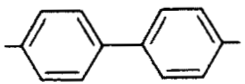
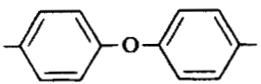
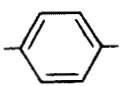
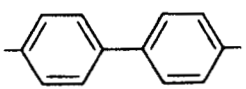
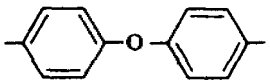
R	X		
H	Nil.	No polymer	1284, 1285, 1443
H		0.36	1284, 1285, 1443
H		0.38	1284, 1285, 1443
H		0.62	1284, 1285, 1443
H		0.08	1284, 1285, 1443
C_6H_5		0.26	1284, 1285, 1443
C_6H_5		0.57	1284, 1285, 1443

TABLE 51 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	[n] (intrinsic viscosity)	Picrate (and other derivs.), m.p. (°C)	References
					
R Ar					
H 			1.0		1282, 1283, 1443
H 			3.1		1282, 1283, 1443
H 			1.6		1282, 1283, 1443
C_6H_5 			3.4		1282, 1283, 1443
C_6H_5 			4.1		1282, 1283, 1443

R	Ar			
C_6H_5			2.0	1282, 1283, 1443

For further polyquinolines prepared by cross-linking, see reference 2351.

(II) Other heteroarylquinolines				
2-(1-Isoquinolyl)-	129			1324a,b
2-(3-Isoquinolyl)-	151.5–152		245.5–246	2352
3-(1-Isoquinolyl)-		210–215/1	228–229	2353
4-(3,4-Dihydro-6,7-methylenedioxy-1-isoquinolyl)-	138		183	1217a
6-(3,4-Dihydro-6,7-methylenedioxy-1-isoquinolyl)-	167		224	1217b
8-(3,4-Dihydro-6,7-methylenedioxy-1-isoquinolyl)-	205		224	1217b
2-(3-Methyl-6,7-methylenedioxy-1-isoquinolyl)-			223–224	2354
3-(3-Methyl-6,7-methylenedioxy-1-isoquinolyl)-2-phenyl-	258–259			2354
2-[3,4-Dihydro-(2*H*)-1-benzopyran-6-yl]-	126–127	230–234/15	210	2247
2-[3,4-Dihydro-(2*H*)-1-benzopyran-6-yl]-6-methyl-	119–120	236–240/16	196	2247
2-[3,4-Dihydro-(2*H*)-1-benzothiopyran-6-yl]-	96		188	2355
2-[3,4-Dihydro-(2*H*)-1-benzothiopyran-6-yl]-3-methyl-	118		192–194	2355
6-(9-Acridinyl)-	218–220			2356
2-[Benzo(*f*)quinolin-3-yl]-	212			1356, 2357, 2358
6-[Benzo(*f*)quinolin-3-yl]-	225–226			2358
2-[1-Methylbenzo(*f*)quinolin-3-yl]-	187		Methiodide, 270	2210, 2358
2-[1-Phenylbenzo(*f*)quinolin-3-yl]-	285			1356, 2358
2-[1-(4-Acetylphenyl)benzo(*f*)quinolin-3-yl]-	266–267			1353
2-[1-(4-Bromophenyl)benzo(*f*)quinolin-3-yl]-	280–281			1353, 2358

TABLE 51 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	[*n*] (intrinsic viscosity)	Picrate (and other derivs.), m.p. (°C)	References
2-[1-(4-Chlorophenyl)benzo(*f*)quinolin-3-yl]-	258–259				2358
2-[1-(4-Fluorophenyl)benzo(*f*)quinolin-3-yl]-	251–252				2358
2-[1-(4-Methoxyphenyl)benzo(*f*)quinolin-3-yl]-	247–248				1353
2-[1-(4-Methylphenyl)benzo(*f*)quinolin-3-yl]-	247–248				2358
2-[1-(4-Nitrophenyl)benzo(*f*)quinolin-3-yl]-	270–271				1353
2-[1-(1,1'-Biphenyl-4-yl)benzo(*f*)quinolin-3-yl]-	259–260				1353
2-[1-(*x*-Acetyl-1,1'-biphenyl-4-yl)benzo(*f*)-quinolin-3-yl]-	275–276				1353
2-[1-(Terphenyl-4-yl)benzo(*f*)quinolin-3-yl]-	297–298				1353
2-[1-(3-Pyridyl)benzo(*f*)quinolin-3-yl]-	293–294				2358
2-[1-(2-Thienyl)benzo(*f*)quinolin-3-yl]-	253–254				2358
2-[1-(2-Phenylethenyl)benzo(*f*)quinolin-3-yl]-	211				2210, 2211
2-{1-[2-(4-Nitrophenyl)ethenyl]benzo-(*f*)quinolin-3-yl}-	220–221				2210
2-{1-[2-(2-quinolyl)ethenyl]benzo(*f*)-quinolin-3-yl}-	200–201				2211
2-{1-[2-(4-Quinolyl)ethenyl]benzo(*f*)-quinolin-3-yl}-	262				2210, 2211
2-{1-[2-(6-Quinolyl)ethenyl]benzo(*f*)-quinolin-3-yl}-	231–232				2210, 2211
3-(2-Quinolyl)benzo(*f*)quinoline-1-carbonyl-chloride	247–249				2357
3-(2-Quinolyl)benzo(*f*)quinoline-1-carboxylic acid	259–260				1511, 2357

3-(2-Quinolyl)benzo(*f*)quinoline-2-carboxylic acid	216	1511
3-(2-Quinolyl)benzo(*f*)quinoline-1-carboxylic acid, pentyl ester	119–120	2357
NN-Diethyl-3-(2-quinolyl)benzo(*f*)-quinoline-1-carboxamide	188	2357
N-Phenyl-3-(2-quinolyl)benzo(*f*)-quinoline-1-carboxamide	325–326	2357
4-[1-(4-Bromophenyl)benzo(*f*)quinolin-3-yl]-	215.5–217	2358
4-[1-(4-Chlorophenyl)benzo(*f*)quinolin-3-yl]-	209–210	2358
4-[1-(4-Fluorophenyl)benzo(*f*)quinolin-3-yl]-	173–174	2358
4-[1-(4-Methylphenyl)benzo(*f*)quinolin-3-yl]-	222	2358
4-[1-(3-Pyridyl)benzo(*f*)quinolin-3-yl]-	217	2358
6-[1-Methylbenzo(*f*)quinolin-3-yl]-	169–170	2358
6-[1-Phenylbenzo(*f*)quinolin-3-yl]-	170–171	2358
6-[1-(4-Bromophenyl)benzo(*f*)quinolin-3-yl]-	230–231	2358
6-[1-(4-Chlorophenyl)benzo(*f*)quinolin-3-yl]-	226	2358
6-[1-(4-Fluorophenyl)benzo(*f*)quinolin-3-yl]-	223–224	2358
6-[1-(4-Methylphenyl)benzo(*f*)quinolin-3-yl]-	202–203	2358
6-[1-(3-Pyridyl)benzo(*f*)quinolin-3-yl]-	228	2358
6-[1-(2-Thienyl)benzo(*f*)quinolin-3-yl]-	193–194	2358
2-[Benzo(*f*)quinolin-3-yl]-4-phenyl-	229–230	1356, 2358
2-[1-Phenylbenzo(*f*)quinolin-3-yl]-4-phenyl-	322–323	1356
2-[1-(4-Bromophenyl)benzo(*f*)quinolin-3-yl]-4-phenyl-	320–321	1353
2-[1-(4-Hydroxyphenyl)benzo(*f*)quinolin-3-yl]-4-phenyl-	317–318	1353
2-[1-(4-Methoxyphenyl)benzo(*f*)quinolin-3-yl]-4-phenyl-	293–294	1353

TABLE 51 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	[*n*] (intrinsic viscosity)	Picrate (and other derivs.), m.p. (°C)	References
2-[1-(4-Nitrophenyl)benzo(*f*)quinolin-3-yl]-4-phenyl-	340–341				1353
2-[1-(1,1'-Biphenyl-4-yl)benzo(*f*)-quinolin-3-yl]-4-phenyl-	330–331				1353
2-[1-(Terphenyl-4-yl)benzo(*f*)quinolin-3-yl]-	380–382				1353
3-(4-Phenyl-2-quinolyl)benzo(*f*)-quinoline-1-carbonyl chloride	251–253				2357
3-(4-Phenyl-2-quinolyl)benzo(*f*)-quinoline-1-carboxylic acid	271–272				2357
3-(4-Phenyl-2-quinolyl)benzo(*f*)-quinoline-1-carboxylic acid, pentyl ester	191–192				2357
NN-Diethyl-3-(4-phenyl-2-quinolyl)-benzo(*f*)quinoline-1-carboxamide	219				2357
N-Phenyl-3-(4-phenyl-2-quinolyl)-benzo(*f*)quinoline-1-carboxamide	338–339				2357
2-[2,3-Dihydro-(1*H*)-naphtho(2,1-*b*)-thiopyran-8-yl]-6-methyl-	147				2359
2-[1,2,3,4-Tetrahydrobenzo(*a*)-phenanthridin-5-yl]-	133				1356
2-[1,2,3,4-Tetrahydrobenzo(*a*)-phenanthridin-5-yl]-4-phenyl-	176–177				1356
2-[(10*H*)-Indeno(1,2-*g*)quinolin-2-yl]-	281–282				1357
2-[4-Phenyl-(10*H*)-indeno(1,2-*g*)quinolin-2-yl]-	305–306				1357
2-[(10*H*)-Indeno(1,2-*g*)quinolin-2-yl]-4-phenyl-	270–272				1357
2-[4-Phenyl-(10*H*)-indeno(1,2-*g*)quinolin-2-yl]-4-phenyl-	310–312				1357

(C) TWO HETEROATOMS			
2-(5-Pyrimidinyl)-	139–140		1532
4-(5-Pyrimidinyl)-	149–152		1532
2-(4-Amino-5-pyrimidinyl)-	201–201.5		2360
4-(4-Amino-5-pyrimidinyl)-	246–247		2360
6-(4-Amino-5-pyrimidinyl)-	194–195		2360
8-(4-Amino-5-pyrimidinyl)-	186–187		2360
2-(2,4-Diamino-6-methyl-5-pyrimidinyl)-		Hydrochloride, 303–305	1220
2-(2-Pyrazinyl)-	156–157		1532
(D) TWO HETEROATOMS—Benzo derivatives, etc.[a,b,d,e]			
3-(2-Quinoxalinyl)-	214–215	238–239	1216, 2361
3-[6(7)-Chloro-2-quinoxalinyl]-	236–239		1216
3-[6(7)-Methyl-2-quinoxalinyl]-	210–212		1216
3-[6(7)-Nitro-2-quinoxalinyl]-	270–272		1216
2-(3-Phenyl-2-quinoxalinyl)-	132		2297
2-(3-Quinolyl)quinoxaline-6(7)-carboxylic acid	330+		1216
2-(2-Quinoxalinyl)-3,4-diphenyl-	No data		1326
2-(4-Phenylcinnolin-3-yl)-	162–163	219–220	1055
2-[4-(4-Methoxyphenyl)cinnolin-3-yl]-	151–152		937, 1055
2-[4-(4-Methylphenyl)cinnolin-3-yl]-	153–154		1055
2-(6-Chloro-4-phenylcinnolin-3-yl)-	205–206		1055
2-(Phenazin-2-yl)-	211–212		2056
2-(5,10-Dihydrophenazin-2-yl)-	202		2056
2-(5,10-Diacetyl-5,10-dihydrophenazin-2-yl)-	190–192		2056
3-[2-Benzo(*g*)quinoxalinyl]-	181–183		1216
2-[(10*H*)-phenothiazin-2-yl]-	80–81		2057
2-(2-Phenoxathiinyl)-	132	223	2362
2-(2-Thianthrenyl)-	165–166		2363

[a] Compounds substituted on the heteroaryl ring are listed first, followed by compounds substituted on the quinoline ring.

[b] Compounds with substituents on both heteroaryl and quinoline rings are listed last.

[d] Heteroatoms present are generally listed in the order N, O, S. Within each series compounds are grouped in increasing order of number of substituents present and listed in order of position of substituents.

[e] Compounds have generally been arranged in ascending order of position numbers of heteroatoms.

TABLE 51 (*cont.*)

Compound	M.p. (°C)	B.p. (°C/mmHg)	[*n*] (intrinsic viscosity)	Picrate (and other derivs.), m.p. (°C)	References
2-(2-Thianthrenyl)-5,7-dimethyl-	155				2364
2-(2-Thianthrenyl)-6,8-dimethyl-	193				2364
2-[Dibenzo(*a*,*c*)phenazin-2-yl]-	274				2204
2-[Dibenzo(*a*,*c*)phenazin-3-yl]-	262				2204
(E) THREE HETEROATOMS[a,b,d,e]					
2-(5,6-Dimethyl-1,2,4-triazin-3-yl)-	185				1221a
2-(5,6-Diphenyl-1,2,4-triazin-3-yl)-	188–189				2365
2-[5,6-Di-(2-pyridyl)-1,2,4-triazin-3-yl]-	176–177				2365
4-(5,6-Diphenyl-1,2,4-triazin-3-yl)-	281–282				2366
4-(4,6-Diamino-1,3,5-triazin-2-yl)-	318–322				2367
4-(4,6-Diamino-1,3,5-triazin-2-yl)-2-phenyl-	240				2368
(F) POLYQUINOLYLHETEROARENES[a]					
2,6-Di(2-quinolyl)pyridine	227–228			214	784, 1328, 2315, 2370
3,5-Di(2-pyridyl)pyridine	233–234				1532
2,6-Bis(6-methyl-2-quinolyl)pyridine	286				784
2,6-Di(2-quinolyl)-4-phenylpyridine	295–296				2371
1,3-Di(2-quinolyl)benzo(*f*)quinoline	243				2358
1-(2-Quinolyl)-3-(4-quinolyl)benzo(*f*)-quinoline	210–211				2358
1-(2-Quinolyl)-3-(6-quinolyl)benzo(*f*)-quinoline	227–228				2358

[a] Compounds substituted on the heteroaryl ring are listed first, followed by compounds substituted on the quinoline ring.

[b] Compounds with substituents on both heteroaryl and quinoline rings are listed last.

[d] Heteroatoms present are generally listed in the order N, O, S. Within each series compounds are grouped in increasing order of number of substituents present and listed in order of position of substituents.

[e] Compounds have generally been arranged in ascending order of position numbers of heteroatoms.

[h] For polyquinolylbiquinolyl derivatives see sections B(1)(vi) and (vii) in this table.

4,6-Dimethyl-5-(2-quinolylmethyl)-2-(2-quinolyl)pyrimidine	270–271		2372
2,3-Di(2-quinolyl)quinoxaline	187		1215
2,3-Bis(6-methyl-2-quinolyl) quinoxaline	202–203		475
3-(4-Dimethylaminophenyl)-5,6-di-(2-quinolyl)1,2,4-triazine	231–232		2373
2-Amino-4,6-di(2-quinolyl)-1,3,5-triazine	355–356		1222
2,4,6-Tri(2-quinolyl)-1,3,5-triazine	270–271 ($+1\frac{1}{2}$ H_2O)		
	(2) SEVEN-MEMBERED RINGS[a,b,d,e]		
2-(2,3,4,5-Tetrahydro-1-benzoxepin-7-yl)-6-methyl-	111.5	195	2250
2-(2,3,4,5-Tetrahydro-1-benzothiepin-7-yl)-	98	163	2374
2-(2,3,4,5-Tetrahydro-1-benzothiepin-7-yl)-6-methyl-	135	160	2375

[a] Compounds substituted on the heteroaryl ring are listed first, followed by compounds substituted on the quinoline ring.
[b] Compounds with substituents on both heteroaryl and quinoline rings are listed last.
[d] Heteroatoms present are generally listed in the order N, O, S. Within each series compounds are grouped in increasing order of number of substituents present and listed in order of position of substituents.
[e] Compounds have generally been arranged in ascending order of position numbers of heteroatoms.

VIII. References

1. J. T. Hackmann, J. P. Wibaut and H. P. L. Gitsels, *Rec. Trav. Chim.*, **62**, 229 (1943).
2. T. S. Perrin and J. R. Bailey, *J. Amer. Chem. Soc.*, **55**, 4136 (1933).
3. B. S. Biggs and J. R. Bailey, *J. Amer. Chem. Soc.*, **55**, 4141 (1933).
4. G. R. Lake and J. R. Bailey, *J. Amer. Chem. Soc.*, **55**, 4143 (1933).
5. A. C. Bratton and J. R. Bailey, *J. Amer. Chem. Soc.*, **59**, 175 (1937).
6. C. L. Key and J. R. Bailey, *J. Amer. Chem. Soc.*, **60**, 763 (1938).
7. W. N. Axe and J. R. Bailey, *J. Amer. Chem. Soc.*, **60**, 3028 (1938).
8. W. N. Axe, *J. Amer. Chem. Soc.*, **61**, 1017 (1939).
9. W. N. Axe and J. R. Bailey, *J. Amer. Chem. Soc.*, **61**, 2609 (1939.
10. L. M. Schenck and J. R. Bailey, *J. Amer. Chem. Soc.*, **62**, 1967 (1940).
11. R. A. Glenn and J. R. Bailey, *J. Amer. Chem. Soc.*, **63**, 637 (1941).
12. R. A. Glenn and J. R. Bailey, *J. Amer. Chem. Soc.*, **63**, 639 (1941).
13. L. M. Schenck and J. R. Bailey, *J. Amer. Chem. Soc.*, **63**, 1364 (1941).
14. L. M. Schenck and J. R. Bailey, *J. Amer. Chem. Soc.*, **63**, 1365 (1941).
15. J. R. Bailey and C. L. Key, *U.S. Pat.* 2,237,542 (1941); *Chem. Abstr.*, **35**, 4398[2].
16. F. Runge and P. Pfeiffer, *Chem. Ber.*, **90**, 1757 (1957).
17. S. K. Ganguli and P. C. Guha, *J. Indian Chem. Soc.*, **11**, 197 (1934).
18. O. Kruber and L. Ruppen, *Chem. Ber.*, **81**, 483 (1948).
19. W. Swietoslawski, A. Bylicki and D. Rostafinska, *Przem. Chem.*, **9**, 367 (1953); *Chem. Abstr.*, **49**, 9905e.
20. O. Kruber and R. Oberkobusch, *Chem. Ber.*, **86**, 309 (1953).
21. H. B. Nisbet and A. M. Pryde, *J. Inst. Fuel*, **27**, 58 (1954).
22. E. Profft and G. Buchmann, *Chem. Tech. (Berlin)*, **8**, 30 (1956).
23. L. Fedotova and G. Vanags, *Latv. PSR Zinat. Akad. Vestis*, No. 5, 93 (1958); *Chem. Abstr.*, **53**, 1348a.
24. C. Karr and T. C. L. Chang, *J. Inst. Fuel*, **31**, 522 (1958).
25. L. Fedotova and G. Vanags, *Latv. PSR Zinat. Akad. Kim. Inst. Zinat. Raksti*, **2**, 53 (1958); *Chem. Abstr.*, **53**, 21941f.
26. L. Fedotova and G. Vanags, *Latv. PSR Zinat. Akad. Vestis*, No. 2, 75 (1959); *Chem. Abstr.*, **54**, 526f.
27. M. M. Potashnikov, *Zh. Prikl. Khim.*, **33**, 223 (1960); *Chem. Abstr.*, **54**, 10283d.
28. M. M. Potashnikov, *Zh. Prikl. Khim.*, **34**, 700 (1961); *Chem. Abstr.*, **55**, 18075d.
29. H. Wille, R. Oberkobusch and L. Rappen, *Ger. Pat.* 1,110,644 (1961); *Chem. Abstr.*, **55**, 25214h.
30. G. N. Kulsrestha, G. S. Murty, A. R. Panicker, H. S. Rao and A. Lahiri, *J. Sci. Ind. Res. (India)*, **20D**, 108 (1961).
31. B. E. Kogan, *Koks Khim.*, No. 12, 48 (1961); *Chem. Abstr.*, **56**, 9025d.
32. G. Buchmann, *E. Ger. Pat.*, 23,129 (1962); *Chem. Abstr.*, **58**, 32446.
33. G. Buchmann, *Chem. Tech. (Berlin)*, **14**, 741 (1962); *Chem. Abstr.*, **58**, 11147e.
34. G. Buchmann, *Wiss. Z. Tech. Hochsch. Chem. Leuna-Merseburg*, **4**, 235 (1963); *Chem. Abstr.*, **59**, 3685d.
35. S. Malankowski, *Przem. Chem.*, **42**(9), 497 (1963); *Chem. Abstr.*, **60**, 332d.
36. E. Proksch, *Oesterr. Chem.-Ztg.*, **67**(4), 105 (1966); *Chem. Abstr.*, **64**, 19251h.
37. B. E. Kogan, A. M. Zubok, E. I. Berkutoua and B. E. Kotlik, *Koks Khim.* (**10**) 40 (1968); *Chem. Abstr.*, **70**, 87506.
38. H. Pichler and P. Hennenberger, *Brennst. Chem.*, **50**(11), 341 (1969); *Chem. Abstr.*, **72**, 34138.
39. L. I. Mariich and Zh. K. Lenkevich, *Koks Khim.*, No. 7, 32 (1973); *Chem. Abstr.*, **80**, 5617.
40. G. R. Clemo, *Tetrahedron*, **29**(23), 3987 (1973).
41. J. Vymetal, *Erdöl, Kohle, Erdgas, Petrochem. Brennst. Chem.*, **27** (1), 8 (1974); *Chem. Abstr.*, **81**, 138391.
42. O. G. Vitzthum, P. Werkhoff. and P. Hubert, *J. Argic. Food Chem.*, **23**(5), 999 (1975).
43. Z. Fujinaga and N. Yoshida, *Yakugaku Zasshi*, **63**, 489 (1943); *Chem. Abstr.*, **44**, 7044i.
44. Y. Fushizaki, *Technol. Rept. Osaka Univ.*, **1**, 309 (1951); *Chem. Abstr.*, **46**, 7746i.
45. E. Demole and D. Berthet, *Helv. Chim. Acta*, **55**(6), 1866 (1972).
46. A. V. Kotova, L. N., Tokareva, A. Ya. Lanchuk and I. D. Leonov, *Tr. Inst. Khim. Nefti Prir. Solei, Akad. Nauk. Kaz. SSR*, No. 3, 100 (1970); *Chem. Abstr.*, **77**, 154651.

47. H. L. Lochte and H. W. H. Meyer, *J. Amer. Chem. Soc.*, **78**, 2150 (1956).
48. S. L. Gusinskaya, *Nauchn. Tr. Tashk. Gos. Univ.*, No. 399, 54 (1970); *Chem. Abstr.*, **78**, 32268.
49. E. J. Poth, W. A. Schulze, W. A. King, W. C. Thompson, W. M. Slagle, W. W. Floyd and J. R. Bailey, *J. Amer. Chem. Soc.*, **52**, 1239 (1930).
50. E. V. Brown, *Tob. Health Workshop Conf., Proc., 3rd*, 158 (1972). *Chem. Abstr.*, **79**, 50794.
51. E. V. Brown and I. Ahmad, *Phytochemistry*, **11**(12), 3485 (1972).
52. S. L. Gusinskaya, *Neftekhim. Akad. Nauk. Turkm. SSR*, **1963**, 126; *Chem. Abstr.*, **60**, 13069h.
53. S. L. Gusinskaya, *Dokl. Akad. Nauk Usbek. SSR*, No. 11, 33 (1958); *Chem. Abstr.*, **53**, 12643e.
54. V. G. Ben'kovskii, A. Ya. Baikova, N. S. Lyubopytova, Yu. N. Popov, E. A. Kruglov, A. I. Stekhun and F. N. Latypova, *Neftekhimiya*, **14**(6), 891 (1974); *Chem. Abstr.*, **82**, 127279.
55. R. F. Cane, *Papers Proc. Roy. Soc. Tasmania*, **1941**, 55 (Pub. 1942); *Chem. Abstr.*, **38**, 6357.
56. G. Neurath and M. Duenger, *Beitr. Tabakforsch.*, **5**(1), 1 (1969); *Chem. Abstr.*, **72**, 11072.
57. B. Kh. Zharekeev, Kh. N. Khashimov, M. V. Telezhenetskaya and S. Yu. Yunusov, *Khim. Prir. Soedin.*, **10**(2), 264 (1974); *Chem. Abstr.*, **81**, 13681.
58. K. Chmel and V. Chmeloya-Hlauata, *J. Chromatogr.*, **118**(2), 276 (1976).
59. J. Le Men, *Bull. Soc. Chim. Fr.*, **1950**, 599.
60. F. A. L. Anet and L. Marion, *Chem. Ind. (London)*, **1954**, 1232.
61. F. A. L. Anet and L. Marion, *Can. J. Chem.*, **33**, 849 (1955).
62. B. P. Moore and L. Marion, *Can. J. Chem.*, **31**, 952 (1953).
63. L. Marion and R. H. F. Manske, *Can. J. Res.*, **20B**, 153 (1942).
64. N. Yu. Novgorodova, S. Kh. Maekh and S. Yu. Yunusov, *Khim. Prir. Soedin.*, No. 2, 196 (1973); *Chem. Abstr.*, **79**, 32150.
65. E. Spath and J. Pikl, *Ber.*, **62B**, 2244 (1929).
66. E. Spath and J. Pikl, *Monatsh.*, **55**, 352 (1930).
67. M. F. Bartlett, D. F. Dickel and W. I. Taylor, *J. Amer. Chem. Soc.*, **80**, 126 (1958).
68. Z. Valenta, P. Deslongchamps, M. H. Rashid, R. H. Wightman and J. S. Wilson, *Tetrahedron Lett.*, **1963**, 1559.
69. Z. Valenta, P. Deslongchamps, M. H. Rashid, R. H. Wightman and J. S. Wilson, *Can. J. Chem.*, **44**(21), 2525 (1966).
70. J. Vymetal, *Chem. Listy*, **68**(12), 1234 (1974); *Chem. Abstr.*, **82**, 75217.
71. M. Conrad and L. Limpach, *Ber.*, **20**, 76 (1887).
72. A. Baeyer and O. R. Jackson, *Ber.*, **13**, 115 (1880).
73. O. Widman, *Ber.*, **19**, 255 (1886).
74. E. Wohnlich, *Arch. Pharm.*, **251**, 526 (1913); *Chem Abstr.*, **8**, 1110.
75. L. Knorr, *Ann.*, **236**, 94 (1886).
76. S. Gabriel and A. Thieme, *Ber.*, **52B**, 1079 (1919).
77. F. W. Neumann, N. B. Sommer, C. E. Kaslow, and R. L. Shriner, in *Organic Syntheses*, ed. H. Adkins, Vol. 26, p. 45 (1946), Wiley, New York.
78. H. Kammerer, L. Horner and H. Beck, *Chem. Ber.*, **91**, 1376 (1958).
79. D. S. Breslow, M. S. Bloom, J. C. Shivers, J. T. Adams, M. J. Weiss, R. S. Yost and C. R. Hauser, *J. Amer. Chem. Soc.*, **68**, 1232 (1946).
80. G. Beck, H. Heitzer and H. Holtschmidt, *Justus Liebigs Ann. Chem.*, **1975**, 415
81. G. I. Mikhailov, *Russ. Pat.*, 39,104 (1934); *Chem. Abstr.*, **30**, 3446[4].
82. Unpublished observations by the authors (1975).
83. J. Guareschi, *Ber.*, **26**, IV, 944 (1893).
84. J. Guareschi, *Atti Accad. Sci. Torino*, **28**, 719 (1893).
85. L. Knorr, *Ber.*, **16**, 2596 (1883).
86. A. J. Ewins, *J. Chem. Soc.*, **103**, 97 (1913).
87. E. Spath, *Monatsh.*, **40**, 93 (1919).
88. W. Robson, *Biochem. J.*, **22**, II, 1163 (1928).
89. L. Knorr, *Ann.* **245**, 357 (1888).
90. W. Von Miller, *Ber.*, **23**, 2252 (1890).
91. A. J. Ewins and H. King, *J. Chem. Soc.*, **103**, 104 (1913).
92. O. Starke, *Ber.*, **40**, 3425 (1907).
93. W. Koenigs, *Ber.*, **31**, 2364 (1898).
94. W. Koenigs, *Ber.*, **32**, 223 (1899).
95. E. Thielepape, *Ber.*, **55B**, 136 (1922).

96. S. Nagaoka, *Yakugaku Zasshi*, **81**, 479 (1961).
97. V. M. Rodionov and M. A. Berkenheim, *J. Gen. Chem. (USSR)*, **16**, 483 (1946); *Chem. Abstr.*, **41**, 966.
98. E. V. Brown, A. C. Plasz, R. Isbrandt and H. H. Baver, *Org. Prep. Proced. Int.*, **6**(5), 239 (1974).
99. E. Fischer and H. Kuzel, *Ber.*, **16**, 163 (1883).
100. E. Jacobsen and K. L. Reimer, *Ber.*, **16**, 1082 (1883).
101. B. Heymann and W. Koenigs, *Ber.*, **21**, 1424 (1888).
102. W. H. Mills and R. Raper, *J. Chem. Soc.*, **127**, 2466 (1925).
103. E. Spath, G. Kubiczek and E. Dubensky, *Ber.*, **74B**, 873 (1941).
104. E. Von Crabski, *Ber.*, **35**, 1956 (1902).
105. G. Gasda, *Ber.*, **38**, 3699 (1905).
106. R. C. Fuson, A. P. Kosacik and J. T. Eaton, *J. Amer. Chem. Soc.*, **55**, 3799 (1933).
107. R. C. Fuson, L. L. Alexander, E. Ellingboe and A. Hoffman, *J. Amer. Chem. Soc.*, **58**, 1979 (1936).
108. S. Biniecki and W. Modrzejewska, *Acta Pol. Pharm.*, **25**(3), 213, (1968); *Chem. Abstr.*, **70**, 28795.
109. E. Jantzen, *Dechema-Monographie*, No. 48, p. 135, Verlag Chemie, Berlin, 1932.
110. A. C. Plasz, E. V. Brown and H. H. Bauer, *J. Chem. Soc. Chem. Commun.*, **1972**, 527.
111. W. Borsche and H. Groth, *Ann.*, **549**, 238 (1941).
112. (a) Ashland Oil Inc., *Fr. Pat.* 2,208,864 (1974); *Chem. Abstr.*, **82**, 139603.
(b) D. K. Chapman, J. W. Newman and W. S. Green, *U.S. Pat.* 3,718,704; *Chem. Abstr.*, **78**, 147547 (1973).
113. D. M. Fenton, *U.S. Pat.* 3,825,545 (1974); *Chem. Abstr.*, **81**, 105315.
114. F. Bertini, T. Caronna, A. Citterio, L. Grossi and F. Minisci, *Chim. Ind. (Milan)*, **56**(4), 272 (1974).
115. M. G. Reinecke, G. Grins, L. R. Kray and R. F. Francis, *Ann. N.Y. Acad. Sci.*, **145**(1), 116 (1967).
116. G. A. Collins, *Brit. Pat.* 845,562 (1960); *Chem. Abstr.*, **55**, 5543f.
117. C. R. Wagner, *U.S. Pat.* 2,592,625 (1952); *Chem. Abstr.*, **47**, 6446g.
118. G. Pieper and R. Wegler, *Ger. Pat.* 831,099 (1952); *Chem. Abstr.*, **52**, 92238.
119. C. Schuster, *Ger. Pat.* 858,698 (1952); *Chem. Abstr.*, **52**, 5484b.
120. S. F. Orochena and W. M. Kutz, *U.S. Pat.* 2,510,134 (1950); *Chem. Abstr.*, **44**, 7354i.
121. H. J. Steinbach and G. Buchmann, *Z. Chem.*, **2**, 339 (1962); *Chem. Abstr.*, **59**, 1587f.
122. H. Gilman and S. M. Spatz, *J. Amer. Chem. Soc.*, **63**, 1553 (1941).
123. W. Oldham and I. B. Johns, *J. Amer. Chem. Soc.*, **61**, 3289 (1939).
124. K. Ziegler and H. Zeiser, *Ann.*, **485**, 174 (1931).
125. J. J. Eisch and D. R. Comfort, *J. Organomet. Chem.*, **43**(2), C17 (1972).
126. (a) J. J. Eisch and D. R. Comfort, *J. Org. Chem.*, **40**(16), 2288 (1975).
(b) D. R. Comfort, *Diss. Abstr. Int. B.*, **34** (2), 590 (1973); *Chem. Abstr.*, **79**, 136253.
(c) J. J. Eisch and D. R. Comfort, *J. Organomet. Chem.*, **38**(2), 209 (1972).
127. E. D. Thorsett and F. R. Stermitz, *J. Heterocycl. Chem.*, **10**(2), 243 (1973).
128. E. C. Taylor and S. F. Martin, *J. Amer. Chem. Soc.*, **94** (8), 2874 (1972).
129. E. C. Taylor and S. F. Martin, *J. Amer. Chem. Soc.*, **96**(26), 8095 (1974).
130. T. Kudo, A. Nose, and M. Hamana, *Yakugaku Zasshi*, **95**(5), 521 (1975); *Chem. Abstr.*, **83**, 146716.
131. C. E. Crawforth, C. A. Russell and O. Meth-Cohn, *J. Chem. Soc. D*, **1970**, 1406.
132. C. E. Crawforth, O. Meth-Cohn and C. A. Russell, *J. Chem. Soc., Perkin Trans. 1*, **1972**, 1176.
133. G. Magnus and R. Levine, *J. Org. Chem.*, **22**, 270 (1957).
134. G. A. Russell and S. A. Weiner, *J. Org. Chem.*, **31**, 248 (1966).
135. A. E. Chichibabin, *Ger. Pat.* 676,144 (1939); *Chem. Abstr.*, **33**, 6345^6.
136. P. H. Dirstine and F. W. Bergstrom, *J. Org. Chem.*, **11**, 55 (1946).
137. D. E. Ames, C. S. Franklin and T. F. Grey, *J. Chem. Soc.*, **1956**, 3079.
138. B. A. Tertov and S. E. Panchenko, *Zh. Obshch. Khim.*, **33**(4), 1277 (1963).
139. G. Buchmann and H. J. Steinbach, *J. Prakt. Chem.*, **28**(1-2), 82 (1965); *Chem. Abstr.*, **62**, 146256.
140. F. M. Elkobaisi and W. J. Hickinbottom, *J. Chem. Soc.*, **1960**, 1286.

141. M. Z. A. Badr and H. A. H. El-Sherief, *Can. J. Chem.*, **50**(2), 259 (1972).
142. M. H. Palmer and P. S. McIntyre, *Tetrahedron Lett.*, **1968**, 2147.
143. K. C. Bass and P. Nababsing, *J. Chem. Soc. C*, **1969**, 388.
144. (a) K. C. Bass and P. Nababsing, *J. Chem. Soc. C*, **1972**, 2169. (b) B. McIntosh, *Ph.D. Thesis*, City University, London, 1973.
145. B. M. Bertilsson, B. Gustafsson, I. Kuhn and K. Torssell, *Acta Chem. Scand.*, **24**(10), 3590 (1970).
146. F. Minisci and O. Porta, in *Advances in Heterocyclic Chemistry*, ed. A. R. Katritzky and A. J. Boulton, Vol. 16, pp. 123–180, Academic Press, New York, San Francisco and London, 1974.
147. T. Caronna, G. P. Gardini and F. Minisci, *J. Chem. Soc., Chem. Commun.*, **1969**, 201.
148. F. Minisci, R. Galli, M. Cerere, V. Malatesta and T. Caronna, *Tetrahedron Lett.*, **1968**, 5609.
149. F. Minisci, R. Galli, V. Malatesta and T. Caronna, *Tetrahedron*, **26**(17), 4083 (1970).
150. G. P. Gardini and F. Minisci, *Ann. Chim. (Rome)*, **60**(10–11), 746 (1970); *Chem. Abstr.*, **74**, 87128.
151. F. Minisci, R. Bernardi, P. Bertini, R. Galli and M. Perchinunno, *Tetrahedron*, **27**(15), 3575 (1971).
152. F. Minisci, F. Bertini, R. Galli and A. Quilico, (a) *Ger. Offen.* 2,153,234 (1972); *Chem. Abstr.*, **77**, 48278; (b) *Ital. Pat.* 906,418 (1972), *Chem. Abstr.*, **83**, 58667.
153. F. Bertini, T. Caronna, R. Galli, F. Minisci and O. Porta, *Chim. Ind. (Milan)*, **54**(5), 425 (1972).
154. R. Galli, M. Pershinunno and R. Bernardi, *Chem. Ind. (Milan)*, **54**(12), 1067 (1972); *Chem. Abstr.*, **78**, 97537.
155. A. Clerici, F. Minisci and O. Porta, *Tetrahedron*, **29**(18), 2775 (1973).
156. M. Kahn, *Ber.*, **18**, 3361 (1885).
157. M. L. Simon, *Ann. Chim. Phys.*, **9**(VII Series), 433 (1896).
158. F. A. Al-Tai, G. Y. Sarkis and J. M. Al-Janabi, *Bull. Coll. Sci. Univ. (Baghdad)*, **9**, 55 (1966); *Chem. Abstr.*, **68**, 39436.
159. W. Mathes and W. Savermilch, *Chem. Ber.*, **90**, 758 (1957).
160. A. Skita and C. Wulff, *Ber.*, **59B**, 2683 (1926).
161. G. Ornstein, *Ber.*, **40**, 1088 (1906).
162. F. S. Beattie, *Amer. Chem. J.*, **40**, 425 (1908).
163. Z. von Jakubowski, *Ber.*, **43**, 3026 (1910).
164. P. Jacquignon, N. P. Buu-Hoi and M. Dufour, *Bull. Soc. Chim. Fr.*, **1966**, 2765.
165. N. P. Buu-Hoi and P. Jacquignon, *Bull. Soc. Chim. Fr.*, **1958**, 1567.
166. N. Okuda, *Yakugaku Zasshi.*, **71**, 1275 (1951); *Chem. Abstr.*, **46**, 6128g.
167. R. von Walther, *J. Prakt. Chem.*, **67**, 504 (1903).
168. C. Englelhard, *J. Prakt. Chem.*, **57**, 467 (1898).
169. S. Niementowski and B. Orzechowski, *Ber.*, **28**, 2809 (1895).
170. J. Slouka and P. Pec, *Acta Univ. Palacki. Olomuc. Fac. Rerum. Nat.*, **21**, 243 (1966).
171. L. Reher, *Ber.*, **20**, 2734 (1887).
172. L. Reher, *Ber.*, **19**, 2995 (1886).
173. E. E. Blaise and M. Maire, *C. R. Acad. Sci.*, **144**, 93 (1907).
174. E. E. Blaise and M. Maire, *Bull. Soc. Chim. Fr.*, **3**, 667 (1908).
175. E. Rrosenhauer and T. Grafenberger, *J. Prakt. Chem.*, **108**, 91 (1924).
176. P. A. Claret and G. H. Williams, *J. Chem. Soc. C*, **1969**, 146.
177. J. Kuthan, N. V. Koshmina, J. Palacek and V. Skala, *Collect. Czech. Chem. Commun.*, **35**, 2787 (1970).
178. P. A. Claret, A. G. Osborne and G. H. Williams, previously unpublished results.
179. G. Heller and A. Sourlis, *Ber.*, **41**, 2692 (1908).
180. J. Tafel, *Ber.*, **27**, 824 (1894).
181. G. L. Ciamician and A. Piccinini, *Ber.*, **29**, 2465 (1896).
182. G. L. Ciamician and A. Piccinini, *Gazz. Chim. Ital.*, **27**(I), 69 (1897).
183. H. O. Jones and P. E. Evans, *J. Chem. Soc.*, **99**, 334 (1911).
184. M. G. Edwards, R. E. Garrod and H. O. Jones, *J. Chem. Soc.*, **101**, 1376 (1912).
185. R. E. Garrod, H. O. Jones and P. E. Evans, *J. Chem. Soc.*, **101**, 1389 (1912).
186. J. Meisenheimer and M. Schutze, *Ber.*, **56B**, 1353 (1923).
187. J. Meisenheimer, E. Stotz and K. Bauer, *Ber.*, **58B**, 2320 (1925).

188. W. R. Vaughan, in *Organic Syntheses*, ed. E. C. Horning, Collect. Vol. III, p. 329, Wiley, New York, 1955.
189. D. Craig, *J. Amer. Chem. Soc.*, **60**, 1458 (1938).
190. C. Engler and P. Riehm, *Ber.*, **18**, 2245 (1885).
191. I. Levin and P. Riehm, *Ber.*, **19**, 1394 (1886).
192. P. Riehm, *Ann.*, **238**, 1 (1887).
193. E. Knoevenagel and H. Bahr, *Ber.*, **55**, 1912 (1922).
194. E. Knoevenagel and O. Goos, *Ber.*, **55**, 1929 (1922).
195. E. Knoevenagel, *Ber.*, **56**, 2414 (1923).
196. R. C. Elderfield and J. R. McCarthy, *J. Amer. Chem. Soc.*, **73**, 975 (1951).
197. Knoll and Co., *Ger. Pat.* (a) 363,582 (1921) and (b) 363,583 (1921).
198. G. Reddelien and A. Thurm, *Ber.*, **65**, 1511 (1932).
199. H. Nozaki, Y. Yamamoto and R. Noyori, *Tetrahedron Lett.*, **1966**, 1123.
200. Y. Ogata, A. Kawasaki and S. Suyama, *Tetrahedron*, **25**(6), 1361 (1969).
201. H. Gilman, J. Eisch and T. S. Soddy, *J. Amer. Chem. Soc.*, **81**, 4000 (1959).
202. H. Gilman, J. L. Towle and R. K. Ingham, *J. Amer. Chem. Soc.*, **76**, 2920 (1954).
203. S.-I. Huzise and K. Tiba, *Bull. Chem. Soc. Jap.*, **14**, 478 (1939); *Chem. Abstr.*, **34**, 1987[8].
204. D. Craig, *U.S. Pat.* 2,095,126 (1937); *Chem. Abstr.*, **31**, 8550[8].
205. A. E. Chichibabin, *Bull. Soc. Chim. Fr.*, **3**(5), 1607 (1936).
206. F. W. Bergstrom, *J. Amer. Chem. Soc.*, **53**, 4065 (1931).
207. J. D. Kendall and H. O. Edwards, *Brit. Pat.* 618,894 (1949); *Chem. Abstr.*, **43**, 5807f.
208. T. Yoshikawa, *Yakugaku Zasshi*, **81**, 1601 (1961).
209. G. Heller, W. Dietrich and G. Reichardt, *J. Prakt. Chem.*, **118**(2), 138 (1928).
210. M. E. C. Biffin, G. Bocksteiner, J. Miller and D. B. Paul, *Aust. J. Chem.*, **27**(4), 789 (1974).
211. S. Kozuka, T. Akasaka, S. Furumai and S. Oae, *Chem. Ind. (London)*, **1974**, 452.
212. R. K. Hill and G. R. Newkome, *Tetrahedron Lett.*, No. 49, 5059 (1968).
213. (a) F. R. Stermitz, C.-C. Wei and C. M. O'Donnell, *J. Amer. Chem. Soc.*, **92**(9), 2745 (1970). (b) F. R. Stermitz, C.-C. Wei and W. H. Huang, *J. Chem. Soc., Chem. Commun.*, **1968**, 482.
214. C.-C.Wei, *Ph.D. Thesis*, Colorado State University, 1969; *Diss. Abstr. Int. B*, **31**(3), 118 (1970); *Chem. Abstr.*, **76**, 59818.
215. H. Nozaki, M. Kato, R. Noyori and M. Kawanisi, *Tetrahedron Lett.*, No. 43, 4259 (1967).
216. R. Noyori, M. Kato, M. Kawanisi and H. Nozaki, *Tetrahedron*, **25**(5), 1125 (1969).
217. E. J. Zobian, W. S. Kelley and H. C. Dunathan, *J. Org. Chem.*, **29**(3), 584 (1964).
218. C. F. Schwender and J. Shavel, Jr., *U.S. Pat.* 3,936,461 (1976); *Chem. Abstr.*, **84**, 164637.
219. R. A. Cutler, A. R. Surrey and J. B. Cloke, *J. Amer. Chem. Soc.*, **71**, 3375 (1949).
220. A. R. Surrey and R. A. Cutler, *U.S. Pat.* 2,838,514 (1958); *Chem. Abstr.*, **52**, 15820d.
221. W. E. Parham, R. W. Davenport and J. B. Biasotti, (a) *Tetrahedron Lett.*, **1969**, 557. (b) *J. Org. Chem.*, **35**(11), 3775 (1970).
222. C. W. Rees and C. E. Smithen, *Chem. Ind. (London)*, **1962**, 1022.
223. G. A. Collins, *Brit. Pat.* 850,405 (1960); *Chem. Abstr.*, **55**, 8436i.
224. M. Avramoff and Y. Sprinzak, *J. Amer. Chem. Soc.*, **78**, 4090 (1956).
225. T. Kato and T. Niitsuma, *Yakugaku Zasshi*, **44**(6), 766 (1974).
226. W. Mathes and A. Wolf, (a) *U.S. Pat.*, 3,042,678 (1962); *Chem. Abstr.*, **57**, 15082e; (b) *Ger. Pat.*, 1,198,366 (1965); *Chem. Abstr.*, **63**, 14825c.
227. R. Stroh and W. Hahn, *Ann.*, **623**, 176 (1959).
228. W. A. Ayer and G. G. Inverach, *Tetrahedron Lett.*, **1960**, 19.
229. Mme. J. and J. Martinet, *Bull. Soc. Chim. Fr.*, **1948**, 71.
230. S. Malanowski, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **9** (1961), (a) 71; (b) 77; (c) 83; *Chem. Abstr.*, **58**, 10746a, 10790c, 10790d.
231. B. Malanowska and J. Wecsile, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **12**(4), 239 (1964); *Chem. Abstr.*, **61**, 6418d.
232. A. Mueller, *Seifen, Oele, Fette, Wasche*, **101**(1), 11 (1975); *Chem. Abstr.*, **82**, 144817.
233. W. A. Felsing and B. S. Biggs, *J. Amer. Chem. Soc.*, **55**, 3624 (1933).
234. R. Riccardi and M. Bresesti, *Ann. Chim. (Rome)*, (a) **49**, 1891 (1959); *Chem. Abstr.*, **54**, 17001i; (b) *Ann. Chim. (Rome)*, **48**, 826 (1958).
235. J. H. Markgraf and R. J. Katt, *Tetrahedron Lett.*, **1968**, 6067.
236. D. Berry, K. Bukka and R. S. Satchell, *J. Chem. Soc., Perkin Trans. 2*, **1976**, 89.

237. M. A. G. Rau and B. N. Narayanaswamy, *Z. Phys. Chem.*, **B26**, 32 (1934).
238. C. G. LeFevre and R. J. W. LeFevre, *J. Chem. Soc.*, **1935**, 1470.
239. M. T. Rogers and T. W. Campbell, *J. Amer. Chem. Soc.*, **75**, 1209 (1953).
240. C. W. N. Cumper, D. G. Redford and A. I. Vogel, *J. Chem. Soc.*, **1962**, 1176.
241. A. Waksmunozki, *Ann. Univ. Mariae Curie-Sklodowska*, (a) Sect. AA, **1**, 7 (1948); *Chem. Abstr.*, **43**, 2845e; (b) Sect. AA, **4**, 47 (1949, pub. 1951); *Chem. Abstr.*, **46**, 69066.
242. M. M. Potashnikov and I. G. Belavina, *Zh. Prikl. Khim.*, **38**(8), 1824 (1965); *Chem. Abstr.*, **63**, 14096e.
243. M. M. Potashnikov and I. G. Belavina, *Zh. Prikl. Khim.*, **38**(7), 1585 (1965).
244. L. Sh. Nasibullina and I. A. Fakhretdinov, *Khim. Vysokomol. Soedin. Neftekhim.*, **1973**, 19; *Chem. Abstr.*, **81**, 17374.
245. V. G. Ben'Kovskii, L. Sh. Nasibullina and I. A. Fakretdinov, *Zh. Fiz. Khim.*, **48**(6), 1603 (1974); *Chem. Abstr.*, **81**, 159720.
246. L. V. Haley and H. F. Hameka, *J. Amer. Chem. Soc.*, **96**(7), 2020 (1974).
247. W. Schaaffs, *Z. Phys. Chem.*, **144**, 28 (1944); *Chem. Abstr.*, **44**, 7064h.
248. (a) Y. Kawazoe, M. Ohnishi and Y. Yoshioka, *Chem. Pharm. Bull. (Tokyo)*, **15**(8), 1225 (1967). (b) A. I. Shatenshtein, *Dokl. Akad. Nauk SSSR*, **60**, 1029 (1950); *Chem. Abstr.*, **44**, 5194c.
249. N. N. Zatsepina, A. V. Kirova and I. F. Tupitsyn, *Reakts. Sposobn. Org. Soedin.*, **5**(1), 70 (1968); *Chem. Abstr.*, **69**, 76469.
250. (a) N. N. Zatsepina, I. F. Tupitsyn, V. P. Dushina, Yu. M. Kapustin and Yu. L. Kaminskii, *Reakts. Sposobn. Org. Soedin.*, **9**(3), 745 (1972); *Chem. Abstr.*, **78**, 147198. (b) N. N. Zatsepina, I. F. Tupitsyn, A. V. Kirova and A. I. Belyashova, *Reakts. Sposobn. Org. Soedin.*, **6**(1), 257 (1969); *Chem. Abstr.*, **71**, 101158.
251. W. N. White and D. Lazdins, *J. Org. Chem.*, **34**(9), 2756 (1969).
252. C. Weiss, F. Hoeppner, S. Becker and W. Blaschke, *Tetrahedron*, **29**(19), 3071 (1973).
253. T. C. Beck and W. J. Pope, *Proc. Chem. Soc.*, **23**, 15 (1907).
254. W. J. Pope and J. Read, *Proc. Chem. Soc.*, **26**, 251 (1910); *J. Chem. Soc.*, **97**, 2199 (1910).
255. J. Thomas, *Proc. Chem. Soc.*, **28**, 108 (1912); *J. Chem. Soc.*, **101**, 725 (1912).
256. J. Meisenheimer and M. Schutze, *Ber.*, **56B**, 1353 (1923).
257. W. E. Parham and P. E. Olson, *J. Org. Chem.*, **39**, 3407 (1974).
258. W. E. Parham and Y. Sayed, *J. Org. Chem.*, **40**(21), 3142 (1975).
259. A. Milossky, *Caryologia*, **12**, 439 (1960); *Chem. Abstr.*, **58**, 4979c.
260. F. E. Denny, *U.S. Pat.*, 2,692,822 (1954); *Chem. Abstr.*, **49**, 2014g.
261. M. Simonet and G. Igolen, *C. R. Soc. Biol.*, **138**, 234 (1944); *Chem. Abstr.*, **39**, 3812^5.
262. W. S. Emerson and R. A. Heimsch, *U.S. Pat.*, 2,665,303 (1954); *Chem. Abstr.*, **48**, 4758g.
263. R. C. Bushland and W. V. King, *U.S. Dept. Agr. Bur. Entemol. Plant Quarantine Paper No. E-585*, 15 pp., Jan. 1943; *Chem. Abstr.*, **37**, 2111^8.
264. W. N. Oldham, *Iowa State Coll. J. Sci.*, **14**, 69 (1939); *Chem. Abstr.*, **34**, 6002^7.
265. G. Buchmann, I. *Wiss. Z. Tech. Hochsch. Chem. Leuna-Merseberg*, **4**(3/4), (1962) (a) 213; (b) 219.
266. G. Ortner and F. Grewe, *Belg. Pat.*, 625,409 (1963); *Chem. Abstr.*, **61**, 16052h.
267. S. Steinberger, *U.S. Pat.* 3,111,492 (1963); *Chem. Abstr.*, **60**, 3931a.
268. B. Muench, *Progressive Fish Culturist*, **20**, 42 (1958); *Chem. Abstr.*, **53**, 20585g.
269. L. L. Marking, *Invest. Fish Control*, No. 23, 10 pp. (1969); *Chem. Abstr.*, **71**, 19894.
270. D. O. Locke, *Invest. Fish Control*, No. 24, 5 pp. (1969); *Chem. Abstr.*, **71**, 19895.
271. E. G. Trams and E. A. B. Brown, *Life Sci.*, **9**(1), (Pt. 2), 27 (1970); *Chem. Abstr.*, **72**, 108413.
272. J. B. Sills, J. L. Allen, P. D. Hardman and C. W. Luhning, *Invest. Fish Control*, No. 55, 12 pp. (1973); *Chem. Abstr.*, **81**, 10127.
273. T. P. Strebkova and Zh. T. Dergaleva, *Rybn. Khoz. (Moscow)*, No. 9, 17 (1975); *Chem. Abstr.*, **84**, 162.
274. A. G. Yudin, A. N. Kost, E. K. Zolotaren and A. N. Mirza, *Vestn Moskov. Univ. Ser. Mat. Mekh. Astron., Fiz. Khim.*, **13**(2), 169 (1958); *Chem. Abstr.*, **53**, 8134i.
275. S. Sakai, K. Minoda, G. Saito, S. Akagi, A Ueno and F. Fukuoka, *Gann*, **46**, 605 (1955); *Chem. Abstr.*, **50**, 11526i.
276. L. Schmidt and E. Seeger, *Arzneim.-Forsch.*, **6**, 22 (1956); *Chem. Abstr.*, **50**, 12308e.
277. L. Schmidt, *Naunyn-Schmiedebergs Arch. Exp. Pathol. Pharmakol.*, **226**, 207 (1955); *Chem. Abstr.*, **50**, 486i.

278. L. Ruzicka, M. W. Goldberg and M. Hurbin, *Helv. Chim. Acta*, **16**, 1335 (1933).
279. A. V. Pamfilov, O. M. Dolgaya and L. P. Ostapova, *Electrokhim. Protsessy Uchastiem Org. Veshchestv.*, **1970**, 142; *Chem. Abstr.*, **74**, 18745.
280. A. V. Pamfilov, P. M. Mel'nik and O. E. Panchuk, *Zh. Prikl. Khim.*, **38**(3), 575 (1965); *Chem. Abstr.*, **62**, 15753g.
281. K. E. Langford, *Electroplat. Met. Finish.*, **9**, 39, 48 (1956).
282. J. Matulis and B. Zileniene, *Liet. TSR Mokslu Akad. Darbai, Ser. B*, No. 1, 71 (1966); *Chem. Abstr.*, **66**, 15912.
283. M. Zukaite, J. Vegys, A. Bodnevas and J. Matulis, *Liet. TSR Mokslu Akad. Darbai, Ser. B*, No. 1, 23 (1967); *Chem. Abstr.*, **67**, 104538.
284. M. Vainilaviciene, A. Bodnevas and J. Matulis, *Liet. TSR Mokslu Akad. Darbai, Ser. B*, No. 2, 49 (1969); *Chem. Abstr.*, **71**, 108304.
285. L. W. Clark, *J. Phys. Chem.*, **62**, 633 (1958).
286. H. Kato and N. Maekawa, *Ger. Pat.* 2,441,961 (1975); *Chem. Abstr.*, **83**, 29201.
287. W. A. Marshall and C. F. Steininger, *U.S. Pat.* 2,766,205 (1956); *Chem. Abstr.*, **51**, 22686.
288. R. Bartonicek and J. Nemcova, *Korose Ochr. Mater.* **1962**, 85; *Chem. Abstr.*, **58**, 12233e.
289. T. P. Hoar *Pittsburgh Int. Conf. Surface Reactions*, **1948**, 127; *Chem. Abstr.*, **43**, 2917e.
290. I. M. Stepanenko and N. A. Saverina, *Izv. Vyssh. Ucheb. Zaved. Mashinostr.*, No. 12, 105 (1966); *Chem. Abstr.*, **67**, 45744.
291. H. Miyazaki and M. Takahashi, *Jap. Pat.*, 74 04445 (1974).
292. L. D. Gluzman, V. M. Pospelov and M. K. Tomashevskaya, *Russ. Pat.*, 202,910 (1967); *Chem. Abstr.*, **69**, 21004.
293. J. L. Allen and J. B. Sills, *J. Ass. Offic. Anal. Chem.*, **53**(1), 20 (1970); *Chem. Abstr.*, **72**, 77550.
294. J. L. Allen and J. B. Sills, *J. Ass. Offic. Anal. Chem.*, **53**(6), 1170 (1970); *Chem. Abstr.*, 74, 10242.
295. C. W. Luhning and P. D. Harman, *J. Fish. Res. Bd. Can.*, **28**(1), 113 (1971); *Chem. Abstr.*, **74**, 75302.
296. T. Jasinski, *Acta Pol. Pharm.*, **14**, 45 (1957); *Chem. Abstr.*, **51**, 15338a.
297. C. B. Riolo and T. F. Soldi, *Ann. Chim. (Rome)*, (a) **53**(11), 1574 (1963); *Chem. Abstr.*, **60**, 13932g. (b) **54**(5), 552 (1964); *Chem. Abstr.*, **61**, 6990c.
298. K. Nikolic and Z. Cupic, *Glas. Hem. Drus., Beograd*, **33**(8–10), 589 (1968); *Chem. Abstr.*, **72**, 136510.
299. S. Ono and J. Nakaya, *J. Electrochem. Soc. Jap.*, **23**, 547 (1955); *Chem. Abstr.*, **50**, 10564a.
300. W. R. Turner and J. T. Stock, (a) *J. Chem. Soc.*, **1965**, 1506. (b) W. R. Turner, *Ph.D. Thesis*, Univ. Connecticut 1964; *Diss. Abstr.*, **25**(8), 4379 (1965); *Chem. Abstr.*, **63**, 3623d.
301. L. J. E. Hofer and E. H. Bean, *Fuel*, **40**, 503 (1961).
302. D. Yamamoto, S. Wako and Y. Naka, *Nippon Kagaku Zasshi*, **85**(12), 851 (1964); *Chem. Abstr.*, **63**, 12405e.
303. K. Nikolic, *Acta Pharm. Jugoslav.*, **20**(1), 11 (1970); *Chem. Abstr.*, **73**, 91267.
304. J. H. Markgraff, R. J. Katt, W. L. Scott and R. N. Shefrin, *J. Org. Chem.*, **34**(12), 4131 (1969).
305. M. Wilk, P. Bluel and J. Rochlitz, *Justus Liebigs Ann. Chem.*, **712**, 84 (1968).
306. M. Wilk, H. Schwab and J. Rochlitz, *Justus Liebigs Ann. Chem.*, **698**, 149 (1966).
307. D. Sutherland and C. Compton, *J. Org. Chem.*, **17**, 1257 (1952).
308. (a) S. B. Knight, R. H. Wallick and C. Balch, *J. Amer. Chem. Soc.*, **77**, 2577 (1955). (b) B. Das, *J. Indian Chem. Soc.*, **46**(5), 479 (1969); *Chem. Abstr.*, **71**, 55168.
309. R. Riccardi and M. Bresesti, *Ann. Chim. (Rome)*, **48**, 826 (1958); *Chem. Abstr.*, **53**, 5829g.
310. (a) M. A. Shashidhar and K. S. Rao, *Curr. Sci. (India)*, **35**(9), 230 (1966); *Chem. Abstr.*, **65**, 3191e. (b) *Indian J. Phys.*, **41**(4), 299 (1967); *Chem. Abstr.*, **69**, 6685.
311. B. B. Bhowmik, D. C. Mukherjee and P. K. Srimani, *Indian J. Chem.*, **13**(12), 1314 (1975); *Chem. Abstr.*, **84**, 157592.
312. I. Ilmet and M. Krasij, *J. Phys. Chem.*, **70**(11), 3755 (1966).
313. T. I. Ershova, O. A. Ershov, V. I. Vysotskii and V. A. Stonik, *Opt. Spektrosk.*, **28**(1), 47 (1970); *Chem. Abstr.*, **72**, 105527.
314. A. A. Kane and I. F. Tupitsyn, *Tr. Gos. Inst. Prikl. Khim.*, No. 66, 107 (1970); *Chem. Abstr.*, **76**, 92296.
315. A. A. Kane and I. F. Tupitsyn, *Tr. Gos. Inst. Prikl. Khim.*, No. 66, 139 (1970); *Chem. Abstr.*, **76**, 92397.

316. H. Shindo and S. Tamura, *Pharm. Bull. (Japan)*, **4**, 292 (1956).
317. A. R. Katritzky and R. A. Jones, *J. Chem. Soc.*, **1960**, 2942.
318. A. Roders and H. H. Perkampus, *Z. Naturforsch.*, **18B**(8), 600 (1963); *Chem. Abstr.*, **59**, 13472d.
319. H. Shindo, *Chem. Pharm. Bull. (Tokyo)*, **8**, 845 (1960).
320. A. Lachowicz, A. Marzec and T. Mazonski, *Rocz. Chem.*, **41**(9), 1543 (1967); *Chem. Abstr.*, **69**, 2844.
321. H. Kamada, S. Tanaka, and K. Arakawa, *Bunseki Kagaku*, **3**, 399 (1954); *Chem. Abstr.*, **49**, 15638e.
322. S. Ghersetti, S. Giorgianni and G. Spunta, *Spectrosc. Lett.*, **6**(8), 505 (1973).
323. G. B. Bonino and R. A. Ansidei, *Mem. Accad. Sci. Inst. Bologna, Classe Sci. Fis.* [9], **1**, Sept., 7 pp. (18.2.34); *Chem. Abstr.*, **29**, 1712^{1}.
324. S. K. K. Jatkar, *Indian J. Phys.*, **10**, 23 (1936); *Chem. Abstr.*, **30**, 3723^{6}.
325. G. B. Bonino, R. Manzoni-Ansidei and M. Rolla, *Ricer. Sci.*, **8**(II), No. 5-6, 3 pp. (1937); *Chem. Abstr.*, **32**, 4846^{3}.
326. H. Luther and C. Reichel, *Z. Phys. Chem.*, **195**, 103 (1950); *Chem. Abstr.*, **44**, 9257e.
327. R. J. Pugmire, D. M. Grant, M. J. Robins and R. K. Robins, *J. Amer. Chem. Soc.*, **91**, 6381 (1969).
328. P. A. Claret and A. G. Osborne, *Spectrosc. Lett.*, **8**(6), 385 (1975).
329. M. Ohtsuru, K. Tori and H. Wantanabe, *Chem. Pharm. Bull. (Tokyo)*, **15**(7), 1015 (1967).
330. H. Rottendorf and S. Sternhell, *Aust. J. Chem.*, **17**(12), 1315 (1964).
331. P. A. Claret and A. G. Osborne, *Org. Magn. Reson.*, **8**, 147 (1976) and previously unpublished results.
332. M. R. Chakrabarty and E. S. Hanrahan, *J. Mol. Spectrosc.*, **30**(2), 348 (1969).
333. G. Barbieri, R. Benassi, P. Lazzeretti, L. Schenetti and F. Taddei, *Org. Mag. Reson.*, **7**(9), 451 (1975).
334. W. Seiffert, *Angew. Chem.*, **74**, 250 (1962).
335. R. Mondelli and L. Merlini, (a) *Nucl. Magn. Reson. Chem., Proc. Symp., Cagliari, Italy, 1964*, 243 (1965); *Chem. Abstr.*, **66**, 2078; (b) *Tetrahedron*, **22**(10), 3253 (1966).
336. I. N. Chernyuk, V. E. Prioan, V. A. Bazhutin and M. Yu. Kornilov, *Zh. Obshch. Khim.* **44**(7), 1584 (1974); *Chem. Abstr.*, **82**, 15847.
337. A. R. Garber, P. E. Garrou, G. E. Hartwell, M. J. Smas, J. R. Wilkinson and L. J. Todd, *J. Organomet. Chem.*, **86**(2), 219 (1975).
338. T. Schaefer, *Can. J. Chem.*, **39**, 1864 (1961).
339. J. Ronayne and D. H. Williams, *J. Chem. Soc. B*, **1967**, 805.
340. R. Pastor, J. Musso and A. Cambon, *Bull. Soc. Chim. Fr.*, **1973**, 3009, *Chem. Abstr.*, **81**, 2961.
341. G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, **66**, 2100 (1944).
342. D. F. Evans, *J. Chem Soc.*, **1959**, 2753.
343. E. Vanderdonckt and C. Vogels, *Spectrochim. Acta, A*, **27**(10), 2157 (1971).
344. I. Janic, in *Lumin. Cryst., Mol., Solutions, Proc. Int. Conf., 1972*, ed. F. Williams, p. 213, Plenum, New York, 1973; *Chem. Abstr.*, **79**, 47484.
345. I. Janic and M. Kakas, *Acta Phys. Pol. A*, **43**(6), 857 (1973); *Chem. Abstr.*, **79**, 85092.
346. S. D. Sample, D. A. Lightner, O. Buchardt and C. Djerrasi. *J. Org. Chem.*, **32** (4), 997 (1967).
347. P. M. Draper and D. B. MacLean, *Can. J. Chem.*, **46**(9), 1487 (1968).
348. T. S. Muraski and C. Djerassi, *J. Org. Chem.*, **33**(7), 2962 (1968).
349. C. W. Koch, R. M. Milberg and J. H. Markgraf, *J. Heterocycl. Chem.*, **10**(6), 973 (1973).
350. P. M. Draper and D. B. MacLean, *Can. J. Chem.*, **48**(5) (1970), (a) 738, (b) 746.
351. C. L. Lau, *Anal. Chim. Acta*, **22**, 239 (1960).
352. B. Zegalska, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **16**(7), (1968), (a) 357; *Chem. Abstr.*, **69**, 90235; (b) 335; *Chem. Abstr.*, **69**, 70487.
353. B. Malanowska and S. Malanowski, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **9**(3), 111 (1961); *Chem. Abstr.*, **62**, 13910d.
354. B. E. Kogan, *Pererab. Vydelenic Anal. Koksokhim. Prod.*, **1961**, 61; *Chem. Abstr.*, **59**, 12232h.
355. G. Buchmann, *E. Ger. Pat.* 17,585 (1959); *Chem. Abstr.*, **55**, 951i.
356. B. E. Kogan, P. D. Pistrova, and O. G. Neznamova, *Khim. Prod. Koksovaniya Uglei. Vostoka SSSR*, No. 5, 257 (1969); *Chem. Abstr.*, **75**, 78948.

357. B. E. Kogan, P. D. Pistrova, O. G. Neznamova, A. M. Zubok and E. I. Berkutova, *Koks Khim.*, No. 7, 42 (1969); *Chem. Abstr.*, **71**, 72744.
358. K. H. Engel, *U.S. Pat.* 2,456,774 (1948); *Chem. Abstr.*, **43**, 2241d.
359. I. G. Belavina and M. M. Potashnikov, *Zh. Prikl. Khim. (Leningrad)*, **41**(8), 1798 (1968); *Chem. Abstr.*, **70**, 23522.
360. M. M. Potashnikov and I. G. Belavina, *Russ. Pat.* 172,806 (1965); *Chem. Abstr.*, **64**, 716f.
361. V. A. Popov, Yu. V. Baboshin, I. G. Belavina, N. Kh. Cherkasov, *Uch. Zap. Sverdl. Gos. Pedagog. Inst.*, No. 153, 151 (1972); *Chem. Abstr.*, **83**, 118345.
362. F. Komatsu, *Kogyo Kagaku Zasshi*, **64**, 1076 (1961); *Chem. Abstr.*, **57**, 3718f.
363. V. A. Popov and I. G. Belavina, *Zh. Prikl. Khim. (Leningrad)*, **41**(8), 1802 (1968); *Chem. Abstr.*, **69**, 90316.
364. V. A. Popov and I. G. Belavina, *Uch. Zap. Sverdl. Gos. Pedagog. Inst.*, No. 74, 133 (1968); *Chem. Abstr.*, **73**, 76529.
365. K. H. Engel, *U.S. Pat.* 2,510,875 (1952); *Chem. Abstr.*, **47**, 4919i.
366. C. Golumbic and M. Orchin, *J. Amer. Chem. Soc.*, **72**, 4145 (1950).
367. C. Golumbic, *Anal. Chem.*, **24**, 1849 (1952).
368. A. G. Hill, E. C. Medcalf and W. M. Sisco, *U.S. Pat.* 2,660,581 (1953).
369. E. Soczewinski and J. Kuczynski, (a) *Chem. Anal. (Warsaw)*, **20**(5), 927 (1975); *Chem. Abstr.*, **84**, 65818; (b) **22**, 247 (1977). *Chem. Abstr.*, **87**, 123373.
370. V. K. Kondratov, N. D. Rus'yanova, T. M. Markacheva and Z. I. Chukhlova, *Zh. Prikl. Khim. (Leningrad)*, **44**(6), 1357 (1971); *Chem. Abstr.*, **75**, 91736.
371. F. E. Cislak and M. M. Otto, *U.S. Pat.* 2,432,064 (1947); *Chem. Abstr.*, **42**, 2289f.
372. D. Jerchel and H. Hippehen, *Ger. Pat.* 1,019,653 (1957); *Chem. Abstr.*, **54**, 1557i.
373. K. W. Wilson, F. E. Anderson and R. W. Donohoe, *Anal. Chem.*, **23**, 1032 (1951).
374. H. Bartels, *Z. Anorg. Allg. Chem.*, **350**(3–4), 143 (1967); *Chem. Abstr.*, **66**, 98809.
375. B. Kamienski, Z. Byco and B. Waligora, *Bull. Int. Acad. Polon. Sci. Classe Sci. Math. Nat. Ser. A*, No. 3–6A, 199 (1951. Pub. 1952); *Chem. Abstr.*, **48**, 3183g.
376. Yu. I. Chumakov and M. S. Alyab'eva, *Khim. Prom. Ukr.*, No. 6, 49 (1970); *Chem. Abstr.*, **75**, 38747.
377. Yu. I. Chumakov and M. S. Alyab'eva, *Khim. Prom. Ukr.*, No. 5, 53 (1970); *Chem. Abstr.*, **74**, 53478.
378. D. M. Jewel and G. K. Hartung *J. Chem. Eng. Data*, **9**(2), 297 (1964).
379. R. N. Fleck and C. G. Wright, *U.S. Pat.* 3,029,242 (1962); *Chem. Abstr.*, **57**, 12445b.
380. D. Brocco, A. Cimmino and M. Possanzini, *J. Chromatogr.*, **84**(2), 371 (1973).
381. H. J. Petrowitz, G. Pastuska and S. Wagner, *Chem.-Ztg.*, **89** (1), 7 (1965); *Chem. Abstr.*, 62, 11125c.
382. C. Troszkiewicz, J. Juwinski and W. Zielinski, *Chem. Anal. (Warsaw)*, **13**(1), 3 (1968); *Chem. Abstr.*, **69**, 24346.
383. Z. Gregorowicz, I. Baranowska, R. Baranowska and W. Karminski, *Chem. Anal. (Warsaw)*, **14**(4), 955 (1969); *Chem. Abstr.*, **72**, 18284.
384. R. A. Heacock and O. Hutzinger, *Mikrochim. Acta*, **2**(1), 101 (1975).
385. L. Zoccolillo, *Ann. Ist. Sup. Sanita*, **9**(Spec. No. 1), 409 (1973); *Chem. Abstr.*, **83**, 151514.
386. E. Soczewinski and W. Golkiewicz, *Chem. Anal. (Warsaw)*, **14**(3), 465 (1969); *Chem. Abstr.*, **71**, 74438.
387. H. J. Petrowicz, *Mitt. Deut. Ges. Holzforsch.*, No. 48, 57 (1961); *Chem. Abstr.*, **57**, 12947f.
388. E. Soczewinski, J. Kuczynski and M. Ciszewska, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **18**(7), 397 (1970); *Chem. Abstr.*, **74**, 35032.
389. E. Soczewinski and W. Maciejewicz, *Chem. Anal. (Warsaw)*, **15**(16), 1199 (1970); *Chem. Abstr.*, **74**, 91540.
390. E. Soczewinski and W. Maciejewicz, *Separ. Sci.*, **2**(3), 293 (1967); *Chem. Abstr.*, **68**, 18467.
391. E. Soczewinski and M. Przyborowska, *Chem. Anal. (Warsaw)*, **11**(5), 849 (1966); *Chem. Abstr.*, **66**, 111311.
392. A. Waksmunozki, E. Soczewinski and R. Aksanowski, *Chem. Anal. (Warsaw)*, **2**, 459 (1957); *Chem. Abstr.*, **52**, 12684b.
393. T. M. Markacheva and L. I. Kornilova, *Khim. Prod. Koksovaniya Uglei Vostoka SSSR, Poloch., Obrab. Ispol'z., Metody Anal., Vost. Nauchn.-Issled. Uglekhim. Inst. Sb. Statei*, No. 3, 320 (1965); *Chem. Abstr.*, **65**, 10c.

394. H. J. Petrowitz, *Chem.-Ztg.*, **85**, 143 (1961); *Chem. Abstr.*, **55**, 16551i.
395. A. M. Luly and K. Sakodynsky, *J. Chromatogr.*, **19**(3), 624 (1965).
396. E. Soczewinski and M. Jarzebska-Kowalczyk, *Ann. Univ. Mariae Curie-Skłodowska, Sect. D*, **28**, 13 (1973); *Chem. Abstr.*, **81**, 54910.
397. V. M. Nabivach and L. A. Venger, *Zh. Anal. Khim.*, **30**(3), 604 (1975).
398. H. Sato and M. Shimamine, *Eisei Shikensho Hokoku*, No. 82, 88 (1964); *Chem. Abstr.*, **65**, 8690a.
399. J. Janak and M. Hrivac, *Collect. Czech. Chem. Commun.*, **25**, 1557 (1960); *Chem. Abstr.*, **57**, 1560h.
400. V. I. Yakerson and L. I. Lafer, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1965**, 611; *Chem. Abstr.*, **63**, 3604c.
401. G. Alberini, V. Cantuti and G. Cartoni, *Gas Chromatogr. Proc. Int. Symp. (Eur.), 1966*, **6**, 258 (1967).
402. Le R. H. Klemm, J. Shabtai and F. H. W. Lee, *J. Chromatogr.*, **51**(3), 433 (1970).
403. A. L. Brown and K. R. Buck, *Chem. Ind. (London)*, **1961**, 714.
404. A. R. Cooper and C. W. P. Crowne, *Trans. Faraday Soc.*, **63**(2), 447 (1967).
405. L. A. Paquette, G. R. Krow and J. R. Malpass, *J. Amer. Chem. Soc.*, **91**(20), 5522 (1969).
406. W. W. Hanneman, *J. Gas Chromatogr.*, **1**(12), 18 (1963).
407. D. E. Durbin and A. Zlatkis, *Advan. Chromatogr., Proc. Int. Symp. 6th*, 159 (1970); *Chem. Abstr.*, **74**, 49403.
408. F. S. Fitzgerald, *Aust. J. Appl. Sci.*, **12**, 51 (1961).
409. J. Janák and M. Hřivác, *J. Chromatogr.*, **3**, 297 (1960).
410. W. Funasaka and T. Kosima, *Kogyo Kagaku Zasshi*, **64**, 769 (1961); *Chem. Abstr.*, **57**, 3717b.
411. V. Rezl, *Chem. Prumysl.*, **12**, 246 (1962); *Chem. Abstr.*, **57**, 7913e.
412. E. Proksch, *Oesterr. Chem.-Ztg.*, **67**(4), 105 (1966); *Chem. Abstr.*, **64**, 19251h.
413. T. M. Markacheva and L. I. Kornilova, *Khim. Prod. Koksovaniya Uglei Vostoka SSSR*, No. 4, 330 (1967); *Chem. Abstr.*, **68**, 88892
414. T. M. Markacheva, (a) *Khim. Prod. Koksovaniya Uglei Vostoka SSSR*, No. 5, 366 (1969); *Chem. Abstr.*, **74**, 144233; (b) No. 6, 220 (1970); *Chem. Abstr.*, **76**, 143238; (c) B. E. Kogan and P. D. Pistrova, No. 6(5), 86 (1970); *Chem. Abstr.*, **75**, 131521.
415. J. Neiser, *Ropa Uhlie*, **9**(6–7), 191 (1967); *Chem. Abstr.*, **68**, 4761a.
416. R. W. Frei, K. Beall and R. M. Cassidy, *Mikrochim. Acta*, **1974**, 859.
417. B. P. Lugovkin and E. T. Zemlyanitskaya, *Nauch. Rab. Inst. Okhr. Tr. Vses. Tsent. Soc. Prof. Soyuzov*, No. 53, 108 (1968); *Chem. Abstr.*, **71**, 104927.
418. S. Y. Chumakov, *Uch. Zap. Permsk. Gos. Ped. Inst.*, No. 28, 157 (1961); *Chem. Abstr.*, **58**, 4518g.
419. H. Suhr and U. Schoech, *Chem. Ber.*, **108** (11), 3469 (1975); *Chem. Abstr.*, **84**, 58223.
420. W. R. Vaughan, *Org. Synth.*, Collect., Vol. III, 329 (1955).
421. J. Craig, *J. Amer. Chem. Soc.*, **60**, 1485 (1938).
422. W. H. Mills and R. Raper, *J. Chem. Soc.*, **127**, 2466 (1925).
423. W. von Miller, *Ber.*, **24**, 1919 (1891).
424. S. Hoogewerff and W. A. van Dorp, *Ber.*, (a) **12**, 747 (1879); (b) **13**, 1640 (1880).
425. W. Koenigs, *Ber.*, (a) **12**, 983 (1879); (b) **13**, 911 (1880); (c) **14**, 98 (1881).
426. S. Hoogewerff and W. A. van Dorp, *Rec. Trav. Chim.*, **2**, 2 (1883).
427. Zd. H. Skraup, *Monatsh.*, **2**, 158 (1881).
428. W. von Miller, *Ber.*, **24**, 1906 (1891).
429. C. Beyer, *J. Prakt. Chem.*, **33**, 393 (1886).
430. O. Mumm and E. Herrendorfer, *Ber.*, **47**, 758 (1914).
431. O. Doebner and W. von Miller, *Ber.*, **18**, 1640 (1885).
432. O. Doebner and W. von Miller, *Ber.*, **15**(II), 3075 (1882).
433. J. P. Wibaut and H. Boer, (a) *Proc. Kon. Ned. Akad. Wetenschap.*, **53**, 19 (1950); *Chem. Abstr.*, **44**, 6860d; (b) *Rec. Trav. Chim.*, **74**, 241 (1955).
434. H. Boer, F. L. J. Sixma and J. P. Wibaut, *Rec. Trav. Chim.*, **70**, 509 (1951).
435. R. A. Glenn and J. R. Bailey, *J. Amer. Chem. Soc.*, **63**, 641 (1941).
436. S. Paraskewas, *Synthesis*, **1974**, 819.
437. F. Komatsu, *Muroran Kogyo Daigaku Kenkyu Hokoku*, **3**, 41 (1958); *Chem. Abstr.*, **53**, 13149f.

438. G. von Georgievics, *Monatsh.*, **12**, 309 (1891).
439. B. Hughes and H. Suschitzky, *J. Chem. Soc.*, **1965**, 875.
440. C. B. Biswell and W. V. Wirth, *U.S. Pat.* 2,109,951 (1938); *Chem. Abstr.*, **32**, 3419[9].
441. E. Bartholome, A. Kreyser, H. J. Nienbury, R. Sinn and K. Scherf, (a) *Ger. Pat.* 1,133,714 (1962); *Chem. Abstr.*, **57**, 16577b; (b) E. Bartholome, H. J. Nienbury, and K. Scherf, *Ger. Pat.* 1,119,842 (1960); *Chem. Abstr.*, **57**, 786b.
442. S. D. Sokolov, E. G. Tikhomirova and V. A. Kukhtin, *Zh. Org. Khim.*, **5**(10), 1894 (1969).
443. E. G. Lellmann and H. Alt, *Ann.*, **237**, 307 (1887).
444. A. N. Christyakov, A. K. Kuz'min, M. I. Bessonova and V. A. Proskiryakov, *USSR Pat.*, 457,701 (1975); *Chem. Abstr.*, **83**, 97056.
445. C. K. Cain, J. N. Plampin and J. Sam, *J. Org. Chem.*, **20**, 466 (1955).
446. H. Weidel, *Monatsh.*, **3**, 75 (1882).
447. E. S. Vassermann, *Tr. Dnepropetrov. Khim.-Tekhnol. Inst. Im. F. E. Dzerzhinskogo, Kafedra Org. Khim.*, **1938**, 68; *Referat. Zhur. Khim.*, **2**, No. 4, 56 (1939); *Chem. Abstr.*, **34**, 1020.
448. Z. von Yakubovskii, *Ber.*, **43**, 3026 (1910).
449. Zd. H. Skraup and P. Brunner, *Monatsh.*, **7**, 140 (1886).
450. R. A. Seibert, T. R. Norton, A. A. Benson and F. W. Bergstrom, *J. Amer. Chem. Soc.*, **68**, 2721 (1946).
451. G. Panajotow, *Ber.*, **20**, 32 (1887).
452. C. Riedel, *Ber.*, **16**, 1609 (1883).
453. K. Harz, *Ber.*, **18**, 3384 (1885).
454. J. Spady, *Ber.*, **18**, 3373 (1885).
455. G. Rhode, *Ber.*, **22**, 267 (1889).
456. Meister, Lucius and Brüning, Farbw., *Ger. Pat.* **35**, 133 (1886).
457. M. A. Dahlen and S. R. Detrick, *U.S. Pat.*, 2,109,957 (1938); *Chem. Abstr.*, **34**, 3424[b].
458. O. Doebner and W. von Miller, *Ber.*, **17**, (1884), (a) 1698; (b) 1712.
459. O. Doebner and W. von Miller, *Ber.*, **16**, 2464 (1883).
460. L. Monti, *Atti Accad. Naz. Lincei*, **18**, 505 (1933); *Chem. Abstr.*, **28**, 4733[5].
461. K. K. Hsu and S. F. Chang, *Tai-wan k'o Hsueh*, **29**(3–4), 51 (1975); *Chem. Abstr.*, **84**, 164725.
462. R. G. Haber and E. Schonberger, *Israeli Pat.* 27,993 (1972); *Chem. Abstr.*, **78**, 147821.
463. F. Gialdi and R. Ponci, *Farm. Sci. Tec. (Pavia)*, **6**, 332 (1951); *Chem. Abstr.*, **45**, 9117e.
464. S. F. MacDonald, *J. Amer. Chem. Soc.*, **69**, 1219 (1947).
465. C. E. Kwartler and H. G. Lindwall, *J. Amer. Chem. Soc.*, **59**, 524 (1937).
466. V. M. Rodionov and M. A. Berkenheim, *Zhur. Obshch. Khim.* **14**, 330 (1944); *Chem. Abstr.*, **39**, 40769.
467. D. Jerchel, J. Heider and H. Wagner, *Ann.*, **613**, 153 (1958); *Chem. Abstr.*, **53**, 5263a.
468. F. Nerdel and J. Kleinwachter, *Naturwissenschaften*, **42**, 577 (1955); *Chem. Abstr.*, **51**, 11151e.
469. H. Kaplan, *J. Amer. Chem Soc.*, **63**, 2654 (1941).
470. F. Linsker and R. L. Evans, *J. Amer. Chem. Soc.*, **68**, 947 (1946).
471. M. Henze, *Ber.*, **67B**, 750 (1934).
472. A. Burger and L. R. Modlin, Jr., *J. Amer. Chem. Soc.*, **62**, 1079 (1940).
473. M. Seyhan, *Rev. Fac. Sci. Univ. Istanbul*, **16A**, 252 (1951); *Chem. Abstr.*, **47**, 3312b.
474. M. Seyhan, *Chem. Ber.*, **85**, 425 (1952).
475. C. A. Buehler and S. P. Edwards, *J. Amer. Chem. Soc.*, **74**, 977 (1952).
476. M. Seyhan and W. C. Fernelius, *Chem. Ber.*, **89**, 2212 (1956).
477. M. Seyhan, *Chem. Ber.*, **90**, 1386 (1957).
478. P. Buballet, A. Godard, G. Queguiner and P. Pastour, *J. Heterocycl. Chem.*, **10**(6), 1079 (1973).
479. T. Ishiguro and I. Utsumi, *Yakugaku Zasshi*, **72**, 865 (1952); *Chem. Abstr.*, **47**, 6416h.
480. W. Mathes and W. Sauermilch, (a) *Chem. Ber.*, **87**, 1179 (1954); (b) *U.S. Pat.* 2,798,071 (1957); *Chem. Abstr.*, **52**, 451d.
481. W. Borsche, *Ber.*, **41**, 2203 (1908).
482. G. Wittig and K. Niethammer, *Chem. Ber.*, **93**, 944 (1960).
483. T. Masamune and G. Homma, *J. Fac. Sci. Hokkaido Univ., Ser. III*, **5**, 64 (1957); *Chem. Abstr.*, **52**, 14581h.
484. V. Boekelheide and W. J. Linn, *J. Amer. Chem. Soc.*, **76**, 1286 (1954).
485. E. Ochiai, H. Tanida and S. Uyeda, *Pharm. Bull. (Tokyo)*, **5**, 188 (1957).
486. E. Ochiai and H. Tanida, *Pharm. Bull. (Tokyo)*, **5**, 621 (1957).

487. R. T. Coutts, K. W. Hindmarsh and G. E. Myers, *Can. J. Chem.*, **48**(15), 2393 (1970).
488. T. Nakashima and I. Suzuki, *Chem. Pharm. Bull. (Tokyo)*, **17**(11), 2293 (1969).
489. M. K. Murshtein and V. N. Kontukhov. *Khim. Prod. Koksovaniya Uglei Vostoka SSSR*, No. 5, 342 (1969); *Chem. Abstr.*, **74**, 3490.
490. G. A. Tolstikov, U. M. Emileev, U. P. Tur'ev, F. B. Gershanov and S. R. Rafikov, *Tetrahedron Lett.*, **1971**, 2807.
491. H. John and G. Behmel, (a) *Ber.*, **66B**, 844 (1933); (b) *Ber.*, **58B**, 1563 (1925).
492. Vereinigte Chemische Fabriken Kreiol Heller and Co., *Fr. Pat.* 702, 183 (1930); *Chem. Abstr.*, **25**, 3919.
493. N. J. Novello, B. Harrow and C. P. Sherwin, *J. Pharmacol. Expt. Therapeut.*, **27**, 242 (1926); *Chem. Abstr.*, **20**, 3030.
494. Y. Hashimoto, *J. Jap. Biochem. Soc.*, **20**, 17 (1948); *Chem. Abstr.*, **43**, 6267c.
495. Y. Mizuno, *Yakugaku Zasshi*, **69**, 126 (1949); *Chem. Abstr.*, **44**, 1985i.
496. Y. Kobayashi, I. Kumadaki and S. Taguchi, *Chem. Pharm. Bull. (Tokyo)*, **20**(4), 823 (1972).
497. D. S. Tarbell, J. F. Bunnett, R. B. Carlin and V. P. Wystram, *J. Amer. Chem. Soc.*, **67**, 1582 (1945).
498. S. Yamaguchi, *Yakagaku Zasshi*, **46**, 556 (1926); (b) **46**, 749 (1926); *Chem. Abstr.*, **21**, 2696.
499. K. W. Rosenmund, F. Zymalkowski and N. Schwarte, *Chem. Ber.*, **87**, 1229 (1954).
500. W. P. Neumann, (a) *Angew. Chem.*, **70**, 401 (1958); (b) *Ann.*, **618**, 90 (1958).
501. (a) A. A. Grabetskii and V. V. Levchenko, *Zhur. Obshch. Khim.*, **17**, 1564 (1947); *Chem. Abstr.*, **42**, 2255f. (b) V. V. Levchenko, *Zhur. Obshch. Khim.*, **17**, 1656 (1947); *Chem. Abstr.*, **42**, 2187c.
502. F. B. Ahrens, *Z. Elektrochem.*, **2**, 577 (1895); *Chem. Zentralbl.*, **I**, 1127 (1896).
503. (a) G. Heller and A. Sourlis, *Ber.*, **41**, 2692 (1908); (b) G. Heller, *Ber.*, **44**, 2106 (1911); (c) C. Heller, *Ber.*, **47**, 2893 (1914).
504. V. V. Levchenko, *Zh. Obshch. Khim. Zhur. Obshch. Khim.*, (a) **18**, 1237 (1948); (b) **18**, 1245 (1948).
505. V. V. Levchenko and A. A. Zats, (a) *Zhur. Obshch. Khim.*, **22**, 1253 and 1301 (1952); *Chem. Abstr.*, **47**, 421i; (b) 2071; *Chem. Abstr.*, **47**, 9328b.
506. V. V. Levchenko and A. A. Zats, *Zhur. Obshch. Khim.* **22**, 2076 (1952); *Chem. Abstr.*, **47**, 9328e.
507. (a) H. Dunathan, I. W. Elliott, Jr., and P. Yates, *Tetrahedron Lett.*, **1961**, 781; (b) I. W. Elliott Jr., E. S. McCaskill, M. S. Robertson and C. H. Kirksey, *Tetrahedron Lett.*, **1962**, 291.
508. (a) I. W. Elliott, W. T. Bowie and D. L. T. Wong, *J. Heterocycl. Chem.*, **9**(6), 1425 (1972); (b) J. Bordner and I. W. Elliott, *Cryst. Struct. Commun.*, **3**(4), 689 (1974).
509. L. Palfray and S. Sabetay, *Bull. Soc. Chim. Fr.*, **5**(5), 1423 (1938).
510. S. Tsushima and S. Sudzuki, *Nippon Kagaku Kaishi*; **64**, 1295 (1943); *Chem. Abstr.*, **41**, 3801
511. T. H. Yeh and I. V. Kalechits, *K'o Hsueh T'ung Pao*, No. 15, 474 (1958); *Chem. Abstr.*, **53**, 13149b.
512. V. Yu. Telly, S. L. Gusinskaya and Z. Sabirov *Dokl. Akad. Nauk Uzb. SSR*, **27**(3), 37 (1970); *Chem. Abstr.*, **80**, 3365.
513. F. W. Vierhapper and E. L. Eliel, (a) *J. Amer. Chem. Soc.*, **96**(7), 2256 (1974); (b) *J. Org. Chem.*, **40**(9), 2729 (1975).
514. J. von Braun, A. Petzold and J. Seeman, *Ber.*, **55B**, 3779 (1922).
515. J. von Braun, W. Gmelin and A. Schultheiss, *Ber.*, **56B**, 1338 (1923).
516. J. von Braun, W. Gmelin and A. Petzold, *Ber.*, **57B**, 382 (1924).
517. S. G. P. Plant and R. J. Rosser, (a) *J. Chem. Soc.*, **1929**, 1861; (b) **1930**, 2444.
518. R. Hardman and M. W. Partridge, *J. Chem. Soc.*, **1958**, 614.
519. A. S. Sultanov, A. Safaev, T. Faiziev and A. I. Akhundzhanov, *Russ. Pat.* 239,961 (1969); *Chem. Abstr.*, **71**, 49797.
520. M. S. Raasch, *U.S. Pat.* 2,707,681 (1955).
521. W. S. Emerson and J. W. Davis, *J. Amer. Chem. Soc.*, **61**, 2830 (1939).
522. R. Escourrov, *Bull. Soc. Chim. Fr.*, **5**(5), 1184 (1938).
523. M. Lamchen, W. Pugh and A. M. Stephen, *J. Chem. Soc.*, **1954**, 4418.
524. H. Sato, *Eisei Shikensho Hokoku*, **77**, 44 (1959); *Chem Abstr.*, **55**, 14282a.
525. R. C. Elderfield and B. H. Wark, *J. Org. Chem.*, **27**, 543 (1962).
526. G. Buchmann and R. Schmuck, (a) *Wiss. Z. Tech. Hochsch. Chem. Leuna-Merseberg.*, **4**, 127 (1961–62); *Chem. Abstr.*, **59**, 3892f; (b) *Z. Chem.*, **2**(1), 11 (1962); *Chem. Abstr.*, **57**, 16555b.

527. B. A. Lugovik, L. G. Yudin, A. M. Popov and M. A. Kovaneva, *Vestn. Mosk. Univ. Khim.*, **12**(15), 601 (1971); *Chem. Abstr.*, **76**, 46057.
528. L. Knorr and C. Klotz, *Ber.*, **19**, 3299 (1886).
529. E. Bamberger and P. Wulz, *Ber.*, **24**, 2055 (1891).
530. W. König and G. A. Becker, *J. Prakt. Chem.*, **85**, 353 (1912).
531. J. Ziegler, *Ber.*, **21**, 862 (1888).
532. L. Berend, *Ber.*, **18**, 3165 (1885).
533. J. A. J. Tonella, *Rec. Trav. Chim.*, **16**, 361 (1897).
534. E. H. Wikander, *Ber.*, **33**, 646 (1900).
535. S. Cybulski, *J. Russ. Phys. Chem. Soc.*, **35**, 219 (1903).
536. F. Bayer & Co., *Ger. Pat.* 305,347 (1918); *Chem. Abstr.*, **13**, 825.
537. A. Ferantini, *Gazz. Chim. Ital.*, **23**, 105 (1893).
538. A. Ferratini, *Ber.*, **26**, 1811 (1893).
539. E. Fischer and J. Meyer, *Ber.*, **23**, 2628 (1890).
540. G. Darzens, *C. R. Acad. Sci.*, **149**, 1001 (1909).
541. S. Y. Yanusov and G. P. Sidyakin, *Zh. Obshch. Khim.*, **25**, 2009 (1955); *Chem. Abstr.*, **50**, 9435.
542. E. Schering, *Ger. Pat.* 24,317 (1883).
543. O. Fischer, G. Scheibe, P. Merkel and R. Muller, *J. Prakt. Chem.*, **100**, 86 (1919).
544. M. Avramoff and Y. Sprinzak, *J. Org. Chem.*, **22**, 571 (1957).
545. G. Buchmann and H. Pracht, *J. Prakt. Chem.*, **16**, 55 (1962); *Chem. Abstr.*, **58**, 90236.
546. V. I. Artyukin, D. V. Sokolov, L. K. Orazbaeva and G. S. Litvinenko, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.*, **17**(5), 57 (1967); *Chem. Abstr.*, **68**, 114401.
547. P. Sabatier and M. Murat, *C. R. Acad. Sci.*, **158**, 309 (1914); *Chem Abstr.*, **8**, 1564.
548. W. H. Perkin, Jr., and S. G. P. Plant, *J. Chem. Soc.*, **1928**, 2583.
549. W. H. Perkin, Jr., and W. G. Sedgwick, *J. Chem. Soc.*, **125**, 2437 (1924).
550. J. von Braun, A. Petzold and A. Schultheiss, *Ber.*, **56B**, 1347 (1923).
551. E. Hayashi and T. Nagao, *Yakugaku Zasshi*, **84**(2), 198 (1964); *Chem. Abstr.*, **61**, 30716.
552. A. S. Nakhmanovich and I. V. Kalechits, *Katal. Reakts. Zhidk. Faze, Tr. Vses. Konf.*, **1962**, 166 (1963); *Chem. Abstr.*, **60**, 10497f.
553. A. K. Sheinkman, A. N. Kost, A. N. Prilepskaya and N. A. Kltuev, *Khim. Geterotsikl. Soedin.*, 1105 (1972); *Chem. Abstr.*, **77**, 139767.
554. I. W. Elliott, *J. Org. Chem.*, **29**(2), 305 (1964).
555. D. A. Archer, H. Booth and P. C. Crisp, *J. Chem. Soc.*, **1964**, 249.
556. J. von Braun and A. Steindorf, *Ber.*, **37**, 4723 (1904).
557. Y. Kawazoe and M. Maeda, *Kagaku no Ryoiki. Zokan*, **107**, 78 (1975); *Chem. Abstr.*, **84**, 134695.
558. W. E. Parham and P. E. Olson, *Tetrahedron Lett.*, **1973**, 4783.
559. F. W. Bergstrom, *J. Amer. Chem. Soc.*, **53**, 3027 (1931).
560. R. E. Wright and F. W. Bergstrom, *J. Org. Chem.*, **1**, 179 (1936).
561. A. E. Chichibabin, (a) *Bull. Soc. Chim. Fr.*, **5**(5), 436 (1938); (b) *Rec. Trav. Chim.*, **57**, 582 (1938); *Chem. Abstr.*, **32**, 7459^2.
562. J. A. Eberle, M. Y. Sargant, C. P. Fauran and G. J. Huguet, *U.S. Pat.* 3,573,304 (1971); *Chem. Abstr.*, **75**, 63807.
563. O. Compagnon and P. L. Compagnon, *Bull. Soc. Chim. Fr.*, **1973**, 3385.
564. R. E. Lyle, D. E. Portlock, M. J. Kane and J. A. Bristol, *J. Org. Chem.*, **37**, (24), 3967 (1972).
565. (a) J. Howitz and J. Philipp, *Ann.*, **396**, 23 (1913); (b) J. Howitz and P. Nother, *Ber.*, **39**, 2705 (1906).
566. J. H. Ridd, in *Physical Methods in Heterocyclic Chemistry*, ed. A. R. Katritzky, Vol. I, p.109, Academic Press, New York and London, 1963.
567. M. Hasegawa, *Yakugaku Zasshi*, **71**, 256 (1951); *Chem. Abstr.*, **46**, 510h.
568. B. Prijs, R. Gall, R. Hinderling and H. Erlenmeyer, *Helv. Chim. Acta*, **37**, 90 (1954).
569. M. Hasegawa, *Pharm. Bull. (Tokyo)*, **1**, 47 (1953).
570. B. R. Brown, *J. Chem. Soc.*, **1949**, 2577.
571. D. Ll. Hammick, *J. Chem. Soc.*, **123**, 2882 (1923).
572. F. Raschig GmbH, *Brit. Pat.* 909,080 (1962); *Chem. Abstr.*, **58**, 9035e.
573. W. Mathes and H. Schuely, *Ger. Pat.* 1,204,231 (1965); *Chem. Abstr.*, **64**, 2063e.

574. W. Mathes and H. Schuely, *Angew. Chem.*, **75**, 235 (1963).
575. M. Fukushima, S. Tsuruta, H. Mitamoto and K. Fukatsu, *Jap. Pat.* 73 05,598 (1973); *Chem. Abstr.*, **78**, 136106.
576. M. Peinberg, E. Jansons and P. Kagans, *Uch. Zap. Latv. Gos. Univ.*, **117**, 174 (1970); *Chem. Abstr.*, **77**, 19502.
577. D. Beke, K. Lempert, J. Seress and L. Gyermek, *Magy. Kem. Foly.*, **61**, 190 (1955); *Chem. Abstr.*, **52**, 9124.
578. D. Ll. Hammick, *J. Chem. Soc.*, **1926**, 1302.
579. K. N. Campbell, J. Fakerman and B. K. Campbell, *J. Amer. Chem. Soc.*, **71**, 2905 (1949).
580. K. N. Campbell and G. E. Ullyot, *U.S. Pat.* 2,640,828 (1953); *Chem. Abstr.*, **48**, 40016.
581. R. D. Goeschke, *Ger. Pat.* 2,310,773 (1973); *Chem. Abstr.*, **80**, 27119.
582. J. Bankovskis, Z. Misulovina, A. Ivins and M. Buka, *Latv. PSR Zinat. Akad. Vestis*, No. 11, 103 (1960); *Chem. Abstr.*, **55**, 14458h.
583. T. Mazonski and Z. Kulicki, *Zesz. Nauk. Politech. Slask. Chem.*, No. 2, 21 (1957); *Chem. Abstr.*, **52**, 46466.
584. H. C. Richards, *S. Afr. Pat.* 68 03,636 (1968); *Chem. Abstr.*, **71**, 30369.
585. B. R. Brown and D. Ll. Hammick, (a) *J. Chem. Soc.*, **1950**, 628; (b) *Nature*, **164**, 831 (1949).
586. T. Takahashi, S. Nishigaki and H. Taniyama, *Yakugaku Zasshi*, **64**, 237 (1944).
587. Midland Tar Distillers Ltd., *Belg. Pat.* 667,939 (1966); *Chem. Abstr.*, **65**, 5447h.
588. B. R. Brown, D. Ll. Hammick and B. H. Thewlis, *J. Chem. Soc.*, **1951**, 1145.
589. L. M. Yagupolskii, V. S. Mikhailov and G. I. Matyushecheva, *Zh. Org. Khim.*, **8**(4), 838 (1972).
590. E. Jansons and O. Stirks, *Latv. PSR Zinat. Akad. Vestis Kim. Ser.*, **1975**, 753; *Chem. Abstr.*, **84**, 74066
591. P. P. Karpukhin, A. I. Slachinskaya, L. I. Sergeeva and V. M. Spengler, *Vestn. Khar'kov Politekh. Inst.*, No. 60, 50 (1971); *Chem. Abstr.*, **79**, 115905.
592. J. Ciernik, *Collect. Czech. Chem. Commun.*, **37**(7), 2273 (1972); *Chem. Abstr.*, **78**, 5378.
593. J. F. Wolfe, D. E. Portlock and D. J. Feuerbach, *J. Org. Chem.*, **39**(14), 2006 (1974).
594. J. F. Wolfe and T. P. Murray, *J. Org. Chem.*, **36**(2), 354 (1971).
595. H. Feuer and J. P. Lawrence, (a) *J. Org. Chem.*, **37**(23), 3662 (1972); (b) *J. Amer. Chem. Soc.*, **91**(7), 1856 (1969).
596. M. Ishikawa and I. Kikkawa, *Yakugaku Zasshi*, **75**, 36 (1955); *Chem. Abstr.*, **50**, 1007i.
597. A. Busch and W. Koenigs, *Ber.*, **23**, 2679 (1890).
598. R. Buchmann, C. M. McCloskey and J. A. Seneker, *J. Amer. Chem. Soc.*, **69**, 380 (1947).
599. E. Roberts and E. E. Turner, *J. Chem. Soc.*, **1927**, 1832.
600. J. L. C. Marais and O. G. Backeberg, *J. Chem. Soc.*, **1950**, 2207.
601. P. A. Claret and A. G. Osborne, *Tetrahedron*, **33**, 1765 (1977).
602. M. T. Bogert and H. L. Fischer, *J. Amer. Chem. Soc.*, **34**, 1569 (1912).
603. E. Noelting and E. Trautmann, *Ber.*, **23**, 3654 (1890).
604. J. D. Capps, *J. Amer. Chem. Soc.*, **69**, 179 (1947).
605. S. Sakai, K. Minoda and S. Akagi, *Jap. Pat.* 61 3872 (1961); *Chem. Abstr.*, **58**, 10181d.
606. E. Ochiai and J. Takeuchi, *Yakugaku Zasshi*, **70**, 389 (1950); *Chem. Abstr.*, **45**, 2476c.
607. E. Ochiai and M. Shimizu, *Yakugaku Zasshi*, **63**, 398 (1943).
608. C. C. Price, B. H. Velzen and D. B. Guthrie, *J. Org. Chem.*, **12**, 203 (1947).
609. E. Roberts and E. E. Turner, *J. Chem. Soc.*, **1927**, 1832.
610. D. M. Bowen, R. W. Belfit, Jr., and R. A. Walser, *J. Amer. Chem. Soc.*, **75**, 4307 (1953).
611. A. J. Lin, B. J. Lillis and A. C. Sartorelli, *J. Med. Chem.*, **18**, 917. (1975).
612. L. M. Schenck and H. R. Henze, *J. Amer. Chem. Soc.*, **64**, 1499 (1942).
613. W. R. Vaughan, *J. Amer. Chem. Soc.*, **70**, 2294 (1948).
614. E. Hayashi and R. Goto, *Yakugaku Zasshi*, **85**(7), 645 (1965); *Chem. Abstr.*, **63**, 9913a.
615. K. Nomoto, *Pharm. Bull. (Tokyo)*, **5**, 297 (1957).
616. F. W. Bergstrom, T. R. Norton and R. A. Seibert, *J. Org. Chem.*, **10**, 452 (1945).
617. M. A. Ai'perovich and I. K. Ushenko, *Zh. Obshch. Khim.*, **29**, 3384 (1959).
618. C. E. Kaslow and B. Buchner, *J. Org. Chem.*, **23**, 271 (1958).
619. O. H. Johnson and C. S. Hamilton, *J. Amer. Chem. Soc.*, **63**, 2864 (1941).
620. G. E. McCasland, *J. Org. Chem.*, **11**, 277 (1946).
621. E. Schering, *Ger. Pat.* 29,819 (1884).
622. A. Busche and W. Koenigs, *Ber.*, **23**, 2679 (1890).

623. J. Herzfeld, *Ber.*, **17**, (1884), (a) 903; (b) 1550.
624. A. Claus and A. Kaufmann, *J. Prakt. Chem.*, **55**, 524 (1897).
625. E. von Lellmann, and H. Ziemssen, *Ber.*, **24**, 2116 (1891).
626. E. Noelting and J. Fruhling, *Ber.*, **21**, 3156 (1888).
627. L. Berend, *Ber.*, **17**, 2716 (1884).
628. A. Edinger and J. B. Ekeley, (a) *J. Prakt. Chem.*, **66**, 214 (1902); (b) *Ber.*, **35**, 96 (1902).
629. A. P. Edinger and A. Schumaker, *Ber.*, **33**, 2886 (1900).
630. L. P. Zalukaev and T. I. Zheltukhina, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **9**(4), 631 (1966); *Chem. Abstr.*, **66**, 85687.
631. T. Kato, H. Yamanaka and T. Shimizu, *Yakugaku Zasshi*, **93**(1), 73 (1973); *Chem. Abstr.*, **78**, 97453.
632. T. Ukai, *Yakugaku Zasshi*. (a) **48**, 812 (1928); *Chem. Abstr.*, **23**, 839; (b) **51**, 542 (1931); *Chem. Abstr.*, **25**, 5427.
633. A. Sturkis and J. Bankovskis, *Khim. Geterotsikl. Soedin. Sb. 1: Azotsoderzhashchie Geterotsikly*, **1967**, 269; *Chem. Abstr.*, **70**, 87517.
634. (a) M. Cirule, J. Bankovskis and A. Sturis, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, **1974**, 617; *Chem. Abstr.*, **82**, 139922.
(b) M. Cirule, Yu. A. Bankovskii and A. Sturis, **1975**, 300; *Chem. Abstr.*, **83**, 178764.
(c) A. Sturis, Yu. A. Bankovskii and U. Tomsons, **1974**, 355; *Chem. Abstr.*, **81**, 120409.
(d) A Sturis, Yu. A. Bankovskii and A. Deme, **1974**, 498; *Chem. Abstr.*, **81**, 169416.
(e) Yu. A. Bankovskii, A. Sturis, M. Cirule and J. Cirule, **1975**, 581; *Chem. Abstr.*, **84**, 59139.
(f) A. Sturis and Yu. A. Bankovskii, **1975**, 585; *Chem. Abstr.*, **84**, 59140.
(g) A. Sturis and Yu. A. Bankovskii, **1974**, 624; *Chem. Abstr.*, **82**, 43147.
635. N. Marekov, *C. R. Acad. Bulg. Sci.*, **6**, 35 (1956); *Chem. Abstr.*, **52**, 18418e.
636. M. T. Leffler, in *Organic Reactions*, ed. R. Adams, Vol. I, Wiley, New York and Chichester, 1942, (a) pp. 91–104; (b) p. 94; (c) p. 100; (d) pp. 102–104.
637. F. W. Bergstrom, *J. Amer. Chem. Soc.*, **53**, 3027 (1931).
638. T. Kametani, H. Nemoto and S. Takano, *Yakugaku Zasshi*, **88**(4), 453 (1968); *Chem. Abstr.*, **69**, 106492.
639. T. Kametani and H. Nemoto, *Chem. Pharm. Bull. (Tokyo)*, **15**(12), 1910 (1967).
640. F. E. Bergstrom, *J. Org. Chem.*, **3**, 233 (1938).
641. T. Kametani, H. Nemoto and S. Takano, *Chem. Pharm. Bull. (Tokyo)*, **16**(2), 367 (1968).
642. A. E. Chichibabin, *Ber.*, **56B**, 1879 (1923).
643. A. E. Chichibabin, *J. Russ. Phys. Chem. Soc.*, **55**, 7 (1924); *Chem. Abstr.*, **19**, 1572.
644. A. E. Chichibabin and A. I. Kirsanova, *J. Russ. Phys. Chem. Soc.*, **62**, 1211 (1930); *Chem. Abstr.*, **25**, 2727.
645. W. H. Rieger, *U.S. Pat.* 2,502,174 (1950); *Chem. Abstr.*, **44**, 5396g.
646. W. R. Thomas, *Ph.D. Thesis*, University of Missouri, 1975; *Diss. Abstr.*, **36B**(2), 729 (1975).
647. E. M. Kaiser, G. J. Bartling, W. R. Thomas, S. B. Nichols and D. R. Nash, *J. Org. Chem.*, **38**(1), 71 (1973).
648. E. M. Kaiser and W. R. Thomas, *J. Org. Chem.*, **39**(17), 2659 (1974).
649. K. Konishi, Y. Onari, S. Goto and K. Takahashi, *Chem. Lett.*, **1975**, 717; *Chem. Abstr.*, **83**, 146648.
650. A. M. Jones and C. A. Russell, *J. Chem. Soc. C*, No. 17, 2246 (1969).
651. Lithium Corp. of America, *Brit. Pat.* 1,213,409 (1970).
652. C. G. Screttas, *Fr. Pat.* 1,585,052 (1970).
653. A. M. Jones, C. A. Russell and S. Skidmore, *J. Chem. Soc. C.*, **1969**, 2245.
654. N. N. Goldberg and R. Levine, *J. Amer. Chem. Soc.*, **74**, 5217 (1952).
655. S. M. Spatz, *Iowa State Coll. J. Sci.*, **17**, 129 (1942); *Chem. Abstr.*, **37**, 34343.
656. R. J. W. Le Fevre and F. C. Mathur, *J. Chem. Soc.*, **1930**, 2236.
657. F. Minisci, A. Selva, O. Porta, P. Barilli and G. P. Gardini, *Tetrahedron*, **28**, 2415 (1972).
658. K. Schwetlick and R. Lungwitz, *Z. Chem.*, **4**, 458 (1964).
659. H. J. M. Dou, G. Vernin and J. Metzger, *Bull. Soc. Chim. Fr.*, **1971**, 102.
660. M. Araki, M. Maeda and Y. Kawazoe, *Tetrahedron*, **32**(3), 337 (1976).
661. T. Caronna, G. Fronza, F. Minisci, O. Porta and G. P. Gardini, *J. Chem. Soc. Perkin Trans. 2*, **1972**, 1477.

662. T. Caronna, G. Fronza, F. Minisci and O. Porta, *J. Chem. Soc. Perkin Trans. 2*, **1972**, 2035.
663. G. P. Gardini, *Tetrahedron Lett.*, **1972**, 4113.
664. F. Minisci, F. Bertini, R. Galli, M. Perchinunno and A. Quilico, *Ital. Pat.* 918,225 (1972).
665. H. Itokawa, S. Kameyama, T. Inaba, T. Tazaki, S. Mihashi and Y. Kawazoe, *Chem. Pharm. Bull. (Tokyo)*, **23**(3), 487 (1975).
666. F. Minisci, A. Citterio, M. Perchinunno and F. Bertini, *Gazz. Chim. Ital.*, **105**(9–10), 1083 (1975); *Chem. Abstr.*, **84**, 163786.
667. F. Minisci, R. Galli, M. Cerere, M. Perchinunno and A. Quilico *Ital. Pat.* 909,170 (1972); *Chem. Abstr.*, **84**, 59237.
668. A. Arnone, M. Cerere, R. Galli, F. Minisci, M. Perchinunno, O. Porta and G. Gardini, *Gazz. Chim. Ital.*, **103**(1–2), 13 (1973); *Chem. Abstr.*, **79**, 52563.
669. W. Buratti, G. P. Gardini, F. Minisci, F. Bertini, R. Galli and M. Perchinunno, *Tetrahedron*, **27**, 3655 (1971).
670. A. Ledwith, P. J. Russel and L. H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, **1971**, 970.
671. F. R. Stermitz, C. C. Wei and C. M. O'Donnell, *J. Amer. Chem. Soc.*, **92**, 2745 (1970).
672. T. T. Chen, W. Dorscheln, H. Goth, M. Hesse and H. Schmid, *Helv. Chim. Acta*, **51**, 632 (1968).
673. S. Jerumais and A. Martell, *Can. J. Chem.*, **48**, 1716 (1970).
674. G. P. Gardini, F. Minisci, G. Palla, A. Arnone and R. Galli, *Tetrahedron Lett.*, **1971**, 59.
675. Y. Otsuji, K. Yutani and E. Imoto, *Bull. Chem. Soc. Jap.*, **44**(2), 520 (1971); *Chem. Abstr.*, **74**, 99833.
676. E. M. Kaiser and J. D. Petty, *J. Org. Chem.*, **41**(4), 716 (1976).
677. F. D. Popp, *Adv. Heterocycl. Chem.*, **9**, 1 (1968).
678. F. D. Popp, W. Blount and P. Meluin, *J. Org. Chem.*, **26**, 4930 (1961).
679. E. D. Snoke and F. D. Popp, *J. Heterocycl. Chem.*, **10**(1), 99 (1973).
680. C. A. Russel, A. M. Jones and O. Meth-Cohn, *J. Chem. Soc.*, **1971**, 2453.
681. R. Fusco and F. Sannicolo, *Gazz. Chim. Ital.*, (a) **105**(5–6), 465 (1975); *Chem. Abstr.*, **83**, 206079; (b) **105**(9–10), 1105 (1975); *Chem. Abstr.*, **84**, 135444; (c) **106**, 85 (1976); *Chem. Abstr.*, **85**, 142220.
682. R. A. Abramovitch and T. Takata, *J. Org. Chem.*, **37**(12), 2022 (1972).
683. R. N. Pratt, G. A. Taylor and S. A. Proctor, *J. Chem. Soc. C*, **1967**, 1569.
684. (a) O. Diels, K. Alder, T. Kashimoto, W. Friedrichsen, W. Eckardt and H. Klare, *Ann.*, **498**, 16 (1932).
(b) O. Diels, K. Alder, W. Friedrichsen, E. Pertersen, Brodersen, and H. Kach, *Ann.*, **510**, 87 (1934).
(c) O. Diels, K. Alder, W. Friedrichsen, H. Klare, H. Winckler, and Schrum, *Ann.*, **505**, 103 (1933).
685. B. S. Thyagarajan, (a) *Chem. Rev.*, **54**, 1019 (1954); (b) *Adv. Heterocycl. Chem.*, **5**, 291 (1965).
686. R. M. Acheson, *Adv. Heterocycl. Chem.*, **1**, 125 (1963).
687. R. M. Acheson, J. M. F. Gagan and D. R. Harrison, *J. Chem. Soc. C*, **1968**, 362.
688. R. M. Acheson and D. F. Nisbet, (a) *J. Chem. Soc. C.*, **1971**, 3291; (b) *J. Chem. Soc. Perkin Trans. 1*, **1973**, 1338.
689. R. M. Acheson, G. Procter and S. R. Critchley, (a) *J. Chem. Soc., Chem. Commun.*, **1976**, 692; (b) *Acta Cryst.* **B33**, 916 (1977).
690. R. M. Acheson and G. Procter, *J. Chem. Soc., Perkin Trans. 1*, **1977**, 1924.
691. R. M. Acheson, P. J. Abbott, R. A. Forder, D. J. Watkin and C. J. Carruthers, (a) *Acta Cryst*, **B33**, 898 (1977); (b) **B32**, 1927 (1976).
692. O. Gerngross, *Ber.*, **42**, 398 (1909).
693. R. Spallino and E. Cucchiaroni, *Gazz. Chim. Ital.*, **42**(I) 517 (1912); *Chem. Abstr.*, **6**, 2419.
694. H. Kondo and T. Matsuno, *Yakugaku Zasshi*, **49**, 445 (1929); *Chem. Abstr.*, **23**, 4218.
695. H. John, *Ber.*, **58B**, 2799 (1925).
696. J. Lindner and J. Hager, *Monatsh.*, **72**, 361 (1939); *Chem. Abstr.*, **33**, 6853°.
697. B. R. Brown, D. L. Hammick and R. Robinson, *J. Chem. Soc.*, **1950**, 780.
698. C. E. Kaslow and R. D. Stayner, *J. Amer. Chem. Soc.*, **67**, 1716 (1945).
699. R. S. Tipson, *J. Amer. Chem. Soc.*, **67**, 507 (1945).
700. R. C. Elderfield, J. S. Covey, J. B. Geiduschek, U. L. Meyer, A. B. Ross and J. H. Ross, *J. Org. Chem.*, **23**, 1749 (1958).

701. V. A. Petrow, *J. Chem. Soc.*, **1945**, 18.
702. G. M. Bennett and G. H. Willis, *J. Chem. Soc.*, **1928**, 1960.
703. G. M. Bennett and W. L. C. Pratt, *J. Chem. Soc.*, **1929**, 1465.
704. B. M. Mikhailov and G. S. Ter-Sarkisyan, *Izv. Akad. Nauk SSSR., Otd. Khim. Nauk*, **1954**, 846.
705. H. L. Kehlstadt, *Helv. Chim. Acta*, **27**, 685 (1944).
706. H. Gilman and G. Karmas, *J. Amer. Chem. Soc.*, **67**, 342 (1945).
707. (a) Y. Ogata, A. Kawasaki and H. Hirata, *J. Chem. Soc., Perkin Trans. 2*, **1972**, 1129. (b) S. M. Lynch and M. Gordon, *J. Heterocycl. Chem.*, **9**(4), 789 (1972).
708. J. Stañek and M. Horak, *Collect. Czech. Chem. Commun.*, **15**, 1037 (1951); *Chem. Abstr.*, **46**, 71000.
709. H. John, *Ber.*, **59B**, 722 (1926).
710. A. A. Alberts and G. B. Bachmann, *J. Amer. Chem. Soc.*, **57**, 1284 (1935).
711. E. Graef, J. M. Fredericksen and A. Burger, *J. Org. Chem.*, **11**, 257 (1946).
712. G. B. Backman and D. D. Micucci, *J. Amer. Chem. Soc.*, **70**, 2381 (1948).
713. R. Oda, K. Teramura, S. Tanimoto, M. Nomura, H. Suda and K. Matsuda, *Bull. Inst. Chem. Res. Kyoto Univ.*, **33**, 117 (1955); *Chem. Abstr.*, **51**, 11355b.
714. M. M. Koton and O. K. Surnina, *Dokl. Akad. Nauk SSSR*, **113**, 1063 (1957); *Chem. Abstr.*, **51**, 14725e.
715. A. G. Kalle, *Brit. Pat.* 946,108 (1964); *Chem. Abstr.*, **60**, 11526f.
716. G. Buchmann and O. Wolniak, *J. Prakt. Chem.*, **25**(1–2), 101 (1964); *Chem. Abstr.*, **61**, 11969a.
717. C. T. Bahner, D. Brotherton, W. H. Chapman, Jr., W. Longmire, H. B. Orr, L. M. Rives, E. M. Senter and W. Yee, *J. Med. Chem.*, **8**(2), 269 (1965).
718. E. S. Kagan and B. I. Ardashv, *Khim. Geterotsikl. Soedin.*, **1967**, 701; *Chem. Abstr.*, **68**, 114408.
719. W. Koenigs and E. Bischkopf, *Ber.*, **34**, 4322 (1901).
720. F. Eisele, *Ber.*, **20**, 2043 (1887).
721. R. Spallino and G. Salimei, *Gazz. Chim. Ital.*, **42**(1), 607 (1912); *Chem. Abstr.*, **6**, 2742.
722. A. E. Porai-Koshits, *J. Russ. Phys. Chem. Soc.*, **38**(1), 1281 (1906); *Chem. Abstr.*, **1**, 2127.
723. Von Ismailsky, *J. Prakt. Chem.*, **85**, 90 (1911); *Chem. Abstr.*, **6**, 1141.
724. L. F. Werner, *J. Amer. Chem. Soc.*, **42**, 2309 (1920).
725. J. Troger and E. Dunker, *J. Prakt. Chem.*, **112**, 196 (1926); *Chem. Abstr.*, **20**, 1626.
726. T. W. J. Taylor and C. P. Woodhouse, *J. Chem. Soc.*, **1926**, 2971.
727. U. N. Brahmachari and T. Bhattacharjee, *J. Indian Chem. Soc.*, **7**, 527 (1930); *Chem. Abstr.*, **24**, 5752.
728. H. H. Hodgson and E. W. Smith, *J. Chem. Soc.*, **1933**, 315.
729. F. C. Mathur and R. Robinson, *J. Chem. Soc.*, **1934**, 1520.
730. H. Rupe, H. Hagenbach and A. Collin, *Helv. Chim. Acta*, **18**, 1395 (1935).
731. U. Basu, *Sci. Cult.*, **2**, 55 (1936); *Chem. Abstr.*, **30**, 7118[7].
732. K. Maurer and H. Starck, *Ber.*, **70B**, 2054 (1937).
733. A. F. Walton, R. S. Tipson and L. H. Cretcher, *J. Amer. Chem. Soc.*, **67**, 1501 (1945).
734. J. M. Smith, Jr., *U.S. Pat.* (a) 2,482,521 (1949); *Chem. Abstr.*, **44**, 2570i; (b) 2,512, 180 (1950); *Chem. Abstr.*, **44**, 9487c.
735. E. K. Fields, *J. Amer. Chem. Soc.*, **71**, 1495 (1949).
736. D. Papa, E. Schwenk and E. Klingsberg, (a) *J. Amer. Chem. Soc.*, **73**, 253 (1951); (b) *U.S. Pat.* 2,558,777 (1951); *Chem. Abstr.*, **46**, 15946.
737. M. C. Chiang and C. K. Lu, *J. Chin. Chem. Soc.*, **18**, 198 (1951); *Chem. Abstr.*, **46**, 5588a.
738. C. T. Bahner and E. S. Pace, *J. Amer. Chem. Soc.*, **74**, 3932 (1952).
739. F. W. Bergstrom and A. Furst, *J. Amer. Chem. Soc.*, **75**, 5415 (1953).
740. L. Horwitz, *J. Amer. Chem. Soc.*, **77**, 1687 (1955).
741. E. D. Parker and A. Furst, *J. Org. Chem.*, **23**, 201 (1958).
742. V. A. Izmail'skii and P. A. Solodkov, *Zh. Obshch. Khim.*, **29**, 3930 (1959); *Chem. Abstr.*, **54**, 21092b.
743. G. Buchmann and H. J. Steinbach, *J. Prakt. Chem.*, **25**, 7, (1964); *Chem. Abstr.*, **62**, 519h.
744. A. N. Kost and A. K. Sheinkman, *USSR Pat.* 167,878 (1965); *Chem. Abstr.*, **62**, 16214a.
745. J. Michalski and R. Bodalski, *Polish Pat.* 50,521 (1966); *Chem. Abstr.*, **66**, 55408.
746. S. Biniecki and W. Modrzejewska, *Acta Pol. Pharm.*, **24**(6), 561 (1967); *Chem. Abstr.*, **69**, 10338.

747. M. Hasegawa, Y. Suzuki, F. Suzuki and H. Nakanishi, (a) *J. Polym. Sci. Part A-1*, 7(2), 743 (1969); *Chem. Abstr.*, **71**, 13415; (b) *Jap. Pat.* 71 22,758 (1971); *Chem. Abstr.*, **75**, 119203.
748. W. Reid, D. Piechaczek and E. Vollberg, *Justus Liebigs Ann. Chem.*, **734**, 13 (1970); *Chem. Abstr.*, **73**, 14765.
749. A. E. Lipkin and Z. P. Bespalova, *Khim.-Farm. Zh.*, **4**(1), 24 (1970); *Chem. Abstr.*, **72**, 111193.
750. H. Pommer and W. Sarnecki, *Ger. Pat.* 1,903,191 (1970); *Chem. Abstr.*, **73**, 77068.
751. G. Berkelhammer, G. Asato and E. L. Moon, *U.S. Pat.* 3,505,346 (1970); *Chem. Abstr.*, **73**, 77237.
752. K. Loew, *Ber.*, **36**, 1666 (1903).
753. O. Wallach and M. Wusten, *Ber.*, **16**, 2007 (1883).
754. C. H. Browning, J. B. Cohen, S. Ellingworth and R. Gulbransen, *Proc. Roy. Soc.* (*B*), **100**, 293 (1926).
755. M. Hoffmann, *Ber.*, **38**, 3709 (1905).
756. S. K. Dzierzgowski, *Ber.*, **27**, 1979 (1894).
757. O. Bialon, *Ber.*, **35**, 2786 (1902).
758. I. G. Farbenindustrie A.G., *Ger. Pat.* 440,008 (1927).
759. C. Renz and K. Loew, *Ber.*, **36**, 4330 (1903).
760. M. Nencki, *Ber.*, **27**, 1969 (1894).
761. E. Noetting and E. Witte, *Ber.*, **39**, 2749 (1906).
762. J. Troger and E. Dunker, *J. Prakt. Chem.*, **112**, 196 (1926).
763. S. Skraup and K. Bohm, *Ber.*, **59**, 1007 (1926).
764. H. Gilman and G. C. Gainer, *J. Amer. Chem. Soc.*, **71**, 2327 (1949).
765. W. Konig and O. Treichel, *J. Prakt. Chem.*, **102**, 63 (1921).
766. (a) R. C. Fuson, L. L. Alexander, E. Ellingboe and A. Hoffman, *J. Amer. Chem. Soc.*, **58**, 1979 (1936).
(b) R. C. Fuson, A. P. Kozacik and J. T. Eaton, *J. Amer. Chem. Soc.*, **55**, 3799 (1933).
(c) A. Hoffman, M. W. Farlow and R. C. Fuson, *J. Amer. Chem. Soc.*, **55**, 2000 (1933).
767. R. S. Tipson and A. F. Walton, *J. Amer. Chem. Soc.*, **70**, 892 (1948).
768 (a) C. T. Bahner, C. Cook, J. Dale, J. Fain, E. Franklin, J. C. Goan, W. Stump, and J. Wilson, *J. Org. Chem.*, **22**, 682 (1957) and C. T. Bahner, J. Wilson, M. West, G Browder, J. C. Goan, C. Cook, J. Fain, E. Franklin and A. Myers, *J. Org. Chem.*, **22**, 683 (1957).
(b) C. T. Bahner, J. Dale, J. Fain, E. Franklin, J. C. Goan, W. Stump, M. West and J. Wilson, *J. Org. Chem.*, **22**, 1110 (1957)
(c) C. T. Bahner, C. Cook, J. Dale, J. Fain, F. Hannan, P. Smith and J. Wilson, *J. Org. Chem.*, **23**, 1060 (1958).
769. A. N. Kost, A. K. Sheinkman and A. N. Rozenberg, *Zh. Obshch. Khim.*, **34**(12), 4046 (1964); *Chem. Abstr.*, **62**, 9101g.
770. C. Shiele and D. Staudacher, *Tetrahedron*, **24**(1), 471 (1968).
771. H. Guesten and D. Schulte-Frohlinde, *Chem. Ber.*, **104**(2), 402 (1971); *Chem. Abstr.*, **74**, 99840.
772. S. Nasakeno, M. Sumitani, and K. Iguchi, *Jap. Pat.* 73 24,487 (1973); *Chem. Abstr.*, **80**, 134916.
773. S. Varbanova *C. R. Acad. Bulg. Sci.*, **16**(8), 829 (1963); *Chem. Abstr.*, **61**, 4309e.
774. M. Tramontini, *Ann. Chim.* (*Rome*), **55**(11), 1154 (1965); *Chem. Abstr.*, **64**, 6610h.
775. W. Koenigs, *Ber.*, **32**, 3599 (1899).
776. W. Steinkopf, R. Leitsmann, A. H. Muller and H. Wilhelm, *Ann.*, **541**, 260 (1939); *Chem. Abstr.*, **34**, 756[7].
777. W. Reid and S. Hinsching, *Ann.*, **600**, 47 (1956); *Chem. Abstr.*, **51**, 4381i.
778. C. F. Boehringer and Soehne, GmbH, *Belg. Pat.* 616,437 (1962); *Chem. Abstr.*, **59**, 12770e.
779. K. Miura, T. Ohashi, S. Matsuda and Y. Igarashi, *Yakugaku Zasshi*, **83**, 771 (1963).
780. K. Miura, *Belg. Pat.* 638,220 (1964); *Chem. Abstr.*, **62**, 9106h.
781. B. P. Lugovkin, *Khim. Geterotsikl. Soedin. Akad. Nauk Latv. SSR*, **1965**, 382; *Chem. Abstr.*, **63**, 14842f.
782. Y. Hara, M. Kashihara and I. Hirao, *Nippon Kagaku Zasshi*, **86**(11), 1192 (1965).
783. S. Minami, A. Fujita, J. Matsumoto, K. Fujimoto, M. Shimizu and Y. Takase, *Jap. Pat.* 65 23,662 (1965); *Chem. Abstr.*, **64**, 35046.

784. C. T. Bahner, H. Kindner and L. Gutman, *J. Med. Chem.*, **8**(3), 397 (1965).
785. S. Biniecki and W. Modrzejewska, *Acta Pol. Pharm.*, **24**(6), 559 (1967).
786. S. Hillers, M. Lidaks, N. M. Sukhova and K. Venters, *Russ. Pat.* 242,174 (1969).
787. G. Berkelhammer and G. Asato, *U.S. Pat.* 3,598,830 (1971); *Chem. Abstr.*, **76**, 34239.
788. G. Berkelhammer, G. Asato and E. L. Moon, *U.S. Pat.* 3,674,780 (1972); *Chem. Abstr.*, **77**, 101575.
789. Y. Muroyama and M. Matsuo, *Jap. Pat.* 74 72,262 (1974); *Chem. Abstr.*, **83**, 116960.
790. S. Hillers, M. Lidaks, K. Venters and N. M. Sukhova, *Russ. Pat.* 255,942 (1976); *Chem. Abstr.*, **84**, 150323.
791. A. Eibner and O. Lange, *Ann.*, **315**, 303 (1901).
792. W. Von Miller and F. Kinkelin, *Ber.*, **18**, 3234 (1885).
793. J. O. Sapek, *Ber.*, **20**, 2044 (1887).
794. M. Kohn and A. Klein, *Monatsh.*, **33**, 929 (1912).
795. L. G. S. Brooker, R. H. Sprague, C. P. Smyth and G. L. Lewis, *J. Amer. Chem. Soc.*, **62**, 1116 (1940).
796. D. J. Cook and M. Stamper *J. Amer. Chem. Soc.*, **69**, 1467 (1947).
797. K. Miura, M. Ikeda, T. Ohashi, Y. Igarashi, I. Okada, T. Shikimi and S. Ishii, *Yakugaku Zasshi*, **85**(4), 289 (1965).
798. C. F. Boehringer and Soehne GmbH, *Brit. Pat.* 1,107,790 (1968); *Chem. Abstr.*, **69**, 86828.
799. S. Biniecki and A. Bulacinski, *Acta Polon. Pharm.*, **26**(2), 101 (1969); *Chem. Abstr.*, **71**, 38768.
800. L. G. S. Brooker and R. H. Sprague, *J. Amer. Chem. Soc.*, **63**, 3203 (1941).
801. W. H. Mills and P. E. Evans, *J. Chem. Soc.*, **117**, 1035 (1920).
802. C. T. Bahner and J. N. Fain, *J. Org. Chem.*, **22**, 1109 (1957).
803. C. Compton and W. Bergmann, *J. Org. Chem.*, **12**, 363 (1947).
804. (a) W. Wislicenus and E. Kleisinger, *Ber.*, **42**, 1140 (1909).
(b) W. Wislicenus and H. Elvert, *Ber.*, **42**, 1144 (1909); *Chem. Abstr.*, **3**, 2130.
805. F. W. Bergstrom and A. Moffat, *J. Amer. Chem. Soc.*, **59**, 1494 (1937).
806. W. Borsche and R. Manteuffel, *Ann.*, **534**, 56 (1938); *Chem. Abstr.*, **32**, 4587[3].
807. M. J. Weiss and C. R. Hauser, *J. Amer. Chem. Soc.*, (a) **71**, 2023 (1949); (b) **71**, 2026 (1949).
808. C. R. Hauser and W. J. Humphlett, *J. Amer. Chem. Soc.*, **72**, 3805 (1950).
809. A. W. Hofmann, *Ber.*, **20**, 4 (1887).
810. E. Jacobsen, *Ger. Pat.* (a) 19, 306 (1882); (b) 23,967 (1883); (c) 23,188 (1883); (d) 25,144 (1883).
811. A.G.F.A., *Ger. Pat.* 40,420 (1887).
812. (a) A. Eibner and E. Simon, *Ber.*, **34**, 2303 (1901); (b) A. Eibner and H. Merkel, *Ber.*, **35**, 2297 (1902); (c) A. Eibner and H. Merkel, *Ber.*, **37**, 3006 (1904); (d) A. Eibner and K. Hofmann, *Ber.*, **37**, 3011 (1904); (e) A. Eibner, *Ber.*, **37**, 3605 (1904).
813. M. C. Traub, *Ber.*, **16**, 297 (1883).
814. E. Jacobsen and K. L. Reimer, *Ber.*, **16**, (1883), (a) 513; (b) 2602.
815. S. Ueno and T. Suzuki, *Kogyo! Kagaku Zasshi*, **36**, Suppl. 195 (1933); *Chem. Abstr.*, **27**, 3477.
816. R. Kuhn and F. Bar, *Ann.*, **516**, 143 (1935).
817. W. Koenigs and J. V. Nef, *Ber.*, **19**, 2427 (1886).
818. W. Koenigs and A. Mengel, *Ber.*, **37**, 1322 (1904).
819. R. Geigy and W. Koenigs, *Ber.*, **18**, 2400 (1885).
820. M. Phillips and M. J. Goss, *J. Amer. Chem. Soc.*, **48**, 823 (1926).
821. G. Panajotow, *Ber.*, **28**, 1511 (1895).
822. A. Eibner, *Ger. Pat.* 158,761 (1905).
823. J. Ogilvie, *U.S. Pat.* 1,963,374 (1934).
824. A. Taurins, *J. Prakt. Chem.*, **153**, 189 (1939).
825. L. Zalukajevs and E. Vanags, *Zh. Obshch. Khim.*, **29**, 1639 (1959); *Chem. Abstr.*, **54**, 8835a.
826. A. E. Poraikoshits and I. I. Chizhevskaya, *Zh. Obshch. Khim.*, **26**, 1950 (1956); *Chem. Abstr.*, **51**, 5073b.
827. B. K. Manukian, P. Niklaus and H. Ehrsam, *Helv. Chim. Acta*, **52**(5), 1259 (1969).
828. (a) V. V. Korshak, E. S. Krongauz and A. M. Berlin, *Russ. Pat.* 293,015 (1971); *Chem. Abstr.*, **75**, 37031.
(b) V. V. Korshak, E. S. Krongauz, A. M. Berlin and N. M. Kofman, *Russ. Pat.* 328,140 (1972); *Chem. Abstr.*, **77**, 20353.

829. L. Krasnec and P. Hrnciar, *Chem. Zvesti*, **28**(1), 100 (1974); *Chem. Abstr.*, **81**, 3854.
830. O. Stark and F. Hoffman, *Ber.*, **46**, 2697 (1913).
831. H. Saikachi and T. Hisano, *Chem. Pharm. Bull. (Tokyo)*, **8**, 51 (1960).
832. (a) O. N. Chupakhin, Z. V. Pushkareva, Z. Y. Kokoshko and M. I. Podgornaya, *Zh. Org. Khim.*, **1**(4), 772 (1965); *Chem. Abstr.*, **63**, 5602b.
(b) O. N. Chupakhin, Z. V. Pushkareva and E. P. Darienko, *Zh. Obshch. Khim.*, **33**(7), 2401 (1963); *Chem. Abstr.*, **59**, 13946f.
833. T. Hisano and M. Ichikawa, *Chem. Pharm. Bull. (Tokyo)*, **22**(9), 2051 (1974).
834. S. M. McElvain and H. G. Johnson, *J. Amer. Chem. Soc.*, **63**, 2213 (1941).
835. F. Bell, *J. Chem. Soc.*, **1953**, 3485.
836. A. A. Bothner-by, *J. Amer. Chem. Soc.*, **77**, 749 (1955).
837. J. E. Humphries, *J. Chem. Soc.*, **1926**, 374.
838. T. Heou-Feo, *C. R. Acad. Sci.*, **192**, 1242 (1931); *Chem. Abstr.*, **25**, 4270.
839. W. H. Smith and A. J. Baro, *J. Amer. Chem. Soc.*, **97**(22), 6491 (1975).
840. (a) C. E. Crawforth, O. Meth-Cohn and C. A. Russell, *J. Chem. Soc., Chem. Commun.*, **1972**, 259.
(b) C. E. Crawforth, O. Meth-Cohn and C. A. Russell, *J. Chem. Soc., Perkin Trans. 1*, **1972**, 2807.
(c) D. I. C. Scopes and J. A. Joule, *J. Chem. Soc., Perkin Trans. 1*, **1972**, 22.
841. C. Parkanyi and Y. J. Lee, *Tetrahedron Lett.*, **1974**, 1115.
842. (a) F. R. Stermitz and C. C. Wei, *J. Amer. Chem. Soc.*, **91**(11), 3103 (1969).
(b) F. R. Stermitz, W. H. Huang, D. J. Blythin, A. Hoeft, D. K. Kim and C. M. O'Donnell, *J. Heterocycl. Chem.*, **9**(6), 1289 (1972).
843. A. Castellano, J. P. Catteau and A. Lablache-Combier, *Tetrahedron*, **31**(18), 2255 (1975).
844. (a) O. Buchardt, *Acta Chem. Scand.*, **18**, 1389 (1964).
(b) O. Buchardt, J. Becher and C. Lohse, *Acta Chem. Scand.*, **19**(5), 1120 (1965).
(c) O. Buchardt, P. L. Kamler and C. Lohse, *Acta Chem. Scand.*, **23**, 159 (1969).
845. O. Mumm and C. Bruhn, *Ber.*, **68B**, 176 (1935).
846. S. Vyrbanova, (a) *C. R. Acad. Bulg. Sci.*, **16**(7), 733 (1963); *Chem. Abstr.*, **61**, 5608c; (b) *C. R. Acad. Bulg. Sci.*, **20**(10), 1033 (1967); *Chem. Abstr.*, **68**, 68850; (c) *Nauchn. Tr. Vyssh. Veterinarnomed. Inst., "Prof. G. Pavlov"* **12**, 17 and 25 (1964); *Chem. Abstr.*, **64**, 696d and e.
847. A. Iovchev, I. Kanchovska and S. Vyrbanova, *C. R. Acad. Bulg.* **24**,(2), 223 (1971); *Chem. Abstr.*, **75**, 5650.
848. I. N. Chernyuk, V. V. Shelest, M. Yu. Kornilov and G. T. Pilyugin, *Zh. Obshch. Khim.*, **45**(7), 1559 (1975); *Chem. Abstr.*, **83**, 179223.
849. I. N. Chernyuk, V. V. Shelest, G. T. Pilyugin and I. K. Ushenko, *Russ. Pat.* 448,181 (1974).
850. J. J. Eisch and B. Jaselskis, *J. Org. Chem.*, **28**(10), 2865 (1963).
851. S. Sorriso, G. G. Aloisi and S. Santini, *Z. Phys. Chem. (Frankfurt)*, **94**(1-3), 117 (1975); *Chem. Abstr.*, **82**, 175982.
852. V. G. Krishna and B. B. Bhowmik, *J. Amer. Chem. Soc.*, **90**(7), 1700 (1968).
853. W. Baker, R. F. Curtis and M. G. Edwards, *J. Chem. Soc.*, **1951**, 83.
854. P. E. Verkade and M. van Leeuwen, *Rec. Trav. Chim.*, **70**, 142 (1951); *Chem. Abstr.*, **45**, 79776.
855. G. Y. Sarkis and T. N. Radwan, *J. Indian Chem. Soc.*, **50**(8), 521 (1973); *Chem. Abstr.*, **80**, 149358.
856. A. Kent, D. McNeil and R. M. Cowper, *J. Chem. Soc.*, **1939**, 1858.
857. D. E. Laskowski, D. G. Grabar and W. C. McCrone, *Anal. Chem.*, **25**, 1400 (1953).
858. V. Hoo, T. S. Ma and P. P. T. Sah, *Sci. Rep. Natl. Tsing Hua Univ.*, **2**, 191 (1933); *Chem. Abstr.*, **28**, 3692^3.
859. P. P. T. Sah and K. H. Yuin, *J. Chin Chem. Soc.*, **5**, 129 (1937); *Chem. Abstr.*, **31**, 6140^1.
860. B. E. Christensen, C. H. Wang, I. W. Davies and D. Harris, *Anal. Chem.*, **21**, 1573 (1949).
861. F. M. Taylor, *Brit. Pat.* 909,390 (1962); *Chem. Abstr.*, **58**, 6846a.
862. E. Krause, *Ber.*, **57B**, 813 (1924).
863. H. C. Beachell and D. E. Hoffman, *J. Amer. Chem. Soc.*, **84**, 180 (1962).
864. W. P. Neumann, *Ann.*, **667**, 12 (1963); *Chem. Abstr.*, **60**, 4168h.
865. R. Fricke and F. Robke, *Z. Anorg. Allg. Chem.*, **170**, 25 (1928); *Chem. Abstr.*, **22**, 2721.
866. P. P. Karlik and I. P. Ryazanov, *Zh. Anal. Khim.*, **23**(2), 796 (1968).

867. B. Paul and D. V. R. Rao, *Curr. Sci.*, (a) **37**(22), 642 (1968); *Chem. Abstr.*, **70**, 43503; (b) **40**(5), 106 (1971); *Chem. Abstr.*, **74**, 93917.
868. (a) I. Buric, K. Nikolic and K. R. Velasevic, *Czech. J. Phys.*, **21**(12), 1306 (1971); *Chem. Abstr.*, **76**, 52444.
(b) K. I. Nikolic, K. R. Velasevic and A. B. Dukanovic, *Glas. Hem. Drus. Beograd*, **36**(7–8), 277 (1971); *Chem. Abstr.*, **77**, 159614.
869. H. D. Harot and H. Gechnizdjani, *Z. Anorg. Allg. Chem.*, **397**(1), 16 (1973); *Chem. Abstr.*, **78**, 148043.
870. A. N. Lewin, I. A. Cohen and R. J. Michl, *J. Inorg. Nucl. Chem.*, **36**(9), 1951 (1974); *Chem. Abstr.*, **82**, 25311.
871. S. Fisel, *Acad. Repub. Pop. Rom. Fil. Iasi, Stud. Cercet. Stiint. Chim.*, **9**, 29 (1958); *Chem. Abstr.*, **53**, 18955a.
872. J. Kratsmar-Smogrovic, *Chem. Zvesti*, **20**(5), 321 (1966); *Chem. Abstr.*, **65**, 6705a.
873. J. Kohout and M. Quastlerova, *Chem. Zvesti*, **22**(10), 776 (1968); *Chem. Abstr.*, **70**, 63643.
874. M. Pang, *U.S. Pat.* 3,697,400 (1972); *Chem. Abstr.*, **77**, 167351.
875. J. Kratsmar-Smogrovic, V. Seressova, O. Hulkova, M. Blakhova and M. Melnik, *Chem. Zvesti*, **26**, 348 (1972); *Chem. Abstr.*, **77**, 134443.
876. B. K. Mohapatra, *J. Indian Chem. Soc.*, **51**(7), 705 (1974); *Chem. Abstr.*, **82**, 38101.
877. A. Cirulis and M. Straumanis, *J. Prakt. Chem.*, **162**, 307 (1943); *Chem. Abstr.*, **38**, 19693.
878. J. Ploquin, *C. R. Acad. Sci.*, **233**, 162 (1951); *Chem. Abstr.*, **46**, 1909h.
879. R. Ripan, I. Gainescu and C. Varhelyi, *Rev. Roum. Chim.*, (a) **11**(9), 1051 (1966); *Chem. Abstr.*, **66**, 91240; (b) **11**(6), 717 (1966); *Chem. Abstr.*, **65**, 67028.
880. E. G. V. Percival and W. Warolan, *J. Chem. Soc.*, **1929**, 1505.
881. P. Mesnaro and J. F. Kergonou, *C. R. Acad. Sci., Ser. C*, **263**(2), 167 (1966); *Chem. Abstr.*, **65**, 117366.
882. C. Varhelyi, F. Manok and I. Mostis, *Studia Univ. Babes Bolyai Ser. Chem.*, **11**(1), 93 (1966); *Chem. Abstr.*, **66**, 25571.
883. W. Scheler, P. Mohr, K. Hecht and K. Gustav, *Z. Chem.*, **7**(8), 303 (1967); *Chem. Abstr.*, **67**, 103280.
884. A. A. Schilt and K. R. Kluge, *Talanta*, **15**(10), 1055 (1968).
885. D. J. Booth, G. Marr and B. W. Rockett, *J. Organomet. Chem.*, **32**(2), 227 (1971).
886. E. M. Agres and A. I. Altsybeeva, *Zh. Fiz. Khim.*, **50**(2), 437 (1976); *Chem. Abstr.*, **84**, 164030.
887. S. Guru and D. V. R. Rao, *Curr. Sci.*, **37**(8), 225 (1968); *Chem. Abstr.*, **68**, 118926.
888. K. Nikolic, A. Djukanovic and K. Velasevic, *Acta Pharm. Jugoslav.*, **21**(1), 29 (1971); *Chem. Abstr.*, **75**, 20148.
889. I. Buric and K. Nikolic, *Fizika (Zagreb)*, **5**(1), 27 (1973); *Chem. Abstr.*, **79**, 71816.
890. C. N. Anderson, *U.S. Pat.* 2,085,063 (1937); *Chem. Abstr.*, **31**, 5951.
891. R. H. Wiley, J. L. Hartman, and E. L. De Young, *J. Amer. Chem. Soc.*, **74**, 3452 (1952).
892. D. L. Kepert and D. Taylor, *Aust. J. Chem.*, **27**(6), 1199 (1974).
893. I. S. Ahuja and K. S. Rao, *J. Inorg. Nucl. Chem.*, **37**(2), 586 (1975).
894. K. Brodersen and N. Hacke, *Chem. Ber.*, **107**(10), 3260 (1974).
895. D. G. Bhattacharya and D. C. Bera, *Sci. Cult.*, **41**(5), 225 (1975); *Chem. Abstr.*, **83**, 90150.
896. A. W. Downs and P. A. Ongley, *Chem. Ind. (London)*, **1963**, 493.
897. W. Ludwig and G. Wittmann, *Helv. Chim. Acta*, **47**(5), 1265 (1964).
898. M. K. Misra and D. V. R. Rao, *J. Indian Chem. Soc.*, **46**(7), 672 (1962); *Chem. Abstr.*, **71**, 87261.
899. M. K. Misra and D. V. R. Rao, (a) *J. Inorg. Nucl. Chem.*, **31**(12), 3875 (1969); (b) *Indian J. Chem.*, **8**(1), 86 (1970); *Chem. Abstr.*, **72**, 132241.
900. J. Kohout, M. Jamnicky and E. Jona, *Z. Chem.*, **12**(6), 225 (1972); *Chem. Abstr.*, **77**, 145500.
901. A. V. Leshchenko, V. T. Panyushkin, A. D. Garnovskii and O. A. Osipov, *Zh. Neorgan. Khim.*, **11**(9), 2156 (1966); *Chem. Abstr.*, **65**, 181416; (b) *Zh. Obshch. Khim.*, **37**(5), 1069 (1967); *Chem. Abstr.*, **67**, 104715.
902. D. G. Craciunescu, A. Doadrio and C. Ghirvu, *Z. Phys. Chem. (Leipzig)*, **256**(1), 26 (1975); *Chem. Abstr.*, **83**, 157103.
903. C. C. Yin and A. J. Deeming, *J. Chem. Soc. Dalton Trans.*, **1975**, 2091.
904. V. I. Sokolov, T. A. Sorokina, L. L. Troitskaya, L. I. Solov'eva and O. A. Reutov, *J. Organomet. Chem.*, **36**(2), 389 (1972).

905. D. E. Ryan, *Can. J. Chem.*, **34**, 839 (1956).
906. R. Colton, R. Levitus and G. Wilkinson, *J. Chem. Soc.*, **1960**, 4121.
907. N. A. Subbotina, V. V. Zelentsov and V. I. Spitsyn, *Vestn. Mosk. Univ. Ser. Khim.*, **24**(6), 52 (1969); *Chem. Abstr.*, **72**, 62342.
908. D. G. Tisley and R. A. Walton, *Inorg. Nucl. Chem. Lett.*, **6**(5), 479 (1970).
909. V. V. Zelentsoy, N. A. Subbotina, G. M. Klesova, E. V. Ivanov and V. I. Spitsyn, *Zh. Neorg. Khim.*, **15**(2), 3283 (1970); *Chem. Abstr.*, **74**, 47291.
910. M. Nondyama, *J. Organomet. Chem.*, **92**(1), 89 (1975).
911. W. J. Peard and R. T. Pflaum, *J. Amer. Chem. Soc.*, **80**, 1593 (1958).
912. M. K. Misra, and D. V. R. Rao, *J. Indian Chem. Soc.*, **47**(12), 1162 (1970); *Chem. Abstr.*, **74**, 82644.
913. K. Andra and H. R. Hoppe, *Z. Anorg. Allg. Chem.*, **413**(2), 97 (1975); *Chem. Abstr.*, **83**, 70717.
914. O. Farooq and A. Malik, *Acta Chim. Acad. Sci. Hung.*, **85**(4), 389 (1975); *Chem. Abstr.*, **83**, 209356.
915. F. W. G. Schoening and C. J. Leibenberg, *J. S. Afr. Chem. Inst.*, **20**(2), 61 (1967); *Chem. Abstr.*, **68**, 118174.
916. L. C. Fetterly, *U.S. Pat.* 2,430,632 (1947); *Chem. Abstr.*, **42**, 1397e.
917. H. L. Krauss and G. Gnatz, *Chem. Ber.*, **95**, 1023 (1962).
918. M. Wyler, *Ber.*, **60B**, 398 (1927).
919. S. Guru and D. V. R. Rao, *Z. Anorg. Allg. Chem.*, **362**(1–2), 108 (1968); *Chem. Abstr.*, **70**, 8551.
920. B. K. Mohapatra and D. V. R. Rao, *Z. Anorg. Allg. Chem.*, **372**(3), 332 (1970); *Chem. Abstr.*, **72**, 90237.
921. B. K. Mohapatra, *Curr. Sci.*, **42**(10), 350 (1973); *Chem. Abstr.*, **79**, 26664.
922. M. Pondi, A. Bold, G. Grosu and I. Sirghie, *An. Stiint Univ. "Al I. Cuza" Iasi, Sect 1c*, **12**(1), 17 (1966); *Chem. Abstr.*, **66**, 111162.
923. D. C. Olsen, *Ph.D. Thesis*, Univ. Northern Colorado, 1970; *Diss. Abstr. Int. B*, **31**(12) (Pt. 1) 7193 (1971); *Chem. Abstr.*, **75**, 110164.
924. M. Giua and R. Carpignano, *Gazz. Chim. Ital.*, **83**, 840 (1953); *Chem. Abstr.*, **49**, 6956e.
925. H. Gilman, J. Eisch and T. Soddy, *J. Amer. Chem. Soc.*, **79**, 1245 (1957).
926. W. Borsche and F. Sell, *Chem. Ber.*, **83**, 78 (1950).
927. A. V. El'tsov, H. J. Timpe and N. I. Rtishchev, *Zh. Org. Khim.*, **11**(2), 398 (1975); *Chem. Abstr.*, **83**, 28072.
928. N. P. Buu-Hoi and R. Royer, *Rec. Trav. Chim.*, **66**, 300 (1947); *Chem. Abstr.*, **41**, 6569e.
929. A. Schmidt, *Ber.*, **38**, 3717 (905).
930. E. Besthorn, E. Banzhaf and G. Jaegle, *Ber.*, **27**, 3035 (1894).
931. Meister, Lucius and Brunning Farbw., *Ger. Pat.* 79,173 (1895).
932. W. Borsche and R. Quast, *Ber.*, **52**, 435 (1919).
933. P. Ruggli and A. Disler, *Helv. Chim. Acta*, **10**, 938 (1927).
934. W. H. Mills and F. M. Hamer, *J. Chem. Soc.*, **121**, 2008 (1922).
935. A. A. Rok and L. D. Gluzman, *Sb. Nauchn. Tr., Ukr. Nauchn.-Issled. Uglekhim. Inst.*, No. 16, 136 (1965); *Chem. Abstr.*, **64**, 9679h.
936. L. F. Salisbury, *Brit. Pat.* 632,661 (1949); *Chem. Abstr.*, **44**, 4513g.
937. K. Schofield, *J. Chem Soc.*, **1949**, 2408.
938. J. D. Baty, G. Jones and C. Moore, *J. Org. Chem.*, **34**(11), 3295 (1969).
939. M. Hamana and H. Noda, *Chem. Pharm. Bull. (Tokyo)*, **11**(10), 1331 (1963).
940. J. J. Eisch and F. J. Gadek, *J. Org. Chem.*, **36**(15), 2065 (1971).
941. M. Hasegawa, F. Suzuki, H. Nakanishi and S. Suzuki, *Jap. Pat.* 09,104 (1972); *Chem. Abstr.*, **77**, 63349.
942. P. Bednarek, R. Bodalski, J. Michalski and S. Musierowicz, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.*, **11**(9), 507 (1963); *Chem. Abstr.*, **60**, 5546c.
943. L. Dentimalli, *Gazz. Chim. Ital.*, **93**(8–9), 1093 (1963); *Chem. Abstr.*, **60**, 4108c.
944. B. P. Lugovkin, *Zh. Obshch. Khim.*, **32**, 2544 (1962); *Chem. Abstr.*, **58**, 9059c; (b) **33**, 71 (1963); *Chem. Abstr.*, **59**, 572b.
945. R. A. Abramovitch and D. H. Hey, *J. Chem. Soc.*, **1954**, 1697.
946. B. P. Lugovkin, *Khim. Geterosikl. Soedin.*, **1966**, 571; *Chem. Abstr.*, **66**, 18685.
947. F. Zymalkowski and P. Tinapp, *Justus Liebigs Ann. Chem.*, **699**, 98 (1966); *Chem. Abstr.*, **66**, 55355.

948. D. M. Brown and G. A. R. Kon. *J. Chem. Soc.*, **1948**, 2147.
949. A. Tanaka, *Jap. Pat.* 69 04,975 (1969); *Chem. Abstr.*, **70**, 114996.
950. W. Borsche and R. Manreuffel, *Ann.*, **526**, 22 (1936).
951. M. A. Clapp, and R. S. Tipson, *J. Amer. Chem. Soc.*, **68**, 1332 (1946).
952. C. T. Bahner, W. Chapman, H. Lyons and L. M. Rives, *J. Org. Chem.*, **26**, 2566 (1961).
953. W. Bulach, *Ber.*, **20**, 2046 (1887).
954. M. Q. Doja and D. Prasad, *J. Indian Chem. Soc.*, **20**, 153 (1943); *Chem. Abstr.*, **38**, 3203[9].
955. W. Schneider and A. Pothmann, *Ber.*, **74B**, 471 (1941).
956. E. B. Knott, *J. Chem. Soc.* **1965**, 3793
957. E. K. Fields and A. I. Feinstein, *U.S. Pat.* 3,691,243 (1972).
958. B. W. Bycroft, A. P. Johnson and W. Landon, *J. Chem. Soc. D*, **1969**, 463.
959. (a) M. Yoshida, H. Sugihara, S. Tsushima, E. Mizuta and T. Miki, *Yakugaku Zasshi*, **44**(3), 304 (1974); *Chem. Abstr.*, **81**, 120422.
(b). M. Yoshida, H. Sugihara, S. Tsushima and T. Miki, *J. Chem. Soc. D*, **1969**, 1223.
960. S. Miyano and N. Abe, *Chem. Pharm. Bull. (Tokyo)*, **15**(4), 511 (1967).
961. (a) S. M. Linder, E. I. Becker and P. E. Spoerri, *J. Amer. Chem. Soc.*, **75**, 5972 (1953).
(b) D. Taber, N. Picus, E. I. Becker and P. E. Spoerri, *J. Amer. Chem. Soc.*, **17**, 1010 (1955).
962. S. D. Turk and B. D. Simpson, *U.S. Pat.* 2,996,509 (1961); *Chem. Abstr.*, **56**, 4740e.
963. B. M. Mikhailov and G. S. Ter-Sarkisyan, *Izv. Akad. Nauk SSSR Otdel. Khim. Nauk*, **1956**, 1448; *Chem. Abstr.*, **51**, 8745a.
964. T. Methner, *Ber.*, **27**, 2689 (1894).
965. A. Einhorn and P. Lennkering, *Ann.*, **246**, 160 (1888).
966. A. Benrath, *J. Prakt. Chem.*, **73**(2), 383 (1906).
967. J. Meisenheimer, J. Neresheimer, O. Finn and W. Schneider, *Ann.*, **420**, 190 (1920); *Chem. Abstr.*, **14**, 2927.
968. Z. Y. Kokoshko, V. G. Kitaeva, Z. V. Pushkareva and V. E. Blokhin, *Zh. Obshch. Khim.*, **37**(1), 58 (1967); *Chem. Abstr.*, **66**, 89338.
969. J. Chodkowski and T. Giovanoli-Jakubczak, *Rocz. Chem.*, (a) **43**(5), 1037 (1969); *Chem. Abstr.*, **72**, 11880; (b) **44**(6), 1289 (1970); *Chem. Abstr.*, **73**, 115763.
970. F. Bohlmann, *Chem. Ber.*, **84**, 860 (1951).
971. V. Zanker and G. Schiefele, *Z. Elektrochem.*, **62**, 86 (1958); *Chem. Abstr.*, **52**, 9762b.
972. V. A. Izmail'skii and P. A. Solodkov, *Dokl. Akad. Nauk SSSR*, **75**, 391 (1950); *Chem. Abstr.*, **45**, 4557.
973. M. P. Bhutra and S. P. Tandon, *Z. Naturforsch. B*, **25**(1), 36 (1970); *Chem. Abstr.*, **72**, 72879.
974. R. H. Sprague, H. L. Fichter Jr., and W. P. Hamilton, *U.S. Pat.* 3,102,810 (1963); *Chem. Abstr.*, **59**, 13531e.
975. R. H. Sprague, H. L. Fichter, Jr., and W. P. Hamilton, *U.S. Pat.* 3,095,303; *Chem. Abstr.*, **60**, 1267a.
976. R. H. Sprague and H. L. Fichter, *Photogr. Sci. Eng.*, **8**(2), 95 (1964); *Chem. Abstr.*, **60**, 15333e.
977. National Cash Register Co., *Brit. Pat.* 1,120,094 (1968); *Chem. Abstr.*, **69**, 72834.
978. R. C. Bertelson and K. D. Glanz, *Fr. Pat.* 1,509,687; *Chem. Abstr.*, **70**, 62879.
979. J. M. Lewis, *Brit. Pat.* 1,175,898 (1970); *Chem. Abstr.*, **72**, 61415.
980. E. H. Hazenbosch and A. L. Poot, *Ger. Pat.*, 2,250,752 (1974); *Chem. Abstr.*, **81**, 19237.
981. T. Masuda, Y. Noguchi and H. Katsuyama, *Ger. Pat.*, 2,363,586 (1974); *Chem. Abstr.*, **81**, 84391.
982. V. P. Petro, J. M. Lewis and R. D. Fox, *Ger. Pat.* 1,813,843 (1969); *Chem. Abstr.*, **73**, 9436.
983. T. Goto and K. Kojima, *Jap. Pat.* 74 125,459 (1974); *Chem. Abstr.*, **83**, 19046.
984. Kodak S.A. *Belg. Pat.* 557,439 (1957); *Chem. Abstr.*, **54**, 129c.
985. A. Albert, S. D. Rubbo and M. I. Burvill, *Brit. J. Exp. Path.*, **30**, 159 (1949); *Chem. Abstr.*, **44**, 1560g.
986. C. H. Browning, J. B. Cohen, S. Ellingworth and R. Gulbransen, *Brit. Med. J.*, **II**, 326 (1923); *Chem. Abstr.*, **18**, 1146.
987. C. H. Browning, J. B. Cohen, K. E. Cooper, S. Ellingworth and R. Gulbransen, *Proc. Roy. Soc. (London)*, **B115**, 1 (1934).
988. CIBA Ltd., *Belg. Pat.* 613,604 (1962); *Chem. Abstr.*, **58**, 1441f.
989. A. Taketo, H. Sawada and Y. Takagi, *Biochem. Biophys. Res. Commun.*, **15**(3), 256 (1964).

990. K. Ogasawara, M. Takagi and N. Kato, *Igaku to Seiputsugaku*, **68**(5), 244 (1964); *Chem. Abstr.*, **64**, 10118g.
991. K. Fujimoto, *Chemotherapy (Tokyo)*, **15**(3), 228 (1967); *Chem. Abstr.*, **67**, 97907.
992. L. N. Alekseeva, B. Brizga and N. Saldabols, *Latv. PSR Zinat. Akad. Vestis*, No. 3, 125 (1969); *Chem. Abstr.*, **71**, 10638.
993. S. Yamagishi, Y. Nakajima, Y. Ishikawa and K. Fujii, *Chemotherapy (Tokyo)*, **22**(7), 1159 (1974); *Chem. Abstr.*, **82**, 106909.
994. K. Fujimoto, M. Shimizu, Y. Takase., I. Nakanishi and S. Nakamura, *Chemotherapy (Tokyo)*, **15**(5), 527 (1967); *Chem. Abstr.*, **68**, 47321.
995. G. Berkelhammer and A. Goro, *U.S. Pat.* 3,878,221 (1975); *Chem. Abstr.*, **83**, 79250.
996. T. Ammo, H. Hayashi, S. Kouchiwa and T. Nagayoshi, *Yakugaku Zasshi*, **86**(8), 735 (1966); *Chem Abstr.*, **65**, 16924c.
997. N. A. Leont'Eva, L. N. Yakhontov, Z. V. Idrisova and G. A. Galegov, *Fiz.-Khim. Probl. Sovrem. Biol. Med. Mater. Konf.*, **1970**, 362; *Chem. Abstr.*, **79**, 101054.
998. M. R. Lewis, B. Hughes, C. T. Bahner and A. L. Bates, *Growth*, **19**(1), 1 (1955); *Chem. Abstr.*, **49**, 11186c.
999. B. Hughes, M. R. Lewis and A. L. Bates, *Nature*, **177**, 331 (1956).
1000. M. R. Lewis, B. Hughes and A. L. Bates, *Growth*, **19**, 323 (1955); *Excerpta Med. Sect. V*, **9**, 726 (1956); *Chem. Abstr.*, **51**, 9907c.
1001. C. T. Bahner, *Acta Unio. Int. Cancrum*, **16**, 542 (1960); *Chem. Abstr.*, **54**, 25291b.
1002. A. Haddow, R. J. King, P. D. Lawley and E. M. F. Roe, *Acta Unio. Int. Cancrum*, **16**, 489 (1960); *Chem. Abstr.*, **54**, 25214a.
1003. C. T. Bahner, *Acta Unio. Int. Cancrum*, **20**(1–2), 253 (1964); *Chem. Abstr.*, **61**, 8784b.
1004. C. T. Bahner, L. M. Rives and C. Breder, *J. Med. Chem.*, **7**(6), 818 (1964); *Chem. Abstr.*, **62**, 2761a.
1005. Z. Hadidian, T. N. Fredrickson, E. K. Weisburger, J. H. Weisburger, R. M. Glass and N. Mantel, *J. Nat. Cancer Inst.*, **41**(4), 985 (1968); *Chem. Abstr.*, **70**, 18359.
1006. G. E. Foley, R. E. McCarthy, V. M. Binns, E. E. Snell, B. M. Guirard, G. W. Kidder, V. C. Dewey and P. S. Thayer, *Ann. N.Y. Acad. Sci.*, **76**, 413 (1958); *Chem. Abstr.*, **53**, 9357e.
1007. C. T. Bahner, H. Kinder and T. Rigdon, *J. Med. Chem.*, **8**(1), 137 (1965); *Chem. Abstr.*, **62**, 6457g.
1008. A. Zidermane, I. M. Kravchenko, A. Dauvarte, N. M. Sukhova and M. Lidaka, *Farmakol. Toksikol. (Moscow)*, **33**, 711 (1970); *Chem. Abstr.*, **74**, 62889.
1009. T. Matsuda, *Jap. Pat.* 73 38,851 (1973); *Chem. Abstr.*, **81**, 2552.
1010. W. A. Knapp and L. J. Heuser, *U.S. Pat.* 2,427,286 (1947); *Chem. Abstr.*, **42**, 318a.
1011. Y. Tanaka, Y. Shimura and A. Okada, *Jap. Pat.* 73 84,127 (1973); *Chem. Abstr.*, **80**, 147060.
1012. J. A. Shotton, *U.S. Pat.* 2,927,864 (1960).
1013. K. Ryu, *Jap. Pat.*, (a) 74 99,538 (1974); *Chem. Abstr.*, **82**, 126683; (b) 74 99,332 (1974); *Chem. Abstr.*, **82**, 141749.
1014. Y. Tanaka, Y. Shimura and A. Okada, *Jap. Pat.* 73 84,185 (1973); *Chem. Abstr.*, **80**, 121747.
1015. A. Heller, *Isr. Pat.* 14,445 (1962); *Chem. Abstr.*, **56**, 7518e.
1016. G. F. D'Alelio, *U.S. Pat.*, (a) 2,623,013 (1952); *Chem. Abstr.*, **47**, 2911d; (b) 2,683,124 (1954); *Chem. Abstr.*, **48**, 10957g; (c) 2,739,948 (1956); *Chem. Abstr.*, **50**, 9654c.
1017. (a) M. Morgner, *E. Ger. Pat.* 16,075 (1958); *Chem. Abstr.*, **54**, 16694i.
(b) F. Wolf and M. Morgner, *Ger. Pat.* 1,056,371 (1959); *Chem. Abstr.*, **55**, 5809i.
1018. K. T. Shen, *U.S. Pat.*, (a) 2,771,462 (1956); *Chem. Abstr.*, **51**, 7057e; (b) 2,915,476 (1959); *Chem. Abstr.*, **54**, 5065c.
1019. T. Isojima, R. Yamamoto, M. Nishioka, D. Ono, M. Sasaki and S. Yamagughi, *Jap. Pat.* 66 12,111 (1966); *Chem. Abstr.*, **66**, 3721.
1020. G. B. Bachmann, L. J. Filar, R. W. Finholt, L. V. Heisy, H. M. Hellman, L. L. Lewis and D. D. Micucci, *Ind. Eng. Chem.*, **43**, 997 (1951).
1021. O. D. Ratliff and W. T. McMichael, *U.S. Pat.* 3,049,452 (1962); *Chem. Abstr.*, **59**, 3712c.
1022. F. Mayer, *Fr. Pat.* 1,484,601 (1967); *Chem. Abstr.*, 69, 30638.
1023. Y. Tanaka, Y. Shimura and A. Okada, *Jap. Pat.* 74 93,452 (1974); *Chem. Abstr.*, **82**, 99531.
1024. (a) J. R. Moser and A. A. Schneider, *Ger. Pat.* 2,166,543 (1974); *Chem Abstr.*, **82**, 142643; *Ger. Pat.* 2,126,055 (1971); *Chem. Abstr.*, **76**, 67438.
(b) A. A. Schneider, *U.S. Pat.* 4,010,043 (1977); *Chem. Abstr.*, **85**, 110068.

1025. E. Pernix, *Fr. Pat.* 1,497,474 (1967); *Chem. Abstr.*, **69**, 92421.
1026. E. Ochim and K. Kokeguti, *Yakugaku Zasshi*, **60**, 271 (1940); *Chem. Abstr.*, **35**, 458[2].
1027. B. Heymann and W. Koenigs, *Ber.*, **21**, 2167 (1888).
1028. G. Buchmann and D. Kirstein, *J. Prakt. Chem.*, **18** (No. 3–4), 175 (1962); *Chem. Abstr.*, **58**, 11327b.
1029. J. L. Towle, *Iowa State Coll. J. Sci.*, **26**, 308 (1952); *Chem. Abstr.*, **47**, 8062g.
1030. W. Wartanian, *Ber.*, **23**, 3644 (1890).
1031. G. Buchmann and H. Kirsch, *J. Prakt. Chem.*, **16**, 240 (1962); *Chem. Abstr.*, **59**, 3889g.
1032. T. Sakai, C. Kaneko and S. Mitsui, *Nippon Kaguka Zasshi*, **86** (12), 1328 (1965); *Chem. Abstr.*, **65**, 13648h.
1033. W. Bulach, *Ber.*, **22**, 285 (1889).
1034. A. Boehringer, *Brit. Pat.* 311,387 (1928); *Chem. Abstr.*, **24**, 919.
1035. T. Shono, S. Kodama and R. Oda, *Kogyo Kagaku Zasshi*, **58**, 917 (1955); *Chem. Abstr.*, **50**, 13017h.
1036. G. Buchmann and O. Wolniak, *Pharmazie*, **21** (11), 650 (1966); *Chem. Abstr.*, **68**, 114398v.
1037. V. A. Rao, P. C. Jain and N. Anand, *Indian. J. Chem.*, **12** (4), 425 (1974); *Chem. Abstr.*, **81**, 152193.
1038. D. E. Heitmeier, J. T. Hortenstine and A. P. Gray, *J. Org. Chem.*, **36** (11), 1449 (1971).
1039. P. C. Jain, R. C. Srimal, B. N. Dhawan, N. Anand, J. N. Sharma and V. A. Rao, *Ger. Pat.* 2,421,382 (1975); *Chem. Abstr.*, **84**, 44160.
1040. F. Bergmann, *J. Amer. Chem. Soc.*, **60**, 2811 (1938).
1041. C. W. Hertz, *U.S. Pat.*, (a) 2,745,834 (1956); *Chem. Abstr.*, **51**, 1295b; (b) 2,900,387 (1959); *Chem. Abstr.*, **54**, 1562.
1042. A. Nenz and G. B. Gechele, *Ital. Pat.* 601,911 (1960); *Chem. Abstr.*, **55**, 12934h.
1043. M. M. Koton, (a) *Khim. Teknol. Primen. Proizodnykh Piridina Khinolina Mater. Sovescheh. 1957*, **119** (1960); *Chem. Abstr.*, **55**, 16546g.
(b) *J. Polym. Sci.*, **30**, 331 (1958); *Chem. Abstr.*, **52**, 21223a.
1044. C. Bonsall and P. Holt, *Makromol. Chem.*, **175** (3), 749 (1974).
1045. P. Longi, U. Nordio and E. Pellino, *Ital. Pat.* 726,445 (1966); *Chem. Abstr.*, **69**, 36605.
1046. Y. Shin and O. Fukumoto, *Jap. Pat.* 63 26,585 (1963); *Chem. Abstr.*, **60**, 6979g.
1047. G. E. Ham, *U.S. Pat.* 2,643,990 (1953); *Chem. Abstr.*, **47**, 9025i.
1048. W. F. Fowler, Jr., and D. D. Reynolds, *U.S. Pat.* 2,721,852 (1955); *Chem. Abstr.*, **50**, 2336g.
1049. A. Bonvicini, A. Monaci and V. Cappuccio, *Ital. Pat.* 578,721 (1958); *Chem. Abstr.*, **53**, 22981c.
1050. R. Z. Greenfley, *J. Macromol. Sci. Chem.*, **A9** (4), 505 (1975).
1051. H. Guesten, L. Klasinc and D. Stefanovic, *Org. Mass Spectrom.*, **7** (1), 1 (1973).
1052. C. T. Bahner, C. Cook, W. Longmire and S. V. Hagen, *J. Org. Chem.*, **26**, 2134 (1961).
1053. Ruetgerswerke A.G., *Brit. Pat.* 956,398 (1964); *Chem. Abstr.*, **61**, 5618c.
1054. Y. Makisumi, *Tetrahedron Lett.*, (a) **1964**, 699; (b) **1964**, 1635.
1055. A. J. Nunn and K. Schofield, *J. Chem. Soc.*, **1953**, 3700.
1056. C. E. Loader and C. J. Timmons, *J. Chem. Soc. C*, **1968**, 330.
1057. N. N. Zatsepina, I. F. Tupitsyn and A. I. Belyashova, *Reakts. Sposobn. Org. Soedin.*, **12** (1), 207 (1975); *Chem. Abstr.*, **84**, 164034.
1058. American Cyanamide Co., *Brit. Pat.* 611,991 (1948); *Chem. Abstr.*, **43**, 3045d.
1059. J. M. Smith, Jr., *U.S. Pat.* 2,414,398 (1945); *Chem. Abstr.*, **41**, 5904b.
1060. U. Haug and H. Furst, *Chem. Ber.*, **93**, 593 (1960).
1061. J. M. Smith, Jr., *U.S. Pat.* 2,442,865 (1948); *Chem. Abstr.*, **42**, 7796g.
1062. T. Nakashima, *Yakugaku Zasshi*, **77**, 1298 (1957); *Chem. Abstr.*, **52**, 6345g.
1063. A. I. Kiprianov and G. G. Dyadyusha, *Zh. Obshch. Khim.*, **29**, 1708 (1959); *Chem. Abstr.*, **54**, 8817i.
1064. J. M. Smith, Jr., H. W. Stewart, B. Roth and E. M. Northey, *J. Amer. Chem. Soc.*, **70**, 3997 (1948).
1065. I. K. Ushenko, *Zh. Obshch. Khim.*, **31**, 2854 (1961); *Chem. Abstr.*, **56**, 13048i.
1066. J. H. Blumenthal, *U.S. Pat.* 2,874,162 (1959); *Chem. Abstr.*, **53**, 123116.
1067. J. L. Neumeyer and J. G. Cannon, *J. Pharm. Sci.*, **51**, 804 (1962); *Chem. Abstr.*, **58**, 4514c.
1068. U. Fritzsche and S. Huenig, *Tetrahedron Lett.*, **1972**, 4831.
1069. U. Burckhardt and M. Zimmermann, *Ger. Pat.* 2,209,470 (1972); *Chem. Abstr.*, **77**, 164744.
1070. B. R. Brown, D. Ll. Hammick and B. H. Thewlis, *J. Chem. Soc.*, **1951**, 1145.

1071. J. A. Gautier, M. Miocque and N. M. Hung, *Bull. Soc. Chim. Fr.*, (a) **1961**, 2092; (b) **1961**, 2098; (c) *C. R. Acad. Sci.*, **253**, 128 (1961).
1072. J. C. Carey and W. H. F. Sasse, *Aust. J. Chem.*, **21**(1), 207 (1968).
1073. S. Skidmore and E. Tidd, *J. Chem. Soc.*, **1961**, 1098.
1074. F. M. Hamer, (a) *Q. Rev. Chem. Soc.*, **4**, 327 (1950); (b) *The Cyanine Dyes and Related Compounds*, Interscience, New York, 1963.
1075. (a) G. Scheibe and E. Rossner, *Ber.*, **53B**, 2064 (1920); (b) G. Scheibe and E. Rosner, *Ber.*, **54B**, 786 (1921); (c) H. J. Friedrich, W. Gueckel and G. Scheibe, *Ber.*, **95**, 1378 (1962); (d) G. Scheibe and G. Schmidt, *Ber.*, **55**, 3157 (1922); (e) G. Scheibe, *Ber.*, **56B**, 137 (1923).
1076. G. Scheibe and H. J. Friedrich, *Chem. Ber.*, **94**, 1336 (1961).
1077. B. R. Brown, D. Ll. Hammick, J. Newbould and A. L. Price, *J. Chem. Soc.*, **1959**, 1311.
1078. (a) D. Ll. Hammick, C. N. Lammiman, E. D. Morgan, and A. M. Roe, *J. Chem. Soc.*, **1955**, 2436.
(b) I. M. C. Barfoot, D. Ll. Hammick, E. D. Morgan and A. M. Roe, *J. Chem. Soc.*, **1957**, 1533.
1079. A. Walker, W. E. Baldwin, H. I. Thayer and B. B. Corson, *J. Org. Chem.*, **16**, 1805 (1951).
1080. W. Borsche and G. A. Kienitz, *Ber.*, **43**, 2333 (1910).
1081. C. E. Kaslow and R. A. Reck, *J. Amer. Chem. Soc.*, **69**, 864 (1947).
1082. W. Borsche and R. Meyer, *Ber.*, **54B**, 2841 (1921).
1083. J. Moir, *J. Chem. Soc.*, **127**, 2338 (1925).
1084. W. Konig, *Ber.*, **55**, 3293 (1922).
1085. F. M. Hamer, *J. Chem. Soc.*, **123**, 246 (1923).
1086. D. E. Ames and J. L. Archibald, *J. Chem. Soc.*, **1962**, 1475.
1087. M. Hamana and M. Yamazaki, *Chem. Pharm. Bull. (Tokyo)*, **11**(4), 415 (1963).
1088. R. N. Sen and B. N. Sen, *J. Indian Chem. Soc.*, **7**, 965 (1930); *Chem. Abstr.*, **25**, 2991.
1089. (a) J. von Braun and E. Aust, *Ber.*, **49**, 501 (1916).
(b) J. von Braun and J. Seeman, *Ber.*, **56**, 2163 (1923).
1090. M. Colonna, *Gazz. Chim. Ital.*, **90**, 1179 (1960); *Chem. Abstr.*, **56**, 5930c.
1091. H. Kaplan and H. G. Lindwall, *J. Amer. Chem. Soc.*, **65**, 927 (1943).
1092. W. Neugebauer, O. Sues, M. Tomanek, K. W. Kluepfel and H. Behmenberg, *Ger. Pat.* 1,105,713 (1961); *Chem. Abstr.*, **56**, 8214g.
1093. D. Ll. Hammick, E. Johnston and E. D. Morgan, *J. Chem. Soc.*, **1957**, 5073.
1094. M. Guia, *Gass. Chim. Ital.*, **52**(1), 349 (1922); *Chem. Abstr.*, **16**, 2690.
1095. S. Huenig and I. Stemmler, *Tetrahedron Lett.*, No. 36, 3151 (1974).
1096. S. C. Misra and S. P. Popli, *J. Indian Chem. Soc.*, **39**, 321 (1962).
1097. H. Andrews, S. Skidmore and H. Suschitzky, *J. Chem. Soc.*, **1962**, 2370.
1098. G. Scheibe and G. Kilian, *Z. Phys. Chem. Bodenstein-Festband*, **1931**, 468; *Chem. Abstr.*, **25**, 5675.
1099. G. Scheibe and W. Riess, *Chem. Ber.*, **92**, 2189 (1959).
1100. H. J. Friedrich and G. Scheibe, *Z. Elektrochem.*, **65**, 851 (1961); *Chem. Abstr.*, **57**, 11162i.
1101. J. van Thuijl, C. Romers and E. Havinga, *Rec. Trav. Chim.*, **82**(9–10), 1026 (1963); *Chem. Abstr.*, **60**, 1695c.
1102. E. Daltrozzo, G. Hohlneicher and G. Scheibe, *Ber. Bunsenges. Phys. Chem.*, **69**(3), 190 (1965); *Chem. Abstr.*, **62**, 14468d.
1103. H. J. Friedrich and G. Scheibe, *Z. Elektrochem.*, **65**, 767 (1961); *Chem. Abstr.*, **57**, 11162f.
1104. E. Schell, *Rev. gen. mat. Color.*, **15**, 259 (1911); *Chem. Abstr.*, **6**, 351.
1105. E. Q. Adams and H. L. Haller, *J. Amer. Chem. Soc.*, **42**, 2389 (1920).
1106. H. J. Friedrich, *Z. Naturforsch.*, **18b**(8), 635 (1963); *Chem. Abstr.*, **59**, 14738b.
1107. G. Scheibe and W. Fischer, *Ber.*, **59B**, 502 (1926).
1108. D. Basting, F. P. Schaefer and B. Steyer, *Appl. Phys.*, **3**(1), 81 (1974); *Chem. Abstr.*, **81**, 19043.
1109. F. M. Hamer, *J. Chem. Soc.*, **123**, 246 (1923).
1110. G. Scheibe and H. J. Friedrich, *Z. Elektrochem.*, **64**, 720 (1960); *Chem. Abstr.*, **54**, 24731f.
1111. G. Scheibe, H. J. Friedrich, W. Guckel and H. H. Credner, *Angew. Chem.*, **73**, 273 (1961); *Chem. Abstr.*, **55**, 16250f.
1112. H. J. Friedrich and G. Hohlneicher, *Angew. Chem.*, **74**, 466 (1962); *Chem. Abstr.*, **57**, 8153f.
1113. U. Kuhnes and H. Guesten, *Z. Naturforsch.*, **29B** (1–2), 137 (1974); *Chem. Abstr.*, **81**, 36902.
1114. L. K. Sharp, *J. Pharm. Pharmacol.*, **1**, 395 (1949); *Chem. Abstr.*, **43**, 6207g.

1115. C. A. Buehler and S. P. Edwards, *J. Amer. Chem. Soc.*, **74**, 977 (1952).
1116. M. Bourguel, *Bull. Soc. Chim Fr.*, **45**, 1067 (1929).
1117. E. Noelting and C. Schwartz, *Ber.*, **24**, 1606 (1891).
1118. M. M. Robinson, W. G. Pierson, L. Oorfman, B. F. Lambert and R. A. Lucas, *Tetrahedron Lett.*, **1964**, 1513.
1119. D. M. Clugston, D. B. MacLean and R. H. F. Manske, *Can. J. Chem.*, **45**(1), 39 (1967).
1120. R. Tschesche, D. Kloeden and H. W. Fehlhaber, *Tetrahedron*, **20**(12), 2885 (1964).
1121. R. R. Arndt, A. Jordaan and V. P. Joynt, *J. Chem. Soc.*, **1964**, 5969.
1122. A. Jordaan, V. P. Joynt and R. R. Arndt, *J. Chem. Soc.*, **1965**, 3001.
1123. V. P. Joynt, R. R. Arndt, A. Jordaan, K. Biemann and J. L. Occolowitz, *J. Chem. Soc. B*, **1966**, 980.
1124. H. Gilman, R. V. Christian and S. M. Spatz, *J. Amer. Chem. Soc.*, **68**, 979 (1946).
1125. H. Gilman, J. L. Towle and S. M. Spatz, *J. Amer. Chem. Soc.*, **68**, 2017 (1946).
1126. H. Gilman, W. A. Gregory and S. M. Spatz, *J. Org. Chem.*, **16**, 1788 (1951).
1127. H. Gilman and S. Avakian, *J. Amer. Chem. Soc.*, **76**, 4031 (1954).
1128. H. Gilman and D. A. Shirley, *J. Amer. Chem. Soc.*, 71, 1870 (1949).
1129. D. A. Shirley and P. A. Roussel, *J. Amer. Chem. Soc.*, **75**, 375 (1953).
1130. N. J. Leonard and J. H. Boyer, *J. Amer. Chem. Soc.*, **72**, 2980 (1950).
1131. R. A. Abramovitch, K. S. Ahmed and C.-S. Giam, *Can. J. Chem.*, **41**(7), 1752 (1963).
1132. N. N. Goldberg and R. Levine, *J. Amer. Chem. Soc.*, 77, 3647 (1955).
1133. T. A. Geissman, M. J. Schlatter, I. D. Webb and J. D. Roberts, *J. Org. Chem.*, **11**, 741 (1946).
1134. H. Gilman and S. M. Spatz, *J. Amer. Chem. Soc.*, **66**, 621 (1944).
1135. H. Gilman and T. S. Soddy, *J. Org. Chem.*, **23**, 1584 (1958).
1136. H. Gilman, E. A. Weipert, T. Soddy and F. N. Hayes, *J. Org. Chem.*, **22**, 1169 (1957).
1137. H. Gilman and D. A. Shirley, *J. Amer. Chem. Soc.*, **72**, 2181 (1950).
1138. H. Gilman and G. C. Gainer, *J. Amer. Chem. Soc.*, **69**, 877 (1947).
1139. H. Gilman and L. A. Woods, *J. Amer. Chem. Soc.*, **66**, 1981 (1944).
1140. A. N. Nesmeyanov, V. A. Sazonova, V. I. Romanenko, N. A. Rodionova and G. P. Zol'nikova, *Dokl. Akad. Nauk SSSR.*, **155**(5), 1130 (1964).
1141. K. Schloegl and M. Fried, *Monatsh.*, **94**(3), 537 (1963).
1142. E. Wienhoefer and T. Kauffmann, *Tetrahedron Lett.*, **1974**, 2347.
1143. T. Kauffmann and A. Woltermann, *Angew. Chem. Int. Ed. Engl.*, **11**, 842 (1972).
1144. T. Kauffmann, J. Jackisch, H. J. Streitberger and E. Wienhoeffer, *Angew. Chem. Int. Ed. Engl.* **10**(10), 744 (1971).
1145. D. A. Shirley and P. W. Alley, *J. Amer. Chem. Soc.*, **79**, 4922 (1957).
1146. D. A. Shirley and M. D. Cameron, *J. Amer. Chem. Soc.*, **72**, 2788 (1950).
1147. H. Gilman and M. A. Plunkett, *J. Amer. Chem. Soc.*, **71**, 1117 (1949).
1148. H. Gilman, C. G. Stuckwisch and J. F. Nobis, *J. Amer. Chem. Soc.*, **68**, 326 (1946).
1149. A. Kaufmann and J. M. Playjanini, *Ber.*, **44**, 2670 (1911).
1150. F. W. Bergstrom and S. H. McAllister, *J. Amer. Chem. Soc.*, **52**, 2845 (1930).
1151. F. K. Tcheou and K. L. Lee, *Sci. Rec. (Peking)*, **2**, 70 (1947); *Chem. Abstr.*, **42**, 2605e.
1152. M. Colonna and A. Risaliti, *Gazz. Chim. Ital.*, **83**, 58 (1953); *Chem. Abstr.*, **48**, 8784d.
1153. M. Colonna and A. Risaliti, *Ann. Chim. (Rome)*, **44**, 1029 (1954).
1154. H. E. Jansen and J. P. Wibaut, *Rec. Trav. Chim.*, **56**, 709 (1937); *Chem. Abstr.*, **31**, 6233[1].
1155. T. Kato and H. Yamanaka, *J. Org. Chem.*, **30**(3), 910 (1965).
1156. C. R. Hauser and M. J. Weiss, *J. Org. Chem.*, **14**, 310 (1949).
1157. M. A. Wuonola and R. B. Woodward, (a) *J. Amer. Chem. Soc.*, **95**(1), 284 (1973); (b) *Tetrahedron*, **32**, 1085 (1976).
1158. A. Marsili, *Ann. Chim. (Rome)*, **52**, 3 (1962).
1159. F. Just, *Ber.*, **18**, 2632 (1885)
1160. F. Just, *Ber.*, **19**, 1462 (1886)
1161. F. Just, *Ger. Pat.* 33,497 (1885).
1162. W. von Miller and F. Kinkelin, *Ber.*, **18**, 1900 (1885).
1163. H. Weidel and G. von Geogievico, *Monatsh.*, **9**, 138 (1888).
1164. R. Camps, *Arch. Pharm.*, **237**, 659 (1899).
1165. C. Bulow and G. Issler, *Ber.*, **36** (1903), (a) 2447; (b) 4013.
1166. O. G. Doebner and M. Gieseke, *Ann.*, **242**, 290 (1887).
1167. W. Pfitzinger, *J. Prakt. Chem.*, **38**, 582 (1888).

1168. H. John, (a) *Ber.*, **59B**, 2709 (1926); (b) *J. Prakt. Chem.*, **115**, 279 (1927); *Chem. Abstr.*, **21**, 1814.
1169. W. Pfitzinger, *J. Prakt. Chem.*, **56**, 283 (1897).
1170. O. Doebner and H. Fettback, *Ann.*, **281**, 1 (1894).
1171. H. Hubner, *Ber.*, **41**, 482 (1908); *Chem. Abstr.*, **2**, 1450.
1172. W. Koenigs and G. Jaegle, *Ber.*, **28**, 1046 (1895).
1173. W. Koenigs and J. V. Nef, *Ber.*, **20**, 622 (1887).
1174. O. Doebner, *Ann.*, **249**, 98 (1888).
1175. S. G. P. Plant and R. J. Rosser, *J. Chem. Soc.*, **1929**, 1861.
1176. W. Borsche, *Ber.*, **42**, 4072 (1909).
1177. O. Doebner, *Ann.*, **242**, 265 (1887).
1178. J. von Braun and L. Brauns, *Ber.*, **60B**, 1253 (1927).
1179. T. Kaku, *Yakugaku Zasshi*, (a) **47**, 577 (1927); *Chem. Abstr.*, **21**, 3622; (b) **50**, 235 (1930); *Chem. Abstr.*, **24**, 3511.
1180. J. von Braun, E. Hahn and J. Seeman, *Ber.*, **55B**, 1687 (1922).
1181. H. John and E. Pietsch, *J. Prakt. Chem.*, **143**, 243 (1935); *Chem. Abstr.*, **29**, 7332^2.
1182. W. Steinkopf and M. Kuhnel, *Ann.*, **545**, 33 (1940); *Chem. Abstr.*, **35**, 110^6.
1183. W. E. McEwen, R. H. Terss and I. W. Elliott, *J. Amer. Chem. Soc.*, **74**, 3605 (1952).
1184. P. Cagniant, P. Faller and D. Cagniant, *Bull. Soc. Chim. Fr.*, **1964**, 1525; *Chem. Abstr.*, **61**, 10642h.
1185. N. P. Buu-Hoi, M. Delcey, P. Jacquignon and F. Perin, *J. Heterocycl. Chem.*, **5**(2), 259 (1968).
1186. A. L. Gershuns, A. N. Brizitskaya and P. Ya. Pustavar, *Khim. Geterotsikl. Soedin.*, **1973**, 1536; *Chem. Abstr.*, **80**, 70773.
1187. E. A. Fehnel and D. E. Cohn, *J. Org. Chem.*, **31**(11), 3852 (1966).
1188. J. M. Patterson, C. F. Mayer and W. T. Smith, Jr., *J. Org. Chem.*, **40**(10), 1511 (1975).
1189. D. H. Hey and E. W. Walker, *J. Chem. Soc.*, **1948**, 2213.
1190. K. H. Pausacker, *Aust. J. Chem.*, **11**, 200 (1958).
1191. T. Kosuge, K. Adachi, M. Yokota and T. Nakao, *Yakugaku Zasshi*, **85**(1), 66 (1965); *Chem. Abstr.*, **62**, 10404f.
1192. H. J. M. Dou and B. M. Lynch, *Bull. Soc. Chim. Fr.*, **1966**, 3815; *Chem. Abstr.*, **66**, 104545.
1193. H. J. M. Dou and B. M. Lynch, *C. R. Acad. Sci. Ser. C*, **262**(21), 1537 (1966); *Chem. Abstr.*, **65**, 7004b.
1194. G. Vernin, H. J. M. Dou, and J. Metzger, *Bull. Soc. Chim. Fr.*, **1971**, 2612; *Chem. Abstr.*, **75**, 109709.
1195. W. J. Adams, D. H. Hey, P. Mamalis and R. E. Parker, *J. Chem. Soc.*, **1949**, 3181.
1196. R. A. Abramovitch, *J. Chem. Soc.*, **1954**, 3839.
1197. D. H. Hey and J. M. Williams, *J. Chem. Soc.*, **1950**, 1678.
1198. J. I. G. Cadogan, *J. Chem. Soc.*, **1962**, 4257.
1199. (a) G. Vernin, J. Metzger and C. Parkanyi, *J. Org. Chem.*, **40**(22), 3183 (1975); (b) P. Hassanaly, G. Vernin, H. J. M. Dou and J. Metzger, *J. Heterocycl. Chem.*, **12**(4), 703 (1975).
1200. M. Z. A. Badr and H. A. H. El-Sherief, *Indian J. Chem.*, **12**(10), 1067 (1974); *Chem. Abstr.*, **83**, 43093.
1201. J. Elks and D. H. Hey, *J. Chem. Soc.*, **1943**, 441.
1202. A. K. Shienkman, V. A. Ivanov and S. N. Baranov, *Dopov. Akad. Nauk Ukr. RSR, Ser. B*, **32**(7), 619 (1970); *Chem. Abstr.*, **74**, 76298.
1203. A. K. Shienkman, V. A. Ivanov and S. N. Baranov, *Metody Poluch. Khim. Reakt. Prep.*, (a) No. 23, 72 (1971); *Chem. Abstr.*, **78**, 29580; (b) No. 23, 64 (1971); *Chem. Abstr.*, **78**, 29588.
1204. A. K. Shienkman, V. A. Ivanov, S. N. Baranov and S. G. Potashnikova, (a) *Russ. Pat.* 301,334 (1971); (b) A. K. Shienkman, V. A. Ivanov, S. N. Baravov, S. G. Potashnikova and A. N. Kucherenko, *Tezisy Dokl. Simp. Khim. Tekhnol. Geterotsikl. Soedin. Goryuch Iskop., 2nd*, **1973**, 8; *Chem. Abstr.*, **86**, 29594.
1205. (a) A. K. Shienkman, V. A. Ivanov, N. A. Klyuev and G. A. Mal'tseva, *Zh. Org. Khim.*, **9**(12), 2550 (1973); *Chem. Abs.*, **80**, 82601.
(b) A. K. Shienkman, V. A. Ivanov, L. V. Luk'vanenko and G. F. Filimonova, *Zh. Org. Khim.*, **13**, 450 (1977); *Chem. Abstr.*, **87**, 38477.
1206. E. K. Fields, *U.S. Pat.* 3,891,656 (1975).

1207. T. K. Govindan, *Proc. Indian Acad. Sci.*, **44A**, 123 (1956); *Chem. Abstr.*, **51**, 5084d.
1208. F. H. Case, *J. Heterocycl. Chem.*, **4**(1), 157 (1967).
1209. P. M. Dzadzic, B. L. Bastic and M. V. Piletic, *Glas. Hem. Drus., Beograd*, (a) **36**, (3–4), 137 (1971); *Chem. Abstr.*, **78**, 16096; (b) **37**(5–6), 257 (1972); *Chem. Abstr.*, **79**, 53215.
1210. E. Barni and P. Savarino, *J. Heterocycl. Chem.*, **14**, 937 (1977).
1211. E. Barni and G. di Modica, *Tinctoria*, **74**, 189 (1977); *Chem. Abstr.*, **87**, 153394.
1212. W. Krueger and G. Krueger. *E. Ger. Pat.* 99, 787 (1973); *Chem. Abstr.*, **80**, 95953.
1213. A. L. Gershuns and A. N. Brizitskaya, (a) *Khim. Geterotsikl. Soedin.*, **1969**, 698. *Chem. Abstr.*, **72**, 31672; (b) *Metody Poluch. Khim. Reactiv. Prep.*, No. 18, 38 (1969); *Chem. Abstr.*, **74**, 141693; (c) No. 18, 41 (1969); *Chem. Abstr.*, **75**, 129709.
1214. D. Jerchel, M. Kracht and K. Krucker, *Ann.*, **590**, 232 (1954); *Chem. Abstr.*, **49**, 102716.
1215. C. A. Buehler and J. O. Harris, *J. Amer. Chem. Soc.*, **72**, 5015 (1950).
1216. A. Stener, *Gazz. Chim. Ital.*, **90**, 1365 (1960); *Chem. Abstr.*, **56**, 7308h.
1217. B. S. Alamela and B. B. Dey, (a) *Proc. Natl. Inst. Sci. India*, **7**, 207 (1941); *Chem. Abstr.*, **43**, 1421d; (b) **7**, 215 (1941); *Chem. Abstr.*, **43**, 1241i.
1218. G. Kochendoerfer, *Ger. Pat.* 634,987 (1936); *Chem. Abstr.*, **31**, 418[4].
1219. G. Illuminati and H. Gilman, *J. Amer. Chem. Soc.*, **74**, 2896 (1952).
1220. Burroughs Wellcome & Co. (U.S.A.) Inc., *Brit. Pat.* 735,702 (1955); *Chem. Abstr.*, **50**, 7882d.
1221. R. Metze, (a) *Ber.*, **89**, 2056 (1956); (b) *E. Ger. Pat.* 13,175 (1957); *Chem. Abstr.*, **53**, 7216i.
1222. F. H. Case and E. Koft, *J. Amer. Chem. Soc.*, **81**, 905 (1959).
1223. D. L. Aldous, J. L. Riebsomer and R. N. Castle, *J. Org. Chem.*, **25**, 1151 (1960).
1224. R. P. Williams, V. J. Bauer and S. R. Safir, *J. Med. Chem.*, **12**(5), 1124 (1969); *Chem. Abstr.*, **72**, 31689.
1225. G. F. Holland and J. N. Pereira, *J. Med. Chem.*, **10**(2), 149 (1967).
1226. M. Hamana and H. Noda, *Chem. Pharm. Bull. (Tokyo)*, **13**(8), 912 (1965).
1227. M. Hamana and O. Hoshino, *Yakugaku Zasshi*, **84**, 35 (1964); *Chem. Abstr.*, **61**, 30696.
1228. S. Saeki, A. Yamashita, Y. Matsukura and M. Hamana, *Chem. Pharm. Bull. (Tokyo)*, **22**(10), 2341 (1974).
1229. M. Colonna and P. Bruni, *Boll. Sci. Fac. Chim. Ind. Bologna*, **23**(4), 401 (1965); *Chem. Abstr.*, **64**, 17536f.
1230. G. Wittig and G. Steinhoff, *Ann.*, **676**, 21 (1964); *Chem. Abstr.*, **61**, 14635a.
1231. J. Kacens and O. Neilands, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, **1970**, 606; *Chem. Abstr.*, **74**, 53473.
1232. T. Kato, H. Yamanaka, T. Sakamoto and T. Shiraishi, *Chem. Pharm. Bull. (Tokyo)*, **22**(5), 1206 (1974); *Chem. Abstr.*, **81**, 63456.
1233. T. Kato and H. Yamanaka, *Chem. Pharm. Bull. (Tokyo)*, **12**, 18 (1964).
1234. H. Weidel, *Monatsh.*, **17**, 401 (1896).
1235. W. Meigen, *J. Prakt. Chem.*, **77**, 472 (1908).
1236. J. Biedermann, *Ber.*, **22**, 2761 (1889).
1237. H. Von Dobeneck and W. Goltzsche, *Ber.*, **95**, 1484 (1962).
1238. A. K. Shienkman, A. N. Kost and R. D. Bodnarchuk, *Khim. Geterotsikl. Soedin.*, **1967**, 183; *Chem. Abstr.*, **67**, 54017.
1239. A. K. Shienkmann, A. N. Kost, S. G. Potashnikova, A. O. Ginzburg and S. N. Baranov, *Khim. Geterotsikl. Soedin.*, **7**(5), 648 (1971); *Chem. Abstr.*, **76**, 72342.
1240. A. N. Kost, A. K. Shienkman and A. N. Prilepskaya, *Khim. Geterotsikl. Soedin., Sb. 1, Azotsoderzhashie Geterotsikly*, **1967**, 248; *Chem. Abstr.*, **70**, 87515.
1241. B. Emmert and A. Holz, *Chem. Ber.*, **87**, 676 (1954).
1242. K. Winterfeld and K. Nonn, *Chem. Ber.*, **100**(7), 2274 (1967).
1243. L. H. Klemm and R. E. Merrill, *J. Heterocycl. Chem.*, **9**(2), 293 (1972).
1244. R. L. Cobb and W. E. McEwen, *J. Amer. Chem. Soc.*, **77**, 5042 (1955).
1245. T. Kametani, K. Ogasawara, A. Kozuka and M. Shio, *Yakugaku Zasshi*, **87**(3), 254 (1967); *Chem. Abstr.*, **67**, 54316.
1246. K. Rasheed, *Pakistan J. Sci. Ind. Res.*, **10**(2), 102 (1967); *Chem. Abstr.*, **69**, 58973.
1247. G. W. J. Fleet and I. Fleming, *J. Chem. Soc. C*, **1969**, 1758.
1248. H. Tomishawa, T. Suzuki, H. Sawada, H. Hongo, R. Fujita, H. Kato and C. H. Wang, *Chem. Pharm. Bull. (Tokyo)*, **21**(12), 2602 (1973).
1249. E. M. Burgess and J. P. Sanchez, *J. Org. Chem.*, **39**(7), 940 (1974).
1250. S. Yoshina, *Jap. Pat.*, (a) 75 137,983 (1975); *Chem. Abstr.*, **84**, 164632; (b) 75 137,984 (1975); *Chem. Abstr.*, **84**, 135476.

1251. L. Sobczyk, *Trans. Faraday Soc.*, **57**, 1041 (1961).
1252. C. W. N. Cumper, R. F. A. Ginman and A. I. Vogel, *J. Chem. Soc.*, **1962**, 4518.
1253. N. A. Klyuev, A. K. Shienkman, R. A. Khmel'nitskii, G. A. Mal'tseva and N. R. Kat'nitskii, *Zh. Org. Khim.*, **13**, 1079 (1977); *Chem. Abstr.*, **87**, 84299.
1254. I. B. Johns, E. A. McElhill and J. O. Smith, (a) *J. Chem. Eng. Data*, **7**, 277 (1962); *Chem. Abstr.*, **57**, 10981a; (b) *Ind. Eng. Chem. Prod. Res. Develop.*, **1** (1), 2 (1962); *Chem. Abstr.*, **57**, 14913d.
1255. T. Hisano and M. Ichikawa, *Chem. Pharm. Bull. (Tokyo)*, **22**(8), 1923 (1974).
1256. L. Sobczyk, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **9**, 237 (1961); *Chem. Abstr.*, **59**, 7344h.
1257. A. P. Phillips and P. L. Graham, *J. Amer. Chem. Soc.*, **74**, 1552 (1952).
1258. M. Colonna and A. Risaliti, (a) *Atti Accad. Naz. Lincei Mem., Classe Sci. Fis. Mat. Nat. Rend.*, **14**, 809 (1953); *Chem. Abstr.*, **48**, 8045c; (b) *Ann. Chim. (Rome)*, **48**, 1395 (1958); *Chem. Abstr.*, **53**, 14683d.
1259. H. Ito and H. Fukushima, *Ann. Rep. Fac. Pharm. Tokushima Univ.*, **5**, 12 (1956); *Chem. Abstr.*, **53**, 3877e.
1260. R. E. Atkinson and P. H. R. Speakman, *J. Chem. Soc. B*, **1971**, 2077.
1261. E. D. Thorsett, F. R. Stermitz and C. M. O'Donnell, *Photochem. Photobiol.*, **19**(4), 291 (1974); *Chem. Abstr.*, **80**, 144951.
1262. E. D. Thorsett, *Ph.D. Thesis*, Colorado State Univ., 1973; *Diss. Abstr. Int. B*, **34**(6), 2532 (1973).
1263. M. Yu. Kornilov, L. M. Shulezhko and A. I. Tolmachev, *Teor. Eksp. Khim.*, **10**(4), 508 (1974); *Chem. Abstr.*, **82**, 16216.
1264. Z. S. Faizutoinova and S. Y. Yunusov, *Khim. Prir. Soedin.*, **3**(4), 260 (1967); *Chem. Abstr.*, **67**, 108802.
1265. C. W. Koch, R. M. Milberg, R. J. Katt, J. H. Markgraf and P. M. Wege, *J. Heterocycl. Chem.*, **11**(4), 475 (1974).
1266. N. G. Keats and L. A. Summers, *J. Heterocycl. Chem.*, **13**, 981 (1976).
1267. R. R. Pfeiffer, *Anal. Chem.*, **28**, 206 (1956).
1268. G. J. Di Gregorio, *J. Chromatogr.*, **90**(2), 396 (1974).
1269. M. Johansson, *Physiol. Plant.*, **17**(3), 507 (1964); *Chem. Abstr.*, **61**, 15075f.
1270. H. A. Offe, *Ger. Pat.* 949,059 (1956); *Chem. Abstr.*, **53**, 2256g.
1271. W. H. Dekker, H. A. Selling and J. C. Overeem, *J. Agric. Food Chem.*, **23**(4), 785 (1975); *Chem. Abstr.*, **83**, 109650.
1272. A. Albert and R. Goldacre, *J. Chem. Soc.*, **1943**, 706.
1273. H. Coates, A. H. Cook, I. M. Heilbron and F. B. Lewis, *J. Chem. Soc.*, **1943**, 149.
1274. K. Mukherjee, G. B. Behera and M. K. Rout, *J. Inst. Chem. (India)*, **51**, 138 (1969); *Chem. Abstr.*, **72**, 31573.
1275. S. F. Fakhrutdinov, *Farmakol. Alkaloidov. Ikh. Proizvodnykh* **1972**, 64; *Chem. Abstr.*, **80**, 103863.
1276. R. R. G. Haber, E. Shoenberger and M. E. Stolar, *Ger. Pat.* 2,612,250 (1977); *Chem. Abstr.*, **86**, 139881.
1277. E. Barni and G. Di Modica, (a) *Chim. Ind. (Milan)*, **58**, 293 (1976); *Chem. Abstr.*, **85**, 79650; (b) *Ann. Chim. (Rome)*, **66**, 379 (1976).
1278. E. Barni and A. Bonci, *Tinctoria*, **74**, 217 (1977); *Chem. Abstr.*, **87**, 119142.
1279. A. Harai, *Jap. Pat.* 75 93,638 (1975); *Chem. Abstr.*, **85**, 12308.
1280. L. G. Surovtsen, V. E. Blokhin, Yu. A. Rozin, G. A. Lukina and M. A. Bulatov, *Tezisy Dokl. Simp. Khim. Tekhnol. Geterotsikl. Soedin. Goryuch. Iskop., 2nd*, **1973**, 203; *Chem Abstr.*, **85**, 160609.
1281. B. M. Kovarskaya, V. V. Gur'yanova, Yu. A. Rozin and V. E. Blokhin, *Russ. Pat.* 469,723 (1975); *Chem. Abstr.*, **83**, 98573.
1282. S. O. Norris and J. K. Stille, *Macromolecules*, **9**, 496 (1976); *Chem. Abstr.*, **85**, 63369.
1283. S. O. Norris, *Ph.D. Thesis*, Univ. of Iowa, 1975; *Diss. Abstr. Int. B*, **36**, 6203 (1976); *Chem. Abstr.*, **85**, 63379.
1284. J. F. Wolfe and J. K. Stille, *Macromolecules*, **9**, 489 (1976); *Chem. Abstr.*, **85**, 63368.
1285. J. F. Wolfe, *Ph.D. Thesis*, Univ. of Iowa, 1975; *Diss. Abstr. Int. B*, **36**, 6203 (1976); *Chem. Abstr.*, **85**, 63380.
1286. R. C. Elderfield, W. J. Gensler, T. H. Bembry, T. A. Williamson and H. Weisl, *J. Amer. Chem. Soc.*, **68**, 1589 (1946).
1287. H. John, *J. Prakt. Chem.*, **131**, 266 (1931); *Chem. Abstr.*, **25**, 5427.
1288. J. C. Cochran and W. F. Little, *J. Org. Chem.*, **26**, 808 (1961).

1289. K. Ueda, *Yakugaku Zasshi*, **57**, 654 (1937); *Chem. Abstr.*, **33**, 3380[2].
1290. K. Ueda, *Yakugaku Zasshi*, **57**, 827 (1937); *Chem. Abstr.*, **32**, 563[9].
1291. C. W. Rees and C. R. Sabet, *J. Chem. Soc.*, **1965**, 870.
1292. N. K. Ushenko and T. E. Gorizdra, *Ukr. Khim. Zh.*, **15**, 296 (1949); *Chem. Abstr.*, **48**, 3366h.
1293. A. Risaliti, *Ricerca Sci.*, **24**, 2351 (1954); *Chem. Abstr.*, **49**, 15902c.
1294. A. Risaliti, *Ricerca Sci.*, **26**, 2512 (1956); *Chem. Abstr.*, **52**, 10080c.
1295. J. Glinka, *Rocz. Chem.*, **51**, 577 (1977); *Chem. Abstr.*, **87**, 102140.
1296. M. Protiva, V. Rerioha, M. Borovicka and J. Jilek, *Collect. Czech. Chem. Commun.*, **15**, 532 (1950); *Chem. Abstr.*, **45**, 9521h.
1297. T. Kahu, *Yakugaku Zasshi*, **48**, 693 (1928); *Chem. Abstr.*, **23**, 392.
1298. R. Weil and N. Collignon, *C. R. Acad. Sci. Ser. C*, **275**(4), 299 (1972); *Chem. Abstr.*, **77**, 139748.
1299. M. J. S. Dewar, C. Kaneko and M. K. Bhattacharjee, *J. Amer. Chem. Soc.*, **84**, 4884 (1962).
1300. T. Pozzo-Balbi, G. Ramano and M. T. Bassi, *Ann. Chim. (Rome)*, **55**(8-9), 763 (1965); *Chem. Abstr.*, **64**, 692e.
1301. H. Weidal and M. Bamberger, *Monatsh.*, **9**, 99 (1888).
1302. H. Weidel, *Monatsh.*, **8**, 120 (1887).
1303. See ref. 1173.
1304. E. Besthorn and O. Fischer, *Ber.*, **16**, 68 (1883).
1305. O. Fischer and E. Tauber, *Ber.*, **17**, 2925 (1884).
1306. O. Doebner and W. von Miller, *Ber.*, **19**, 1194 (1886).
1307. W. Koenigs and F. Meimberg, *Ber.*, **28**, 1038 (1895).
1308. Meister, Lucius and Brunning Farbw., *Ger. Pat.* 79,385 (1895).
1309. W. La Coste and C. Sorger, *Ann.*, **230**, 1 (1885).
1310. W. von Miller and F. Kinkelin, *Ber.*, **19**, 525 (1886).
1311. O. Fischer and C. Rudolph, *Ber.*, **15**, 1500 (1882).
1312. (a) M. N. Zemtsoya, A. E. Lipkin, and A. V. Zimichev, *Khim. Geterotsikl. Soedin.*, **1974**, 1327; *Chem. Abstr.*, **82**, 139938. (b) M. N. Zemtsoya, A. E. Lipkin, A. V. Zimichev and P. L. Trakhtenberg, *Tezisy Dokl. Nauch. Sess. Khim. Tekhnol. Org. Soedin. Sery Sernistykh Neftei, 13th*, **1974**, 180; *Chem. Abstr.*, **85**, 159846.
1313. E. Murmann, (a) *Monatsh.*, **13**, 58 (1892); (b) **31**, 1303 (1910); *Chem. Abstr.*, **5**, 1777.
1314. F. W. Bergstrom, *J. Org. Chem.*, **3**, 424 (1938).
1315. D. W. Ockenden and K. Schofield, *J. Chem. Soc.*, **1953**, 3914.
1316. R. F. C. Brown, F. Irvine and R. J. Smith, *Aust. J. Chem.*, **26**(10), 2213 (1973).
1317. L. G. S. Brooker and L. A. Smith, *J. Amer. Chem. Soc.*, **59**, 67 (1937).
1318. T. Kauffmann and A. Mitschker, *Tetrahedron Lett.*, No. 41, 4039 (1973).
1319. L. H. Klemm, D. R. McCoy and C. E. Klopfenstein, *J. Heterocycl. Chem.*, **8**(3), 383 (1971).
1320. R. Weil and N. Collignon, *Bull. Soc. Chim. Fr.*, (a) **1974**, 253; *Chem. Abstr.*, **81**, 63239; (b) **1974**, 258; *Chem. Abstr.*, **81**, 90757.
1321. A. K. Shienkman, A. N. Prilepskaya, A. P. Kucherenko and S. N. Baranov, *Ukr. Khim. Zh.*, **38**(6), 389 (1972); *Chem. Abstr.*, **78**, 15997.
1322. A. L. Gershuns and A. N. Brizitskaya, *Ukr. Khim. Zh.*, **37**(3), 263 (1971); *Chem. Abstr.*, **75**, 29558.
1323. A. L. Gershuns and A. N. Brizitskaya, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, **17**(11), 1626 (1974); *Chem. Abstr.*, **83**, 34950.
1324. J. Hoste, (a) *Meded. Koninkl. Vlaam. Acad. Wetenschap., Belg., Klasse Wetenschap.*, **11**(8), 5 (1949); (b) *Anal. Chim. Acta*, **4**, 23 (1950); *Chem. Abstr.*, **44**, 6333h.
1325. A. L. Gershuns and A. N. Brizitskaya, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, **17**(9), 1301 (1974); *Chem. Abstr.*, **82**, 25274.
1326. P. Kurze, G. Kempter and E. Uhlemann, *Z. Chem.*, **12**(3), 114 (1972); *Chem. Abstr.*, **77**, 54238.
1327. N. N. Bogdashev, A. D. Garnovskii, O. A. Osipov, V. P. Grigor'ev and N. M. Gontmakher, *Zh. Obshch. Khim.*, **46**(2), 675 (1976); *Chem. Abstr.*, **84**, 186588.
1328. R. P. Bonomo, S. Musumeci, E. Rizzarelli and A. Seminara, *Z. Anorg. Allg. Chem.*, **414**(2), 185 (1975); *Chem. Abstr.*, **83**, 21199.
1329. (a) D. M. Klassen, C. W. Hudson and E. L. Shaddix, *Inorg. Chem.*, **14**(11), 2733 (1975); *Chem. Abstr.*, **83**, 187585. (b) D. M. Klassen, *Inorg. Chem.*, **15**(12), 3166 (1976); *Chem. Abstr.*, **85**, 186039.
1330. A. Kasahara, *Bull. Chem. Soc. Jap.*, **41**(5), 1272 (1968); *Chem. Abstr.*, **69**, 73553.

1331. T. J. Giordano, *Ph.D. Thesis*, Univ. of Michigan, 1974; *Diss. Abstr. Int. B*, **35**(5), 2088 (1974); *Chem. Abstr.*, **82**, 79852.
1332. S. Gurrieri, S. Musumeci, E. Rizzarelli and A. Seminara, *J. Inorg. Nucl. Chem.*, **38**(2), 259 (1976); *Chem. Abstr.*, **84**, 115330.
1333. D. J. Booth, B. W. Rockett and J. Ronayne, *J. Organomet. Chem.*, **44**(2), C29 (1972); *Chem. Abstr.*, **78**, 29970.
1334. R. J. Charlton, C. M. Harris, H. Patil and N. C. Stephenson, *Inorg. Nucl. Chem. Lett.*, **2**(12), 409 (1966).
1335. F. H. Jardine, A. G. Vohra and F. J. Young, *J. Inorg. Nucl. Chem.*, **33**(9), 2941 (1971).
1336. F. H. Case and A. Idelson, *J. Org. Chem.*, **27**, 4651 (1962).
1337. K. P. Sivaramakrishnan and S. V. Sunthankar, *J. Sci. Ind. Res. (India)*, **20B**, 223 (1961).
1338. H. P. Ward and M. G. Waring, *J. Amer. Chem. Soc.*, **54**, 1697 (1932).
1339. M. K. O'Rell, *U.S. Pat.* 3,944,553 (1976); *Chem. Abstr.*, **85**, 62951.
1340. M. A. Kunz, G. Kochendoerfer and K. Koberle, to I.G. Farbendindustrie, A.G., *Ger. Pat.* 567,273 (1931); *Chem. Abstr.*, **27**, 1362.
1341. B. I. Ardashev and Z. V. Malina, *Zh. Obshch. Khim.*, **21**, 1349 (1951); **21**, 1473 (1951); *Chem. Abstr.*, **47**, 2761b.
1342. M. Miyatake and S. Ehashi, *Shikizai Kyokaishi*, **44**(7), 316 (1971); *Chem. Abstr.*, **75**, 130760.
1343. L. N. Goloyrev, *Zh. Obshch. Khim.*, **27**, 2837 (1957); *Chem. Abstr.*, **52**, 8140g.
1344. C. V. Ferriss and E. E. Turner, *J. Chem. Soc.*, **117**, 1140 (1920).
1345. I. W. Elliott, *J. Org. Chem.*, **25**, 1256 (1960).
1346. T. Pavolini, F. Gambarin and E. Giusto, *Ann. Chim. (Rome)*, **43**, 242 (1953); *Chem. Abstr.*, **48**, 11419a.
1347. G. Koller and H. Ruppersberg, *Monatsh.*, (a) **58**, 238 (1931); *Chem. Abstr.*, **26**, 459; (b) **52**, 59 (1929); *Chem. Abstr.*, **23**, 4218.
1348. W. H. Mills and H. G. Ordish, *J. Chem. Soc.*, **1928**, 81.
1349. F. H. Case and G. Maerker, *J. Amer. Chem. Soc.*, **75**, 4920 (1953).
1350. (a) J. K. Stille, E. F. Johnson, J. Wolfe, M. F. Wingardner and S. Wratten, *Amer. Chem. Soc. Div. Org. Coat. Plast. Chem. Pap.*, **33**(1), 127 (1973); *Chem. Abstr.*, **82**, 58154. (b) J. K. Stille, *U.S. Pat.* 4,000,187 (1976).
1351. A. L. Gershuns and A. A. Pavlyuk, *Ukr. Khim. Zh.*, **30**(10), 1086 (1964); *Chem. Abstr.*, **62**, 5252d.
1352. A. L. Gershuns and A. A. Verezubova, *Russ. Pat.* 135,489 (1961).
1353. L. P. Adamovich, M. Vil'denkain, A. A. Verezubova and A. L. Gershuns, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, **19**, 1527 (1976); *Chem. Abstr.*, **86**, 89576.
1354. S. G. Waley, *J. Chem. Soc.*, **1948**, 2008.
1355. F. A. Ai-Ta'i *Proc. Iraqi Sci. Soc.*, **1**, 27 (1957); *Chem. Abstr.*, **53**, 2229g.
1356. A. L. Gershuns and A. A. Verezubova, (a) *Khim. Geterotsikl. Soedin.*, **1972**, 1396; *Chem. Abstr.*, **78**, 29585. (b) A. L. Gershuns, A. A. Verezubova, A. N. Brizitskaya, I. A. Rastrepina and P. Ya. Pustovar, *Tezisy Dokl. Simp. Khim. Tekhnol. Geterotsikl. Soedin. Goryuch. Iskop., 2nd*, **1973**, 15; *Chem. Abstr.*, **86**, 29601.
1357. A. L. Gershuns, A. A. Verezubova and L. M. Ptyagina, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, **18**(6), 869 (1975); *Chem. Abstr.*, **83**, 178995.
1358. A. P. Smirnoff, *Helv. Chim. Acta*, **4**, 802 (1921); *Chem. Abstr.*, **16**, 234.
1359. R. B. Woodward and E. C. Kornfield, *J. Amer. Chem. Soc.*, **70**, 2508 (1948).
1360. H. Weidel and M. Glaser, *Monatsh.*, **7**, 308 (1886).
1361. W. Baczynski and S. von Niementowski, *Ber.*, **52**, 461 (1919).
1362. A. Musierowicz, S. V. Niementowski and Z. Tomasik, *Roczn. Chem.*, **8**, 325 (1928).
1363. Z. von Jakubowski and S. von Niementowski, *Ber.*, **42**, 634 (1909).
1364. B. G. Zupancic, (a) *J. Prakt. Chem.*, **35**(3–4), 175 (1967); *Chem. Abstr.*, **67**, 43660; (b) *Ger. Pat.* 1,229,092 (1966); *Chem. Abstr.*, **66**, 37782.
1365. T. Mazonski and W. Karminski, *Zeszyty Nauk. Politech. Slask. Chem.*, **1961**, 149; *Chem. Abstr.*, **61**, 4308g.
1366. A. L. Gershuns and P. Ya. Pustovar, *Khim. Geterotsikl. Soedin.*, **7**(5), 641 (1971); *Chem. Abstr.*, **76**, 59410.
1367. K. von Ihnatowicz and S. von Niementowski, *Ber.*, **52**, 188 (1919); *Chem. Abstr.*, **13**, 1848.
1368. E. Besthorn and I. Ibele, *Ber.*, **37**, 1236 (1904).
1369. W. Koenigs, *Ber.*, **12**, 97 (1879).
1370. H. Weidel, *Monatsh.*, **2**, 491 (1881).

1371. C. G. Williams, *Chem. News*, **37**, 85 (1878).
1372. C. G. Williams, *Chem. News*, **43**, 145 (1881).
1373. A. Einhorn and P. Sherman, *Ann.*, **287**, 26 (1895).
1374. A. Claus, *Ber.*, **14**, 1939 (1881).
1375. E. Carlier and A. Einhorn, *Ber.*, **23**, 2894 (1890).
1376. E. J. V. Conolly, *J. Chem. Soc.*, **127**, 2083 (1925).
1377. W. E. Kramer, L. A. Joo and R. M. Haines, *U.S. Pat.* 3,147,262 (1964); *Chem. Abstr.*, **61**, 13291e.
1378. J. V. Hay, T. Hudlicky and J. F. Wolfe, *J. Amer. Chem. Soc.*, **97**(2), 374 (1975).
1379. A. E. Chichibabin and O. A Zeide, *J. Russ. Phys. Chem. Soc.*, **46**, 1232 (1914).
1380. A. E. Chichibabin and E. V. Zatzepina, *J. Russ. Phys. Chem. Soc.*, **50**, 553 (1920); *Chem. Abstr.*, **18**, 1502.
1381. E. Calzavarra, *Sci. Ind. Photogr.*, **10**, 193 (1939); *Chem. Abstr.*, **34**, 335[4].
1382. A. J. Clarke, S. McNamara and O. Meth-Cohn, *Tetrahedron Lett.*, **1974**, 2372.
1383. F. Ullmann and E. Gilli, *Ann.*, **332**, 80 (1904).
1384. T. Ukai, *Yakugaku Zasshi*, **48**, 1175 (1928).
1385. C. C. Price, H. R. Snyder and E. M. Van Heyningen, *J. Amer. Chem. Soc.*, **68**, 2589 (1946).
1386. C. M. Mehta and D. R. Mehta, *Indian J. Chem.*, **1**, 188 (1963); *Chem. Abstr.*, **59**, 6364a.
1387. S. Nakano, *Yakugaku Zasshi*, (a) **79**, 310 (1959); *Chem. Abstr.*, **53**, 16134a; (b) **79**, 314 (1959); (c) **82**, 498 (1962); *Chem. Abstr.*, **58**, 3391b.
1388. S. Nakano, H. Mori, T. Yoshida and M. Okude, *Meiji Yakka Daigaku Kenkyo Kiyo*, No. 3, 40 (1966); *Chem. Abstr.*, **68**, 104943.
1389. L. G. Vaughan, *U.S. Pat.* 3,755,329 (1973); *Chem. Abstr.*, **79**, 115732.
1390. K. Ueda, *Yakugaku Zasshi*, (a) **57**, 180 (1937); *Chem. Abstr.*, **33**, 608[7]; (b) **57**, 185 (1937); *Chem. Abstr.*, **33**, 608[8]; (c) **51**, 495 (1931).
1391. M. Busch, W. Weber and H. Zink, *J. Prakt. Chem.*, **155**, 163 (1940); *Chem. Abstr.*, **34**, 3725[8].
1392. J. G. Breckenridge, R. W. J. Lewis and L. A. Quick, *Can. J. Res.*, **17B**, 258 (1939).
1393. J. G. Breckenridge, *Can. J. Res.*, **28B**, 593 (1950).
1394. F. H. Case, *J. Org. Chem.*, **23**, 1375 (1958).
1395. T. Kosuge, H. Zenda, H. Sawanishi and Y. Suzuki, *Chem. Pharm. Bull. (Tokyo)*, **17**(10), 2178 (1969).
1396. J. P. Wibaut, H. D. T. Willink, Jr., and W. E. Niewenhuis, *Rec. Trav. Chim.*, **54**, 804 (1935); *Chem. Abstr.*, **30**, 1378[6].
1397. K. Ueda, *Yakugaku Zasshi*, **60**, 537 (1940); *Chem. Abstr.*, **35**, 1790[9].
1398. J. Gillis, J. Hoste and Y. Van Moffaert, *Meded. Koninkl. Vlaam. Acad. Wetenschap. Belg. Kl. Wetenschap.*, **15**(7), 37 (1953).
1399. H. R. Billica and H. Adkins in *Organic Syntheses*, ed. E. C. Horning, Collect. Vol. III, p. 176, Wiley, New York, 1955.
1400. W. H. F. Sasse, *J. Chem. Soc.*, **1960**, 526.
1401. G. M. Badger and W. H. F. Sasse, *J. Chem. Soc.*, **1956**, 616.
1402. G. M. Badger, N. Kowanko and W. H. F. Sasse, *J. Chem. Soc.*, **1959**, 440.
1403. H. Rapoport, R. Iwamoto and J. R. Tretter, *J. Org. Chem.*, **25**, 372 (1960).
1404. California Research Corporation, *Brit. Pat.* 915,950 (1963); *Chem. Abstr.*, **59**, 114536.
1405. J. M. Lesser, *Ph.D. Thesis*, Temple Univ., 1965; *Diss. Abstr.*, **26**(8), 4241 (1966).
1406. G. D. F. Jackson, W. H. F. Sasse and C. P. Whittle, *Aust. J. Chem.*, **16**(6), 1126 (1963).
1407. W. Karminski, *Pol. Pat.* 59,230 (1970); *Chem. Abstr.*, **73**, 45372.
1408. A. L. Gershuns and I. A. Rastrepina, *Metodyz. Poluch. Khim. Reakt. Prep.*, No. 18, 43 (1969); *Chem. Abstr.*, **75**, 76566.
1409. R. Schrader and W. Staedter, *Z. Chem.*, **11**(6), 236 (1971).
1410. A. K. Sheinkman, V. A. Ivanov and S. N. Baranov, *Russ. Pat.* 259,887 (1969).
1411. A. K. Sheinkman, V. N. Kalafat, V. A. Ivanov and N. A. Klyuev, *Khim. Geterotsikl. Soedin.*, **1977**, 385; *Chem. Abstr.*, **87**, 68111.
1412. J. Haginiwa, Y. Higuchi and Y. Fujimoto, *Jap. Pat.* 73 12,746 (1973); *Chem. Abstr.*, **79**, 42366.
1413. J. Haginiwa and Y. Higuchi, *Yakagaku Zasshi*, **93**(2), 144 (1973); *Chem. Abstr.*, **78**, 147751.
1414. J. Zimmermann and A. Muller, *Ber.*, **17**, 1965 (1884).
1415. O. W. Fischer, *Monatsh.*, **5**, 417 (1884).
1416. H. Wieland and E. Haas, *Ber.*, **53B**, 1336 (1920).
1417. B. Emmert, *Ber.*, **42**, 1997 (1909).

1418. S. Kato, J. Nakaya and E. Imoto, *Denki Kagaku*, **40**(10), 708 (1972); *Chem. Abstr.*, **78**, 91770.
1419. S. Reich and H. O. Serpek, *Helv. Chim. Acta*, **3**, 138 (1920).
1420. A. Claus and A. Caroselli, *J. Prakt. Chem.*, **51**, 477 (1895).
1421. O. Fischer and H. van Loo, (a) *Ber.*, **17**, 1899 (1884); (b) **19**, 2471 (1886).
1422. S. Natsume and T. Itai, *Chem. Pharm. Bull. (Tokyo)*, **14**(5), 557 (1966).
1423. V. N. Gogte, K. M. More and B. D. Tilak, *Indian J. Chem.*, **12**(12), 1238 (1974).
1424. A. K. Sheinkman, T. V. Stupniknova and G. V. Somoilenko, *Russ. Pat.* 414,258 (1974); *Chem. Abstr.*, **80**, 133280.
1425. L. T. Bratz and S. v. Niementowski, *Ber.*, **52B**, 189 (1919).
1426. P. Moeckel and G. Staerk, *E. Ger. Pat.* 23, 118 (1962); *Chem. Abstr.*, **58**, 3403b.
1427. K. Pforote and G. Leuschner, *Ann.*, **646**, 30 (1961); *Chem. Abstr.*, **56**, 12458b.
1428. E. Paterno, *Gazz. Chim Ital.*, **44**, 240 (1914).
1429. T. van Schelvin, *Brit. Pat.* 388,087 (1933); *Chem. Abstr.*, **27**, 4685.
1430. R. F. Smirnov, B. I. Tikhomirov, G. V. Marinchenko and A. I. Yakubchik, (a) *Vysokomol. Soedin. Ser. A*, **15**,(4), 740 (1973); *Chem. Abstr.*, **79**, 53852.
1431. I. Kumano, M. Miyatake and S. Ehashi, *Jap. Pat.* 73 32, 765 (1973); *Chem. Abstr.*, **81**, 65369.
1432. C. W. N. Cumper, R. F. A. Ginman and A. I. Vogel, *J. Chem. Soc.*, **1962**, 1188.
1433. N. A. Klyuev, A. K. Sheinkman and A. N. Smirnov, *Khim. Geterotsikl. Soedin.*, **1976**, 812; *Chem. Abstr.*, **85**, 122862.
1434. A. L. Gershuns and L. G. Grineva, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, **18**(12), 1910 (1975); *Chem. Abstr.*, **84**, 104847.
1435. A. L. Gershuns and P. Ya. Pustovar, *Khim. Geterotsikl. Soedin.*, **1977**, 98; *Chem. Abstr.*, **86**, 170620.
1436. A. L. Gershuns, P. Y. Pustovar and V. P. Tkachenko, *Vestn. Khar'k. Univ. Khim.*, **127**(6), 84 (1975); *Chem. Abstr.*, **84**, 120949.
1437. W. H. D. Morgan, *J. Chem. Soc.*, **1950**, 1963.
1438. F. Bell, W. H. D. Morgan and I. F. B. Smyth, *Chem. Ind. (London)*, **1951**, 634.
1439. M. Crawford and I. F. B. Smyth, *J. Chem. Soc.*, **1952**, 4133.
1440. M. Crawford and I. F. B. Smyth, *Chem. Ind. (London)*, **1954**, 346.
1441. M. Crawford and R. B. Ingle, *J. Chem. Soc. B*, **1971**, 1907.
1442. W. Wrasidlo and J. K. Stille, *Macromolecules*, **9**, 505 (1976); *Chem. Abstr.*, **85**, 63485.
1443. W. Wraidlo, S. O. Norris, J. F. Wolfe, T. Katto and J. K. Stille, *Macromolecules*, **9**(3), 512 (1976); *Chem. Abstr.*, **85**, 47257.
1444. R. H. Linnell and A. Kaczmarczyk, *J. Phys. Chem.*, **65**, 1196 (1961); *Chem. Abstr.*, **55**, 21790i.
1445. (a) R. A. Khmel'nitskii, N. A. Klyuev, K. R. Zhigulen and A. K. Sheinkman, *Izv. Timiryazev. Sel'skokhoz. Akad.*, No. 6, 200 (1970); *Chem. Abstr.*, **74**, 52644.
(b) R. A. Khmel'nitskii, N. A. Klyuev and P. B. Terent'ev, *Zh. Org. Khim.*, **7**, 395 (1971).
1446. N. A. Klyuev, R. A. Khmel'nitskii, G. A. Mal'tseva, A. K. Sheinkman, V. A. Ivanov and B. M. Zolotarev, *Khim. Geterotsikl. Soedin.*, **1973**, 979; *Chem. Abstr.*, **79**, 114699.
1447. N. G. Keats and L. A. Summers, *J. Heterocycl. Chem.*, **13**, 369 (1976).
1448. N. G. Keats and L. A. Summers, *J. Heterocycl. Chem.*, **13**, 153 (1976).
1449. A. G. Osborne, *Spectrosc. Lett.*, **10**, 777 (1977).
1450. R. Degeilh, *Ph.D. Thesis*, Indiana Univ., 1956; *Diss. Abstr.*, **17**, 510 (1957); *Chem. Abstr.*, **51**, 10170e.
1451. S. K. Datta, *Ph.D. Thesis*, Indiana Univ., 1959; *Diss. Abstr.*, **20**, 1189 (1959); *Chem. Abstr.*, **54**, 4103c.
1452. K. Folting and L. L. Merpitt, Jr., *Acta Crystallogr.*, **B33**, 3540 (1977); *Chem. Abstr.*, **88**,157178.
1453. M. Lenner and O. Lindgrin, *Acta Crystallogr.*, **B32**(6), 1903 (1976); *Chem. Abstr.*, **85**, 71022.
1454. M. Przyborowska, *Chem. Anal. (Warsaw)*, **20**(6), 1191 (1975); *Chem. Abstr.*, **84**, 189064.
1455. Z. Gregorowicz, J. Kulicka and W. Karminski, *Chem. Anal. (Warsaw)*, **10**(6), 1347 (1965); *Chem. Abstr.*, **64**, 16601b.
1456. W. Roser, *Ber.*, **17**, 1817 (1884).
1457. O. Fischer, *Ber.*, **19**, 1036 (1886).
1458. L. C. Cessna, Jr., *Ger. Pat.* 2,359,861 (1974); *Chem. Abstr.*, **81**, 153541.
1459. G. F. Smith and D. H. Wilkins, *Anal. Chim. Acta*, **10**, 139 (1954); *Chem. Abstr.*, **48**, 5646e.
1460. A. L. Gershuns and I. G. Per'kov, *Uch. Zap. Khar'kovsk. Derz. Univ.*, No. 17, 65–70 (1961); *Chem. Abstr.*, **57**, 13398a.
1461. S. Nakano, *Yakugaku Zasshi*, (a) **81**, 1239 (1961); *Chem. Abstr.*, **57**, 407a; (b) **82**(9), 1256 (1962); *Chem. Abstr.*, **59**, 3303d.

1462. (a) E. Uhlemann, P. Thomas and G. Kempter, *Z. Anorg. Allg. Chem.*, **341**(1-2), 11 (1965); *Chem. Abstr.*, **64**, 9214c.
(b) E. Uhlemann and P. Thomas, *Z. Anorg. Allg. Chem.*, **341**(1-2), 17 (1965); *Chem. Abstr.*, **64**, 9214c.
1463. T. G. Dmitrieva, *Tr. Khar'kov. Med. Inst.*, No. 67, 30 (1966); *Chem. Abstr.*, **69**, 25014.
1464. G. H. Faye, *Can. J. Chem.*, **44**(22), 2729 (1966).
1465. C. M. Harris, H. R. H. Patil and E. Sinn, *Inorg. Chem.*, **6**(6), 1102 (1967); *Chem. Abstr.*, **67**, 39684.
1466. T. G. Dmitrieva and A. L. Gershuns, *Sb. Nauch. Tr. Khar'k. Med. Inst.*, **69**, 42 (1967); *Chem. Abstr.*, **70**, 91306.
1467. H. Bahr and I. Lipinska, *Chem. Anal. (Warsaw)*, **13**(2), 399 (1968); *Chem. Abstr.*, **69**, 73659.
1468. A. L. Gershuns and T. G. Dmitrieva, *Ukr. Khim. Zh.*, **34** (2), 165 (1968); *Chem. Abstr.*, **68**, 111065.
1469. T. G. Dmitrieva and A. L. Gershuns, *Tr. Kom. Anal. Khim. Akad. Nauk SSSR*, **17**, 230 (1969); *Chem. Abstr.*, **72**, 28079.
1470. F. H. Jardine, L. Rule and A. G. Vohra, *J. Chem. Soc. A*, **1970**, 238.
1471. R. Held, F. Dietz and P. Thomas, (a) *Z. Chem.*, **12**(9), 346 (1972); *Chem. Abstr.*, **78**, 57564. (b) O. Guertler, K. P. Dietz and P. Thomas, *Z. Anorg. Allg. Chem.*, **396**(2), 227 (1973); *Chem. Abstr.*, **78**, 78974. (c) O. Guertler, K. P. Dietz and P. Thomas, *Z. Anorg. Allg. Chem.*, **396**(2), 217 (1973); *Chem. Abstr.*, **78**, 83589. (d) O. Guertler, K. P. Dietz and P. Thomas, *Z. Anorg. Allg. Chem.*, **397**(2), 138 (1973); *Chem. Abstr.*, **78**, 142200.
1472. K. Soha-Szalay, *Modszertani Kozl.*, **1**, 53 (1972); *Chem. Abstr.*, **85**, 171157.
1473. A. L. Gershuns, P. Y. Pustovar and G. I. Sukhoivan, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Technol.*, **18**(2), 214 (1975); *Chem. Abstr.*, **83**, 33693.
1474. D. Rehorek and P. Thomas, *Z. Anorg. Allg. Chem.*, **412**(2), 129 (1975); *Chem. Abstr.*, **82**, 92435.
1475. D. Rehorek, H. Spindler and P. Thomas, *Z. Chem.*, **15**(7), 281 (1975); *Chem. Abstr.*, **83**, 157094.
1476. A. L. Gershuns and P. Y. Pustovar, *Khim. Geterotsikl. Soedin.*, **1975**, 976; *Chem. Abstr.*, **83**, 178770.
1477. V. M. Skorobogatov, L. P. Adamovich, A. L. Gershuns and K. D. Kaiser, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, **19**, 1619 (1976); *Chem. Abstr.*, **86**, 61051.
1478. F. Buhl and M. Chwistek, *Chem. Anal. (Warsaw)*, **21**(2), 421 (1976); *Chem. Abstr.*, **85**, 186231.
1479. D. Rehorek and P. Thomas, *Z. Anorg. Allg. Chem.*, **426**, 309 (1976); *Chem. Abstr.*, **86**, 37072.
1480. V. M. Skorobogatov, A. L. Gershuns and L. P. Adamovich, *Zh. Anal. Khim.*, **32**, 1450 (1977); *Chem. Abstr.*, **88**, 79882.
1481. S. C. Watson and J. F. Eastham, *J. Organomet. Chem.*, **9**(1), 165 (1967); *Chem. Abstr.*, **67**, 87540.
1482. H. Berndt and E. Jackwerth, *Fresenius Z. Anal. Chem.*, **282**, 427 (1976); *Chem. Abstr.*, **86**, 60897.
1483. H. Weidel and H. Strache *Monatsh.*, **7**, 280 (1886).
1484. K. Ueda, *Yakugaku Zasshi*, **57**, 817 (1937); *Chem. Abstr.*, **32**, 1265[7].
1485. O. W. Fischer, *Monatsh.*, **6**, 548 (1885).
1486. S. Nakano, *Yakugaku Zasshi*, **80**, 1515 (1960); *Chem. Abstr.*, **55**, 8412a.
1487. H. Noda, M. Minemoto, K. Narimatsu and M. Hamana, *Yakugaku Zasshi*, **95**(9), 1078 (1975); *Chem. Abstr.*, **84**, 30835.
1488. K. Ueda, *Yakugaku Zasshi*, **57**, 312 (1937); *Chem. Abstr.*, **31**, 5361[9].
1489. E. Ostermayer and W. Henrichsen, *Ber.*, **17**, 2444 (1884).
1490. D. L. Morse and M. S. Wrighton, *J. Organomet. Chem.*, **125**, 71 (1977).
1491. G. P. Rabold and L. H. Piette, *Spectrosc. Lett.*, **1**(5), 211 (1968).
1492. A. M. Berlin, N. M. Kofman, E. S. Krongauz and V. V. Korshak, *Dokl. Akad. Nauk SSSR*, **199**(6), 1310 (1971); *Chem. Abstr.*, **76**, 25633.
1493. K. Ueda, *Yakugaku Zasshi*, **57**, 825 (1937); *Chem. Abstr.*, **32**, 1265[8].
1494. Y. Yagi and A. I. Popov, *Inorg. Nucl. Chem. Lett.*, **1**(1), 21 (1965).
1495. B. V. Tronov and O. A. Terekhova, (a) *Tr. Tomskogo Gos. Univ. Ser. Khim.*, **154**, 201 (1962); *Chem. Abstr.*, **60**, 6820c; (b) *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, **3**, 466 (1960); *Chem. Abstr.*, **54**, 24729f.

1496. O. A. Terekhova, *Uch. Zap. Tomsk. Gos. Univ.*, No. 29, 116 (1959); *Chem. Abstr.*, **55**, 13153b.
1497. I. M. Brown and S. I. Weissman, *J. Amer. Chem. Soc.*, **85** (10), 2528 (1963).
1498. M. Schmeisser and M. Weidenbruch, *Chem. Ber.*, **100** (7), 2306 (1967).
1499. A. J. Cantt and G. B. Deacon, *Aust. J. Chem.*, **24** (3), 489 (1971).
1500. R. P. Pantaler, L. D. Alfimova and A. M. Bulgakova, *Zh. Anal. Khim.*, **30**, 1584 (1975); *Chem. Abstr.*, **85**, 103360.
1501. M. A. A. Usmani and D. B. Scaife, *Pak. J. Sci. Ind. Res.*, **19**, 4 (1976).
1502. V. J. Koester, *Chem. Phys. Lett.*, **32** (3), 575 (1975); *Chem. Abstr.*, **83**, 68389.
1503. H. Poradowska and K. Nowak, *Bull. Soc. Chim. Fr.*, **1977**, 535; *Chem. Abstr.*, **88**, 97877.
1504. F. W. Vierhapper and E. L. Eliel, *J. Org. Chem.*, **42**, 51 (1977).
1505. M. Dong, I. Schmeltz and D. Hoffmann, *J. Chromatogr.*, **150**, 269 (1978).
1506. V. G. Ben'kovskii, A. Y. Baikova, Y. N. Popova, E. A. Kruglov, A. I. Stekun, N. Lyubopytova and F. N. Latypova, *Tezisy Dokl. Nauchn. Sess. Khim. Tekhnol. Org. Soedin. Sery Sernistykh Neftei, 13th*, **1974**, 27; *Chem. Abstr.*, **87**, 25665.
1507. G. F. Bol'Shakov, *Tezisy Dokl. Nauchn. Sess. Khim. Tekhnol. Org. Soedin. Sery Sernistykh Neftei, 13th*, **1974**, 25; *Chem. Abstr.*, **87**, 138261.
1508. V. M. Kurilenko, L. P. Basova, O. N. Chupakhin, and V. E. Kurichenko, *Khim.-Farm. Zh.*, **9** (5), 12 (1975); *Chem. Abstr.*, **87**, 126233.
1509. P. V. Prisyazhnik, G. K. Palii, Y. L. Volydnskii, A. I. Lopushanskii and E. P. Opanasenko, *Khim.-Farm. Zh.*, **10** (5), 46 (1976); *Chem. Abstr.*, **85**, 108607.
1510. L. Jasinskas, A. Urbonas and V. Latakas, *Liet. TSR Aukst. Mokyklu Mokslo. Darb. Chem. Chem. Technol.*, **17**, 143 (1975); *Chem. Abstr.*, **85**, 46525.
1511. A. S. Zarif'yan, V. P. Gaidzhurova, L. I. Degtyar and B. I. Ardashev, *Izv. Sev-Kavk Nauchn. Tsentra Vyssh. Shk., Ser. Estestv. Nauk*, **3** (2), 78 (1975); *Chem. Abstr.*, **84**, 43793.
1512. S. K. Johnson, *Tex. Agric. Ext. Serv., Fish Dis. Diagn. Lab. Rep. FDDL-S*, **1974**, FDDL-S4, 2 pp.; *Chem. Abstr.*, **87**, 145574.
1513. L. C. Price, *Am. Assoc. Pet. Geol. Bull.*, **60**, 213 (1976); *Chem. Abstr.*, **86**, 192122.
1514. G. C. Glasiola, Jr., *J. Fish. Biol.*, **10**, 113 (1977); *Chem. Abstr.*, **87**, 161441.
1515. J. Brown and R. E. Williams, *Can. J. Chem.*, **49**, 3765 (1971); *Chem. Abstr.*, **76**, 34562.
1516. J. Brown, D. R. Lauren and R. E. Williams, *Chem. Biol. Fept., Proc. Amer. Pept. Symp., 3rd*, **1972**, 217; *Chem. Abstr.*, **85**, 143484.
1517. K. Tsuji, *Yakugaku Zasshi*, **96**, 479 (1976); *Chem. Abstr.*, **85**, 99075.
1518. F. E. Arnold, *U.S. Pat.* 4,021,409 (1977); *Chem. Abstr.*, **85**, 124991.
1519. D. E. Beattie, R. Crossley, A. C. W. Curran, G. T. Dixon, D. G. Hill, A. N. Lawrence and R. G. Shepherd, *J. Med. Chem.*, **20**, 714 (1977); *Chem. Abstr.*, **86**, 165063.
1520. A. M. Osman, M. Z. A. Badr and A. E. Abel-Rahman, *Bull. Chem. Soc. Jap.*, **49**, 2611 (1976).
1521. T. Hisano, K. Muraoka and M. Ichikawa, *Org. Prep. Proced. Int.*, **9**, 41 (1977).
1522. V. I. Mikhailov, I. I. Popov, E. Sh. Kagan, A. M. Simonov and V. A. Smirnov, *Khim. Geterotsikl. Soedin.*, **1977**, 130; *Chem. Abstr.*, **86**, 139809.
1523. M. Siegmund, J. Bendig and B. Dobslaw, *Z. Phys. Chem. (Leipzig)*, **258**, 513 (1977).
1524. (a) D. Gloyna, K. G. Berndt, H. Koeppel and H. G. Henning, *J. Prakt. Chem.*, **318**, 327 (1976); *Chem. Abstr.*, **85**, 33135. (b) U. Lachmann, H. G. Henning and D. Gloyna, *J. Prakt. Chem.*, **318**, 489 (1976); *Chem. Abstr.*, **85**, 108718.
1525. S. Hillers, M. Lidaks, N. M. Sukhova and K. Venters, *Khim. Geterotsikl. Soedin.*, **1976**, 253; *Chem. Abstr.*, **85**, 32797.
1526. Y. M. Yutilov and L. I. Kovaleva, *Russ. Pat.* 541,846 (1977); *Chem. Abstr.*, **86**, 171448.
1527. G. Gennari, G. Cauzzo and G. Galiazzo, (a) *J. Photochem.*, **5** (5), 409 (1976); *Chem. Abstr.*, **85**, 176609; (b) *J. Phys. Chem.*, **81**, 1551 (1977); *Chem. Abstr.*, **87**, 84218.
1528. T. Tsuneda, (a) *Ger. Pat.* 2,521,917 (1975); *Chem. Abstr.*, **85**, 12337; (b) *Ger. Pat.* 2,521,918 (1975); *Chem. Abstr.*, **85**, 12338.
1529. K. A. Muszkat and S. Sharafi-Ozeri, *Chem. Phys. Lett.*, **42**, 99 (1976); *Chem. Abstr.*, **86**, 88705.
1530. R. I. Yurchenko, O. M. Voitsekhouskaya and A. A. Rykov, *Zh. Obshch. Khim.*, **46**, 2131 (1976); *Chem. Abstr.*, **86**, 43533.
1531. J. Lukevics, T. Lapina, E. Liepins and I. Segals, *Khim. Geterotsikl. Soedin.*, **1977**, 962; *Chem. Abstr.*, **87**, 168124.

1532. T. Koyama, T. Hirota, C. Bashou, T. Nanba, S. Ohmori and M. Yamato, *Chem. Pharm. Bull. (Tokyo)*, **25**, 1923 (1977). *Chem. Abstr.*, **87**, 201464.
1533. A. A. Pasynskii, I. L. Eremenko, T. C. Idrisov and V. T. Kalinnikov, *Koord. Khim.*, **3**, 1205 (1977); *Chem. Abstr.*, **87**, 145077.
1534. E. Hayashi and A. Miyashita, *Yakugaku Zasshi*, **96**, 968 (1976); *Chem. Abstr.*, **86**, 89564.
1535. H. Noda, K. Narimatsu and M. Hamana, *Yakugaku Zasshi*, **96**, 1417 (1976); *Chem. Abstr.*, **86**, 188689.
1536. C. M. Leir, *J. Org. Chem.*, **42**, 911 (1977).
1537. M. Drobnic-Kosorok, K. Jernejc-Pfundner, J. Peternel, B. Standvik and M. Tisler, *J. Heterocycl. Chem.*, **13**, 1279 (1976).
1538. Y. I. Chumakov, B. D. Kabulov and V. F. Novikova, *Tezisy Dokl.-Simp. Khim. Tekhnol. Geterosikl. Soedin. Goryuch. Iskop., 2nd*, **1973**, 171; *Chem. Abstr.*, **85**, 159847.
1539. Y. Akita, K. Misu, T. Watanabe and A. Ohta, *Chem. Pharm. Bull. (Tokyo)*, **24**, 1839 (1976).
1540. (a) Council of Scientific and Industrial Research (India), *Jap. Pat.* 75 149,692 (1975); *Chem. Abstr.*, **85**, 123974.
(b) Council of Scientific and Industrial Research, *Neth. Pat.* 7,406,101 (1975); *Chem. Abstr.*, **85**, 160162.
(c) P. C. Jain, R. C. Srimal, B. N. Dhawan, N. Anand, J. N. Sharma and V. A. Rao, *Fr. Pat.* 2,279,403 (1976); *Chem. Abstr.*, **86**, 16702.
(d) V. A. Murthi, P. C. Jain, J. N. Sharma, R. C. Srimal, B. N. Dhawan and N. Anand, *U.S. Pat.* 3,983,121 (1976); *Chem. Abstr.*, **86**, 89882.
1541. E. F. Nesmelova and G. P. Sidyakin, *Khim. Prir. Soedin.*, **9**(4), 548 (1973); *Chem. Abstr.*, **80**, 105845.
1542. S. A. Sultanov, V. I. Pastukhova and S. Y. Tunusov, *Khim. Prir. Soedin.*, **3**(5), 355 (1967); *Chem. Abstr.*, **68**, 19546.
1543. G. Buchmann and D. Rossner, *J. Prakt. Chem.*, **25**(3–4), 117 (1964); *Chem. Abstr.*, **61**, 16040g.
1544. J. E. Pritchard and P. L. Q. Meyers, *U.S. Pat.* 2,751,323 (1956); *Chem. Abstr.*, **50**, 14271e.
1545. O. E. Schultz and L. Geller, *Arch. Pharm.*, **288**, 234 (1955); *Chem. Abstr.*, **50**, 4142i.
1546. B. P. Lugovkin, *Zh. Obshch. Khim.*, **31**, 1685 (1961); *Chem. Abstr.*, **55**, 22316a.
1547. M. Henze, *Ber.*, **70B**, 1273 (1937).
1548. T. Hisano and H. Koga, *Yakugaku Zasshi*, **91**(2), 180 (1971); *Chem. Abstr.*, **74**, 125559.
1549. I. N. Chernyuk, V. V. Shelest and G. T. Pilyugin, *Ukr. Khim. Zh.*, **38**(12), 1264 (1972); *Chem. Abstr.*, **78**, 71869.
1550. V. P. Lezina, A. U. Stepanyants, L. D. Smirnov, N. A. Andronova and K. M. Dyumaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1972**, 2092; *Chem. Abstr.*, **78**, 3461.
1551. A. Ide and H. Watanabe, *Nippon Nogei Kagaku Kaishi*, **47**(1), 29 (1973); *Chem. Abstr.*, **79**, 5233.
1552. H. Ohta and K. Tokumaru, *Yuki Gosei Kagaku Kyokaishi*, **30**(12), 1006 (1972); *Chem. Abstr.*, **78**, 130473.
1553. R. C. Myerly and K. Weinberg, *U.S. Pat.* 3,428,641 (1969); *Chem. Abstr.*, **71**, 91324.
1554. E. Hayashi and T. Saito, *Yakugaku Zasshi*, **89**(1), 74 (1969); *Chem. Abstr.*, **70**, 96580.
1555. K. Thomae Gmbh, *Fr. Pat.* 1,489,049 (1967); *Chem. Abstr.*, **69**, 27271.
1556. E. C. Kleiderer and E. C. Kornfeld, *J. Org. Chem.*, **13**, 455 (1948).
1557. T. Kato, H. Yamanaka and M. Hikichi, *Yakugaku Zasshi*, **85**(4), 331 (1965); *Chem. Abstr.*, **63**, 4250a.
1558. E. Bergmann and W. Rosenthal, *J. Prakt. Chem.*, **135**, 267 (1932); *Chem. Abstr.*, **27**, 982.
1559. H. J. Steinbach and G. Buchmann, *Z. Chem.*, **3**, 150 (1963); *Chem. Abstr.*, **59**, 9972h.
1560. P. J. Black and M. L. Heffernan, *Aust. J. Chem.*, **17**, 558 (1964).
1561. M. R. Chakrabarty and E. S. Hanrahan, *J. Molec. Spectrosc.*, **30**, 348 (1969).
1562. F. A. L. Anet, *J. Chem. Phys.*, **32**, 1274 (1960).
1563. E. Diaz and P. Joseph-Nathan, *Spectrochim. Acta*, **25A**, 1547 (1969).
1564. K. Konishi, Y. Onari, S. Goto and K. Takahashi, *Chem. Lett.*, **1975**, 717.
1565. R. Noyori, M. Kato, M. Kaiwanisi and H. Nozaki, *Tetrahedron*, **25**, 1125 (1969).
1566. H. Sterk and A. Wachmann, *Z. Naturforsch.*, **31A**, 71 (1976).
1567. W. Seiffert, *Angew. Chem. Int. Ed. Engl.*, **1**, 215 (1962).
1568. N. S. Bhacca, D. P. Hollis, L. F. Johnson, E. A. Pier and J. N. Shoolery, *High Resolution NMR Catalogue*, Varian Associates, 1962, (a) Spectrum No. 578; (b) Spectrum No. 579.
1569. P. A. Claret and A. G. Osborne, Previously unpublished results.

1570. P. A. Claret and A. G. Osborne, *Tetrahedron*, **33**, 1765 (1977).
1571. *Sadtler Standard Spectra*, Sadtler Research Laboratories, Philadelphia, Pa., Spectra Nos. (a) 132; (b) 17130; (c) 21839; (d) 21956; (e) 11784; (f) 24024; (g) 8024; (h) 3971; (i) 11406; (j) 12000; (k) 15251; (l) 25722; (m) 13706; (n) 27764.
1572. P. S. Pregosin, E. W. Randall and A. I. White, *J. Chem. Soc. Perkin Trans. 2*, **1972**, 1.
1573. S. R. Johns and R. I. Willing, *Aust. J. Chem.*, **29**, 1617 (1976).
1574. S. R. Johns, R. I. Willing, P. A. Claret and A. G. Osborne, *Aust. J. Chem.*, **32**, 761 (1979).
1575. P. A. Claret and A. G. Osborne, Unpublished results, assignments based on Ref. 1573.
1576. E. Kleinpeter and R. Borsdorf, *J. Prakt. Chem.*, **315**, 765 (1973).
1577. A. R. Garber, P. E. Garrou, C. E. Hartwell, M. J. Smas, J. R. Wilkinson and L. J. Todd, *J. Organomet. Chem.*, **86**(2), 219 (1975); *Chem. Abstr.*, **82**, 154998.
1578. L. F. Johnson and W. C. Janowski, *Carbon-13 N.M.R. Spectra*, Spectrum 418, Wiley-Interscience, New York, 1972.
1579. P. A. Claret and A. G. Osborne, *Spectrosc. Lett.*, **11**, 351 (1978).
1580. L. W. Reeves and K. O. Stromme, *Can. J. Chem.*, **39**, 2318 (1961).
1581. T. Schaefer, *Can. J. Chem.*, **39**, 1864 (1961).
1582. See also Catalogues in Refs. 1568 and 1571.
1583. S. Sternhell, *Q. Rev. Chem. Soc.*, **23**, 236 (1969).
1584. K. Tori and T. Nakagawa, *J. Phys. Chem.*, **68**, 3163 (1964).
1585. T. A. Bryson, J. C. Wisowaty, R. B. Dunlap, R. R. Fisher and P. D. Ellis, *J. Org. Chem.*, **39**, 1158 (1974).
1586. T. Axenrod and M. J. Wieder, *Org. Magn. Reson.*, **8**, 350 (1976).
1587. *Jeol High Resolution N.M.R. Spectra*, Sadtler Research Laboratories, Philadelphia, Pa. 1967, (a) Spectrum No. 100–138, (b) Spectrum No. 100–139.
1588. C. J. Pouchert and J. R. Campbell, *The Aldrich Library of N.M.R. Spectra*, Vol. 9, Aldrich Chemical Co., Milwaukee, Wisc. 1974, (a) Spectrum No. 97C; (b) Spectrum No. 97D; (c) Spectrum No. 98A; (d) Spectrum No. 98B.
1589. A. Albert and J. N. Phillips, *J. Chem. Soc.*, **1956**, 1294.
1590. J. G. Pritchard and F. A. Long, *J. Amer. Chem. Soc.*, **79**, 2365 (1957).
1591. Tl. Kappe, *Monatsh. Chem.*, **98**(6), 2148 (1967); *Chem. Abstr.*, **68**, 39445.
1592. Y. N. Popov, T. V. Portnova, B. E. Kogan, E. A. Kiva and E. A. Kruglov, *Tezisy Dokl.-Simp. Khim. Tekhnol. Geterotsikl. Soedin. Goryuch. Iskop., 2nd*, **1973**, 160; *Chem. Abstr.*, **86**, 174047.
1593. J. Vymetal, *Chem. Prum.*, **26**(1), 16 (1976); *Chem. Abstr.*, **85**, 94201.
1594. A. Y. Baikova, V. G. Ben'kovskii, Y. N. Popov, E. A. Kruglov and N. S. Lyubopytova, *Neftekhimiya*, **16**(2), 304 (1976); *Chem. Abstr.*, **85**, 110664.
1595. A. I. Stekhun, G. A. Berg, F. G. Unger, A. I. Sumskaya and V. P. Kubrak, *Neftepererab. Neftekhim. (Moscow)*, No. 9, 10 (1973); *Chem. Abstr.*, **80**, 50123.
1596. C. F. Mabery and L. G. Wesson, *J. Amer. Chem. Soc.*, **42**, 1014 (1920).
1597. M. Pailer and W. Jiresch, *Monatsh.*, **100**(1), 121 (1969); *Chem. Abstr.*, **70**, 98426.
1598. R. E. Poulson, H. B. Jensen and G. L. Cook, *Amer. Chem. Soc. Div. Petrol. Chem. Prepr.*, **16**(1), A49 (1971); *Chem. Abstr.*, **78**, 6133.
1599. E. V. Glushchenkova, N. D. Dokshina and S. S. Semenov, *Khim. Tekhnol. Goryuch. Slantsev Prod. Ikh. Pererab.*, **1968**, 56; *Chem. Abstr.*, **71**, 83213.
1600. M. W. Dong, D. C. Locke and D. Hoffmann, *Environ. Sci. Technol.*, **11**, 612 (1977); *Chem. Abstr.*, **87**, 57494.
1601. O. G. Vitzthum, P. Werkhoff and E. Ablanque, *Colloq. Int. Chim. Cafes Vertes, Torrefies Leurs Deriv. (C.R.)*, **7**, 115 (1975); *Chem. Abstr.*, **85**, 158128.
1602. G. A. Evdokimova, V. E. Rakovskii and E. A. Yurkevich, *Kompleks Sn. Ispol'z Torfa*, No. 2, 58 (1968); *Chem. Abstr.*, **73**, 100840.
1603. L. H. Klemm and R. Hartling, *J. Heterocycl. Chem.*, **14**, 165 (1977).
1604. C. De Grand and H. Lund, *Acta Chem. Scand.*, **B31**, 593 (1977).
1605. J. Z. Brzezinski, J. Epsztajn and T. J. Michalski, *Tetrahedron Lett.*, **1976**, 4635.
1606. F. W. Bergstrom and C. H. Horning, *J. Org. Chem.*, **11**, 334 (1946).
1607. (a) A. N. Ivanova and Y. V. Fedorov, *Zashch. Met.*, **12**(3), 330 (1976); *Chem. Abstr.*, **85**, 111433. (b) Y. V. Fedorov, S. P. Miskidzh'yan, A. N. Ivanova and V. F. Voloshin, *Tezisy Dokl.-Simp. Khim. Tekhnol. Geterotsikl. Soedin. Goryuch. Iskop., 2nd*, **1973**, 149; *Chem. Abstr.*, **85**, 146962.
1608. E. M. Agres and A. I. Altsybeeva, *Zh. Fiz. Khim.*, **50**, 3149 (1976); *Chem. Abstr.*, **86**, 112902.

1609. D. L. J. Opdyke, *Food Cosmet. Toxicol.*, (a) **13** (Suppl.), 821 (1975); *Chem. Abstr.*, **86**, 145672; (b) **14** (4), 311 (1976); *Chem. Abstr.*, **86**, 161074.
1610. B. D. Kabulov, *Tr. Samark. Gos. Univ.*, No. 207, 192 (1974); *Chem. Abstr.*, **86**, 184388.
1611. Y. I. Chumakov, B. D. Kabulov, V. F. Novikova and M. S. Alyab'eva, *Tezisye Dokl.-Simp. Khim. Tekhnol. Geterotsikl. Soedin. Goryuch. Iskop., 2nd*, **1973**, 181; *Chem. Abstr.*, **86**, 25657.
1612. E. Soczewinski, G. Matysik and W. Dumkiewicz, *J. Chromatogr.*, **132**, 379 (1977); *Chem. Abstr.*, **86**, 79116.
1613. E. Soczewinski, M. Waksmundzka-Hajnos and M. Bieganowska, *Chem. Anal. (Warsaw)*, **22**, 289 (1977); *Chem. Abstr.*, **87**, 145372.
1614. M. Bieganowska and T. Wawrzynowicz, *Chem. Anal. (Warsaw)*, **21**, 211 (1976); *Chem. Abstr.*, **85**, 52168.
1615. M. Dong, D. C. Locke, D. Hoffmann and N. Dana, *J. Chromatogr. Sci.*, **15**, 32 (1977); *Chem. Abstr.*, **86**, 101529.
1616. K. S. Al-Bahrani and R. J. Martin, *Water Res.*, **10**, 731 (1976); *Chem. Abstr.*, **86**, 21408.
1617. T. M. Markacheva and L. A. Kogan, *Koks Khim.*, No. 5, 36 (1976); *Chem. Abstr.*, **85**, 163100.
1618. P. P. Karlik and V. M. Kynkurogova, *Tezisy Dokl.-Simp. Khim. Tekhnol. Geterotsikl. Soedin. Goryuch. Iskop., 2nd*, **1973**, 20; *Chem. Abstr.*, **86**, 25668.
1619. M. Nagao, T. Yahagi, Y. Seino, T. Sugimura and N. Ito, *Mutat. Res.*, **42**, 335 (1977); *Chem. Abstr.*, **86**, 166197.
1620. A. I. Shatenshtein and E. N. Zuyagintseva, *Dokl. Akad. Nauk SSSR*, **117**, 852 (1957); *Chem. Abstr.*, **52**, 17912b.
1621. N. N. Zatsepina, I. F. Tupitsyn and L. S. Efros, (a) *Zh. Obshch. Khim.*, **33** (8), 2705 (1963); *Chem. Abstr.*, **60**, 5292d; (b) *Dokl. Akad. Nauk SSSR*, **154** (1), 148 (1964); *Chem. Abstr.*, **60**, 9113e; (c) *Zh. Obshch. Khim.*, **34** (12), 4065 (1964); *Chem. Abstr.*, **62**, 8961d; (d) N. N. Zatsepina and I. F. Tupitsyn, *Isotopenpraxis*, **3** (3), 104 (1967); *Chem. Abstr.*, **70**, 118577.
1622. T. I. Abramovitch, I. P. Gragerov and V. V. Perekalin, *Dokl. Akad. Nauk SSSR*, **121**, 295 (1958); *Chem. Abstr.*, **53**, 1342g.
1623. V. Boekelheide and J. Weinstock, *J. Amer. Chem. Soc.*, **74**, 660 (1952).
1624. R. F. Meyer and C. D. Stratton, *U.S. Pat.* 3,794,650; *Chem. Abstr.*, **80**, 108404.
1625. V. M. Rodionov and M. A. Berkenheim, *Zhur. Obshch. Khim.*, **16**, 483 (1946); *Chem.* Abstr., **41**, 9666.
1626. G. W. Gribble and P. W. Heald, *Synthesis*, **1975**, 650.
1627. E. M. Kaiser and G. J. Bartling, *J. Org. Chem.*, **37** (3), 490 (1972).
1628. S. Skidmore and E. Tidd, (a) *Chem. Ind. (London)*, **1954**, 1295; (b) *J. Chem. Soc.*, **1959**, 1641.
1629. W. H. King, *J. Assoc. Off. Agric. Chem.*, **22**, 777 (1939); *Chem. Abstr.*, **34**, 267[4].
1630. Y. Hamada, *Yakugaku Zasshi*, **80**, 1573 (1960); *Chem. Abstr.*, **55**, 10450a.
1631. A. J. Birch and P. C. Lehman, *J. Chem. Soc. Perkin Trans. 1*, **1973**, 2754.
1632. O. Cervinka, A. Fabryova and L. Matouchova, *Collect. Czech Chem. Commun.*, **28**, 535 (1963); *Chem. Abstr.*, **59**, 3888c.
1633. T. C. Christidis and F. W. Heineken, *Magn. Reson. Relat. Phenomena, Proc. Congr. Ampere, 16th, 1970*, **1971**, 551; *Chem. Abstr.*, **78**, 9850.
1634. T. Kato, Y. Goto and M. Kondo, *Yakugaku Zasshi*, **84** (3), 290 (1964); *Chem. Abstr.*, **61**, 3070g.
1635. V. P. Lezina, A. V. Stepanyants, L. D. Smirnov and N. A. Andronova, *Tezisy Dokl.-Simp. Khim. Tekhnol. Geterotsikl. Soedin. Goryuch. Iskop., 2nd*, **1973**, 13; *Chem. Abstr.*, **85**, 192035.
1636. H. Noda, H. Ekimoto and M. Hamana, *Heterocycles*, **5**, 339 (1976); *Chem. Abstr.*, **86**, 55264.
1637. T. Caronna, A. Citterio and M. Bellatti, *J. Chem. Soc. Chem. Commun.*, **1976**, 987.
1638. H. Booth, D. V. Griffiths and M. L. Jozefowicz, *J. Chem. Soc., Perkin Trans. 2*, **1976**, 751.
1639. A. M. Osman, K. M. Hassan, Z. H. Khalil and V. D. Turin, *J. Appl. Chem. Biotechnol.*, **26**, 71 (1976); *Chem. Abstr.*, **85**, 95779.
1640. J. F. Cavalla, *J. Chem. Soc.*, **1954**, 4701.
1641. J. B. Dewitt, E. Bellack and J. F. Welch, *J. Amer. Pharm. Assoc.*, **42**, 695 (1953); *Chem. Abstr.*, **48**, 941b.
1642. M. Szafran, Z. Dega-Szafran and C. Grech, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.*, **24**, 699 (1976).
1643. G. Vanags and A. Lode, *Ber.*, **70B**, 547 (1937); *Chem. Abstr.*, **31**, 3907[4].
1644. P. Tomasik, *Rocz. Chem.*, **39** (3), 483 (1965); *Chem. Abstr.*, **63**, 8308f.

1645. (a) P. C. Roy and D. V. R. Rao, *J. Inst. Chem. (India)*, **49**, 197 (1977); *Chem. Abstr.*, **88**, 15235. (b) J. E. Davies, A. V. Rivera and G. M. Sheldrick, *Acta Crystallogr. Sect. B*, **B33**, 156 (1977); *Chem. Abstr.*, **86**, 113940.
1646. (a) A. A. Pasynskii, T. C. Idrisov, K. M. Suvorova and V. T. Kalinnikov, *Koord. Khim.*, **2**(8), 1060 (1976); *Chem. Abstr.*, **85**, 186054.
(b) A. A. Pasynskii, T. C. Idrisov, K. M. Suvorova, V. T. Kalinnikov and V. M. Novotortsen, *Tezisy Dokl. Khim. Kompliksn. Soedin., 12th*, **3**, 469 (1975); *Chem. Abstr.*, **85**, 192860.
1647. V. L. Katamanov, E. F. Zhuravlev, *Zh. Neorg. Khim.*, **21**(6), 1610 (1976); *Chem. Abstr.*, **85**, 136468.
1648. E. Durcanska, M. Koman and E. Jona, *Z. Chem.*, **16**, 453 (1976); *Chem. Abstr.*, **86**, 64765.
1649. B. Rau and R. Huettel, *J. Organomet. Chem.*, **139**, 103 (1977); *Chem. Abstr.*, **88**, 23118.
1650. S.-I. Fujise and M. Iwakiri, *Bull. Chem. Soc. Jap.*, **11**, 293 (1936).
1651. F. E. Cislak and W. R. Wheeler, *U.S. Pat.* 2,396,457 (1946); *Chem. Abstr.*, **40**, 3142^{8}.
1652. L. M. Yagupol'skii, U. S. Mikhailov and G. I. Matyushecheva, *Zh. Org. Khim.*, **8**(4), 838 (1972); *Chem. Abstr.*, **77**, 19493.
1653. J. J. Baldwin and F. C. Novello, *U.S. Pat.* (a) 4,011,218 (1977); *Chem. Abstr.*, **87**, 5980; (b) 4,032,522 (1977); *Chem. Abstr.*, **87**, 102334.
1654. T. Kauffmann, D. Tigler and A. Woltermann, *Tetrahedron Lett.*, **1977**, 741.
1655. R. J. Butcher and E. Sinn, *Inorg. Chem.*, **16**, 2334 (1977); *Chem. Abstr.*, **87**, 144321.
1656. J. R. Wasson, D. M. Klassen, H. W. Richardson and W. E. Hatfield, *Inorg. Chem.*, **16**, 1906 (1977); *Chem. Abstr.*, **87**, 60345.
1657. M. Ikeda, S. Matsugashita, F. Tabusa and Y. Tamura, *J. Chem. Soc., Perkin Trans. I*, **1977**, 1166.
1658. K. Berg-Nielsen, *Acta Chem. Scand.*, **31B**, 224 (1977).
1659. M. Davis and D. B. Scanlon, *Aust. J. Chem.*, **30**, 433 (1977).
1660. T. Sakamoto, S. Konno and H. Yamanaka, *Heterocycles*, **6**, 1616 (1977); *Chem. Abstr.*, **87**, 167975.
1661. T. Tsuneda, *U.S. Pat.* 4,040,970 (1977); *Chem. Abstr.*, **87**, 175673.
1662. H. Oda, K. Shimada, M. Matsuoka and T. Kitao, *Nippon Kagaku Kaishi*, **1977**, 1186; *Chem. Abstr.*, **87**, 169238.
1663. B. Lorant, *Seifen, Oele, Fette, Wachse*, **103**, 393 (1977); *Chem. Abstr.*, **87**, 189282.
1664. J-A. Su, E. Siew, E. V. Brown and S. L. Smith, *Org. Magn. Reson.*, **10**, 122 (1977).
1665. See ref. 1574.
1666. D. A. Netzel, *Org. Magn. Reson.*, **11**, 58 (1978).
1667. H. A. Stansbury, Jr., and H. F. Lykins, *U.S. Pat.* 2,886,568 (1959).
1668. P. N. Rabinovich and V. K. Dzirkal, *Khim. Farm. Prom.*, **1933**, 273.
1669. Zd. H. Skraup, *Ber.*, **15**, 893 (1882).
1670. W. H. Mills, J. E. G. Harris and H. Lambourne, *J. Chem. Soc.*, **119**, 1294 (1921).
1671. U. Basu, *Ann.*, **512**, 131 (1934).
1672. P. Friedländer and C. F. Gohring, *Ber.*, **16**, 1833 (1883).
1673. C. Schöpf and G. Lehmann, *Ann.*, **497**, 7 (1932).
1674. I. G. Farbenindustrie A. G., *Ger. Pat.* 495,337 (1930).
1675. R. R. Vogt and J. A. Nieuwland, *J. Amer. Chem. Soc.*, **43**, 2071 (1921).
1676. R. H. F. Manske, L. Marion and F. Leger, *Can. J. Res.*, **20B**, 133 (1942).
1677. G. R. Clemo and N.D. Ghatze, *J. Chem. Soc.*, **1955**, 4347.
1678. T. Hèou-Fèo, *Bull. Soc. Chim. Fr.*, **2**, 90 (1935).
1679. L. Zalukajevs and J. Bankovskis, *Dokl. Akad. Nauk SSSR*, **100**, 705 (1955); *Latv. PSR Zinât. Akad. Vēstis*, No. 2, 83 (1955).
1680. T. W. J. Taylor and P. M. Hobson, *J. Chem. Soc.*, **1936**, 181.
1681. W. G. Dauben and C. W. Vaughan, Jr., *J. Amer. Chem. Soc.*, **75**, 4651 (1953).
1682. O. Stark, *Ber.*, **42**, 715 (1909).
1683. L. A. Mikeska, J. K. Stewart and L. E. Wise, *J. Ind. Eng. Chem.*, **11**, 456 (1919).
1684. M. E. Kuehne and P. J. Shearan, *J. Org. Chem.*, **33**, 4406 (1968).
1685. G. Darzens and M. Meyer, *C. R. Acad. Sci.*, **198**, 1428 (1934).
1686. W. von Miller and F. Kinkelin, *Ber.*, **20**, 1916 (1887).
1687. P. A. Claret and A. G. Osborne, *Chem. Ind. (London)*, **1970**, 401.
1688. G. Heller, *Ber.*, **43**, 1907 (1910).
1689. R. T. Coutts, W. N. Pitkethly and D. G. Wibberley, *J. Pharm. Sci.*, **54**, 792 (1965).

1690. B. I. Ardashev and V. I. Minkin, *Zh. Obshch. Khim.*, **28**, 1578 (1958).
1691. S. G. Willimott and I. A. Simpson, *J. Chem. Soc.*, **1926**, 2807.
1692. H. J. Uebel, K. K. Moll and M. Mühlstädt, *J. Prakt. Chem.*, **312**, 263 (1970).
1693. W. P. Utermohlen, Jr., *J. Org. Chem.*, **8**, 544 (1943).
1694. D. Ll. Hammick and B. H. Thewlis, *J. Chem. Soc.*, **1948**, 1457.
1695. L. A. Mikeska, *J. Amer. Chem. Soc.*, **42**, 2396 (1920).
1696. K. N. Campbell, *U.S. Pat.* 2,451,610 (1948).
1697. J. Kenner and F. S. Statham, *Ber.*, **69B**, 16 (1936).
1698. G. I. Mikhailov, *Zh. Obshch. Khim.*, **6**, 511 (1936).
1699. K. N. Campbell and I. J. Schaffner, *J. Amer. Chem. Soc.*, **67**, 86 (1945).
1700. A. E. Tschitschibabin and M. P. Oparina, *Ber.*, **60B**, 1873 (1927).
1701. A. E. Tschitschibabin and M. P. Oparina, *J. Russ. Phys. Chem. Soc.*, **59**, 1129 (1927).
1702. A. E. Tschitschibabin, *Ger. Pat.* 468,303 (1928).
1703. Schering-Kahlbaum A.-G., *Ger. Pat.* 518,291 (1931).
1704. S. E. Krahler and A. Burger, *J. Amer. Chem. Soc.*, **63**, 2367 (1941).
1705. B. I. Ardashev and E. Sh. Kagan, *Zh. Obshch. Khim.*, **34**, 2228 (1964).
1706. B. I. Ardashev, E. Sh. Kagan and N. F. Ovchinnikov, *Khim. Geterotsikl. Soedin.*, **1968**, 857.
1707. B. A. Tertov and B. I. Ardashev, *Zh. Obshch. Khim.*, **27**, 3026 (1957).
1708. N. S. Kozlov and G. P. Korotyshova, *Dokl. Akad. Nauk SSSR*, **222**, 111 (1975).
1709. E. Pouterman and A. Girardet, *Experientia*, **3**, 28 (1947).
1710. L. Bradford, T. J. Elliott and F. M. Rowe, *J. Chem. Soc.*, **1947**, 437.
1711. R. Huisgen, *Ann.*, **559**, 101 (1948).
1712. M. H. Palmer, *J. Chem. Soc.*, **1962**, 3645.
1713. J. G. F. Druce, *Chem. News*, **119**, 271 (1919).
1714. F. Gialdi and R. Ponci, *Farm. Sci. Tec. (Pavia)*, **6**, 327 (1951); *Chem. Abstr.*, **45**, 9117.
1715. L. C. Washburn, T. G. Barbee, Jr., and D. E. Pearson, *J. Med. Chem.*, **13**, 1004 (1970).
1716. W. Mathes and W. Sauermilch, *Chem. Ber.*, **90**, 758 (1957).
1717. C. A. Knueppel, *Ber.*, **29**, 703 (1896).
1718. J. G. F. Druce, *Chem. News*, **117**, 346 (1918).
1719. T. Kametani and H. Nemoto, *Chem. Pharm. Bull. (Tokyo)*, **15**, 1910 (1967).
1720. R. Delaby and J. Hiron, *Bull. Soc. Chim. Fr.*, **47**, 1395 (1930).
1721. R. Delaby and J. Hiron, *Bull. Soc. Chim. Fr.*, **47**, 227 (1930).
1722. S. D. Lesesne and H. R. Henze, *J. Amer. Chem. Soc.*, **64**, 1897 (1942).
1723. W. Bradley and S. Jeffery, *J. Chem. Soc.*, **1954**, 2770.
1724. J. Metzger, H. Larive, R. Dennilauler and E. J. Vincent, *Bull. Soc. Chim. Fr.*, **1967**, 46.
1725. F. L. Warren, *J. Chem. Soc.*, **1936**, 1366.
1726. N. S. Kozlov, Yu. S. Chumakov and S. I. Kozintsev, *Dokl. Akad. Nauk Beloruss. SSR*, **17**, 930 (1973).
1727. R. W. Brown and G. Dougherty, *J. Amer. Chem. Soc.*, **69**, 2232 (1947).
1728. Schering-Kahlbaum A.-G., *Brit. Pat.* 283,577 (1928).
1729. C. Zöllner, *U.S. Pat.* 1,804,045 (1931).
1730. E. D. Amstutz and G. L. Krueger, *U.S. Pat.* 2,894,952 (1959).
1731. P. Rabe and R. Pasternack, *Ber.*, **46**, 1026 (1913).
1732. T. Mazonski, A. Lachowicz and J. Gorniak, *Roczn. Chem.*, **36**, 873 (1962).
1733. W. S. Emerson, R. A. Heimisch and T. M. Patrick Jnr., *J. Amer. Chem. Soc.*, **75**, 2256 (1953).
1734. R. Long and K. Schofield, *J. Chem. Soc.*, **1953**, 2350.
1735. T. Kudo, A. Nose and M. Hamana, *Yakugaku Zasshi*, **95**, 521 (1975).
1736. M. Freund and E. Kessler, *J. Prakt. Chem.*, **98**, 233 (1918).
1737. R. Delaby and J. Hiron, *C. R. Acad. Sci.*, **191**, 845 (1930).
1738. Y. Makisumi and A. Murabayashi, *Tetrahedron Lett.*, **1969**, 2449.
1739. K. von Auwers and R. Kraul, *Z. Phys. Chem.*, **116**, 438 (1925).
1740. J. von Braun, K. Heider and W. Wyczatkowska, *Ber.*, **51**, 1215 (1918).
1741. M. Ferles, O. Kochian and J. Lovy, *Collect. Czech. Chem. Commun.*, **41**, 758 (1976).
1742. J. C. Martin and R. H. Meen, *J. Org. Chem.*, **30**, 4311 (1965).
1743. P. A. Claret and A. G. Osborne, *J. Chem. Tech. Biotechnol.*, **29**, 175 (1979).
1744. A. Lachowicz and T. Mazonski, *Roczn. Chem.*, **40**, 609 (1966).
1745. T. van Hove, *Bull. Acad. Roy. Sci. Belg.*, **1908**, 540.
1746. L. R. Walters, N. T. Iyer and W. E. McEwen, *J. Amer. Chem. Soc.*, **80**, 1177 (1958).

1747. H. R. Henze and D. W. Carroll, *J. Amer. Chem. Soc.*, **76**, 4580 (1954).
1748. T. Okamoto and H. Takayama, *Chem. Pharm. Bull. (Tokyo)*, **11**, 514 (1963).
1749. K. Tamao, S. Kodama, I. Nakajima, T. Nokatsuka, A. Minato and M. Kumada, *Hukusokan Kagaku Toronkai Koen Yoshishu, 8th*, **1975**, 174.
1750. N. P. Buu-Hoi and R. Royer, *J. Chem. Soc.*, **1948**, 106.
1751. T. Higashino, K. Suzuki and E. Hayashi, *Chem. Pharm. Bull. (Tokyo)*, **23**, 746 (1975).
1752. C. Schöpf, *Congr. Int. Chim. Pure Appl., 9th*, **5**, 189 (1934).
1753. M. Ikeda, S. Matsugashita, F. Tabusa and Y. Tamura, *J. Chem. Soc. Perkin Trans. 1*, **1977**, 1166.
1754. J. Eberle, M. Sergant, C. Fauran and G. Huguet, *Brit. Pat.* 1,178,400 (1970).
1755. N. P. Buu-Hoi, R. Royer, N. D. Xuong and P. Jacquignon, *J. Org. Chem.*, **18**, 1209 (1953).
1756. I. G. Farbenindustrie A.-G., *Fr. Pat.* 781,812 (1935).
1757. F. Krafft, *Ber.*, **23**, 2360 (1890).
1758. W. N. White and D. Lazdino, *J. Org. Chem.*, **34**, 2756 (1969).
1759. R. M. Acheson and R. F. Flowerday, *J. Chem. Soc. Perkin Trans. 1*, **1975**, 394.
1760. J. M. F. Gagan and D. Lloyd, *J. Chem. Soc. C*, **1970**, 2488.
1761. S. Goszczynski, *Zesz. Nauk. Politech. Slask., Chem.*, No. 25, 5 (1964).
1762. J. M. F. Gagan and D. Lloyd, *J. Chem. Soc., Chem. Commun.*, **1967**, 1043.
1763. G. Heller, H. Lauth and A. Buchwaldt, *Ber.*, **55B**, 483 (1922).
1764. A. Jaenisch, *Ber.*, **56B**, 2448 (1923).
1765. G. Rohde, *Ber.*, **67B**, 431 (1934).
1766. G. Saint-Ruf, A. De and J. C. Perche, *Bull. Soc. Chim. Fr.*, **1973**, 2514.
1767. N. S. Kozlov and L. E. Olifson, *Zh. Obshch. Khim.*, **7**, 2301 (1937).
1768. N. S. Kozlov, *Zh. Obshch. Khim.*, **7**, 1860 (1937).
1769. E. Knoevenagel, *Ber.*, **56B**, 2414 (1923).
1770. L. A. Mikeska, J. K. Stewart and L. E. Wise, *Ind. Eng. Chem.*, **11**, 456 (1919).
1771. P. Kalnins and W. Grinstein, *Ann.*, **523**, 118 (1936).
1772. D. Craig, *J. Amer. Chem. Soc.*, **60**, 1458 (1938).
1773. W. R. Vaughn, *Org. Synth.*, **28**, 49 (1948); Collect. Vol. III, 329.
1774. M. Julia, *C. R. Acad. Sci.*, **228**, 1807 (1949).
1775. A. M. Spivey and F. H. S. Curd, *J. Chem. Soc.*, **1949**, 2656.
1776. M. Romet, *C. R. Acad. Sci.*, **200**, 1676 (1935).
1777. L. J. Simon, *C. R. Acad. Sci.*, **146**, 1400 (1908).
1778. G. M. Badger, H. P. Crocker, B. C. Ennis, J. A. Gaylor, W. E. Matthews, W. G. C. Raper, E. L. Samuel and T. M. Spotswood, *Aust. J. Chem.*, **16**, 814 (1963).
1779. A. Ermili, R. Giulinao and M. L. Stein, *Ann. Chim. (Rome)*, **46**, 1199 (1956).
1780. British Dyestuffs Corporation and M. Wyler, *Brit. Pat.* 276,156 (1927).
1781. T. Troskiewicz and J. Glinka, *Roczn. Chem.*, **36**, 1387 (1962).
1782. B. I. Ardashev and B. A. Tertov, *Zh. Obshch. Khim.*, **26**, 218 (1956).
1783. A. Prill and R. Wolter, *U.S. Pat.* 1,806,563 (1931).
1784. I. G. Farbenindustrie A.-G., *Brit. Pat.* 308,365 (1930).
1785. A. T. Babayan and N. P. Gambaryan, *Izv. Akad. Nauk Armyan. SSR, Ser. Fiz.-Mat. Nauk*, No. 2, 73 (1953); *Chem. Abstr.*, **49**, 8279.
1786. H. King and J. Wright, *Proc. Roy. Soc. (London)*, **B135**, 27 (1948).
1787. J. A. Gardner and M. Williams, *Brit. Pat.* 198,462 (1923).
1788. L. Berend, *Ber.*, **17**, 1489 (1884).
1789. N. S. Kozlov, V. D. Pak, L. V. Chuklinov and I. N. Levashov, *Russ. Pat.* 435,239 (1974).
1790. D. Horvitz and W. D. Baugh, *U.S. Pat.* 3,705,163 (1972).
1791. T. Joh and N. Hagihara, *Nippon Kagaku Zasshi*, **91**, 378 (1970).
1792. J. B. Zachry, *Ph.D. Thesis*, University of Texas, Austin, 1960; *Diss. Abstr.*, **21**, 3639 (1961).
1793. J. Eliasberg and P. Friedländer, *Ber.*, **25**, 1752 (1892).
1794. K. Murakami, *Sci. Rep. Tôhoku Imp. Univ. 1st Ser.*, **18**, 643 (1929); *Chem. Abstr.*, **24**, 2461.
1795. B. I. Ardashev, *Zhur. Obshch. Khim.*, **20**, 462 (1950).
1796. T. Ozawa and S. Nagaoka, *Yakugaku Zasshi*, **75**, 1405 (1955).
1797. A. L. Searles and H. G. Lindwall, *J. Amer. Chem. Soc.*, **68**, 988 (1946).
1798. H. Bijvanck, *Ber.*, **31**, 2143 (1898).
1799. B. I. Ardashev, *Zh. Obshch. Khim.*, **19**, 1656 (1949).
1800. D. J. Cook and W. E. Schelwalt, *Proc. Indiana Acad. Sci.*, **74**, 183 (1964).

1801. P. A. Claret and A. G. Osborne, *Org. Prep. Proced. Int.*, **6**, 149 (1974).
1802. J. Vahldieck and G. Buchmann, *Pharmazie*, **24**, 196 (1969).
1803. A. Mailhe, *Bull. Chim. Fr.*, **29**, 713 (1921).
1804. A. Mailhe, *C. R. Acad. Sci.*, **173**, 160 (1921).
1805. P. A. Claret and A. G. Osborne, *Org. Prep. Proced.*, **2**, 305 (1970).
1806. S. Uyeo, T. Shingu and H. Harda, *Yakugaku Zasshi*, **85**, 314 (1965).
1807. N. P. Buu-Hoi, M. Mangane and P. Jacquignon, *J. Chem. Soc. C*, **1967**, 662.
1808. G. R. Cliff, G. Jones and J. McK. Wollard, (a) *Tetrahedron Lett.*, **1973**, 2401; (b) *J. Chem. Soc., Perkin Trans. 1*, **1974**, 2072.
1809. Y. Makisumi, *J. Org. Chem.*, **30**, 1989 (1965).
1810. K. W. Bartz, *Ph.D. Thesis*, University of Texas, Austin, 1959; *Diss. Abstr.*, **22**, 63 (1961).
1811. J. N. Le Conte, *J. Elisha Mitchell Sci. Soc.*, **51**, 249 (1935).
1812. A. S. Wheeler and J. N. Le Conte, *J. Amer. Chem. Soc.*, **70**, 386 (1948).
1813. V. I. Minkin, L. E. Nivorozhkin and V. A. Bren, *Zh. Obshch. Khim.*, **35**, 1270 (1965).
1814. M. S. Kharasch, I. Richlin and F. R. Mayo, *J. Amer. Chem. Soc.*, **62**, 494 (1940).
1815. J. von Braun, E. Anton, W. Haensel and G. Werner, *Ann.*, **472**, 1 (1929).
1816. A. T. Nielsen, C. Gibbons and C. A. Zimmerman, *J. Amer. Chem. Soc.*, **73**, 4696 (1951).
1817. Y. Otsuji, K. Yutani and E. Imoto, *Bull. Chem. Soc. Jap.*, **44**, 520 (1971).
1818. T. van Hove, *Bull. Acad. Roy. Sci. Belg.*, **1906**, 650.
1819. W. von Miller, *Ber.*, **24**, 1720 (1891).
1820. G. Ciamician and P. Silber, *Ber.*, **38**, 3813 (1905).
1821. V. I. Minkin and L. E. Nivorozhkin, *Zh. Org. Khim.*, **1**, 1632 (1965).
1822. M. Pang, *U.S. Pat.* 3,787,418 (1974).
1823. G. Kempter and G. Moebus, *J. Prakt. Chem.*, **34**, 298 (1966).
1824. A. Combes, *Bull. Soc. Chim Fr.*, **49**, 89 (1888).
1825. A. Combes, *C. R. Acad. Sci.*, **106**, 142 (1888).
1826. R. Adams and J. Campbell, *J. Amer. Chem. Soc.*, **72**, 1021 (1950).
1827. W. Pfitzinger, *J. Prakt. Chem.*, **38**, 40 (1888).
1828. E. Knoevenagel and H. Bähr, *Ber.*, **55B**, 1912 (1922).
1829. C. Karr, Jr., P. A. Estep and A. J. Papa, *J. Amer. Chem. Soc.*, **81**, 152 (1959).
1830. S. Yamaguchi, *Yakugaku Zasshi*, **44**, 23 (1924).
1831. L. Berend, *Ber.*, **17**, 653 (1884).
1832. W. Merz, *Ber.*, **17**, 1158 (1884).
1833. W. von Miller and J. Plöchl, *Ber.*, **29**, 1462 (1896).
1834. B. I. Ardashev, *Zh. Obshch. Khim.*, **19**, 550 (1949).
1835. F. Piozzi and G. Casnati, *Gazz. Chim. Ital.*, **88**, 161 (1958).
1836. Monsanto Chemicals (Australia) Ltd., *Neth. Pat.*, 6,409,933 (1965).
1837. K. C. John and F. H. Case, *J. Chem. Eng. Data*, **13**, 568 (1968).
1838. C. E. Kaslow and N. B. Sommer, *J. Amer. Chem. Soc.*, **68**, 644 (1946).
1839. M. Gandino, *Belg. Pat.* 667,052 (1965).
1840. B. I. Ardashev and B. A. Tertov, *Zh. Obshch. Khim.*, **24**, 314 (1954).
1841. P. V. Deshmukh, *Sadtler Standard Spectra*, Sadtler Research Labs., Philadelphia, Pa., 1969, Spectrum No. IR-35066.
1842. N. P. Buu-Hoi, P. Jacquignon and O. Roussel, *Bull. Soc. Chim. Fr.*, **1965**, 322.
1843. L. Berend, *Ber.*, **18**, 376 (1885).
1844. N. P. Buu-Hoi, P. Jacquignon and E. Allegrini, *J. Chem. Soc.*, **1961**, 4836.
1845. N. P. Buu-Hoi and P. Jacquignon, *J. Chem. Soc.*, **1959**, 3095.
1846. V. I. Minkin and B. A. Ardashev, *Zh. Obshch. Khim.*, **28**, 2556 (1958).
1847. W. Strubell, *Z. Chem.*, **2**, 29 (1961).
1848. N. P. Buu-Hoi and D. Guettier, *Rec. Trav. Chim.*, **65**, 502 (1946).
1849. L. A. Mikeska and E. Q. Adams, *J. Amer. Chem. Soc.*, **42**, 2394 (1920).
1850. F. H. Case and H. H. Wisneski, *J. Heterocycl. Chem.*, **5**, 789 (1968).
1851. P. A. Claret and A. G. Osborne, *Org. Prep. Proced. Int.*, **4**, 225 (1972).
1852. T. G. Bonner and M. Barnard, *J. Chem. Soc.*, **1958**, 4181.
1853. I. Levin and P. Riehm, *Ber.*, **19**, 1394 (1886).
1854. T. G. Bonner and M. Barnard, *J. Chem. Soc.*, **1958**, 4176.
1855. H. H. Wisneski, *Ph.D. Thesis*, Temple University, Philadelphia, 1964; *Diss Abstr.*, **25**, 4420 (1965).

1856. R. A. Glenn and J. R. Bailey, *J. Amer. Chem. Soc.*, **61**, 2612 (1939).
1857. N. P. Buu-Hoi, B. Eckert and R. Royer, *C. R. Acad. Sci.*, **232**, 1356 (1951).
1858. L. M. Schenck and J. R. Bailey, *J. Amer. Chem. Soc.*, **61**, 2613 (1939).
1859. M. Marty, N. P. Buu-Hoi and P. Jacquignon, *J. Chem. Soc.*, **1961**, 384.
1860. K. Berg-Nielsen, *Acta Chem. Scand.*, **31B**, 224 (1977).
1861. W. Kurtz, *Chem. Ber.*, **108**, 3415 (1975).
1862. A. Castellano and A. Lablache-Combier, *Tetrahedron*, **27**, 2305 (1971).
1863. H. John and E. Pietsch, *J. Prakt. Chem.*, **143**, 236 (1935).
1864. R. Galli, M. Pershinunno and R. Bernardi, *Chim. Ind. (Milan)*, **54**, 1067 (1972).
1865. C. G. Skinner and H. R. Henze, *J. Amer. Chem. Soc.*, **77**, 3810 (1955).
1866. B. A. Lugovik, P. V. Borodin, L. G. Yudin, V. A. Budylin and A. N. Kost, *Khim. Geterotsikl. Soedin.*, **1971**, 977.
1867. K. Mukherjee, G. B. Behera and M. K. Rout, *J. Inst. Chem., Calcutta*, **41**, 138 (1969).
1868. J. H. Markgraf and W. L. Scott, *J. Chem. Soc. Chem. Commun.*, **1967**, 296.
1869. W. Borsche, *Ann.*, **377**, 70 (1910).
1870. R. J. S. Beer, T. Broadhurst and A. Robertson, *J. Chem. Soc.*, **1953**, 2440.
1871. A. Hassner and M. J. Haddadin, *J. Org. Chem.*, **27**, 1911 (1962).
1872. W. E. Hahn and D. Tomczyk, *Roczn. Chem.*, **46**, 837 (1972).
1873. C. F. Koelsch, *J. Org. Chem.*, **16**, 1362 (1951).
1874. J. J. Eisch and F. J. Gadek, *J. Org. Chem.*, **36**, 3376 (1971).
1875. L. E. Kholodov and V. G. Yashunskii, *Khim. Geterotsikl. Soedin.*, **1970**, 1530.
1876. G. Kempter, P. Andratschke, D. Heilmann, H. Krausmann and M. Mietasch, *Z. Chem.*, **3**, 305 (1963).
1877. G. Kempter, P. Andratschke, D. Heilmann, H. Krausmann and M. Mietasch, *Chem. Ber.*, **97**, 16 (1964).
1878. W. Treibs and G. Kempter, *Chem. Ber.*, **92**, 601 (1959).
1879. E. A. Fehnel, *J. Org. Chem.*, **31**, 2899 (1966).
1880. J. J. Eisch, F. J. Gadek and G. Gupta, *J. Org. Chem.*, **38**, 431 (1973).
1881. I. F. Tischenkova, L. E. Kholodov and V. G. Yashunskii, *Khim. Geterotsikl. Soedin.*, **1971**, 102.
1882. M. Los and W. H. Stafford, *J. Chem. Soc.*, **1959**, 1680.
1883. F. H. Case, *J. Org. Chem.*, **21**, 1069 (1956).
1884. D. A. Denton, R. K. Smalley and H. Suschitzky, *J. Chem. Soc.*, **1964**, 2421.
1885. H. J. Roth and E. Schumann, *Arch. Pharm.*, **303**, 268 (1970).
1886. R. Fusco and F. Sannicolo, *Gazz. Chim. Ital.*, **105**, 1105 (1975).
1887. J. Lindner, J. Sellner, E. Hofmann and J. Hager, *Monatsh.*, **72**, 335 (1939).
1888. J. Lindner, A. Berger and W. Mignon, *Monatsh.*, **72**, 354 (1939).
1889. J. Lindner, J. Sellner and A. Berger, *Monatsh.*, **72**, 330 (1939).
1890. J. J. Eisch and G. Gupta, *Tetrahedron Lett.*, **1972**, 3273.
1891. B. D. Tilak, H. Berde, V. N. Gogte and T. Ravindranathan, *Indian J. Chem.*, **8**, 1 (1970).
1892. W. H. Perkin, Jr., and W. G. Sedgwick, *J. Chem. Soc.*, **125**, 2437 (1924).
1893. V. A. Petrow, *J. Chem. Soc.*, **1942**, 693.
1894. G. E. Calf and E. Ritchie, *J. Proc. Roy. Soc. N.S.W.* **83**, 117 (1949).
1895. W. H. Perkin, Jr., and W. G. Sedgwick, *J. Chem. Soc.*, **1926**, 438.
1896. N. P. Buu-Hoi, T. B. Loc and N. D. Xuong, *Bull. Soc. Chim. Fr.*, **1958**, 174.
1897. Y. D. Vankar, V. N. Gogte and B. D. Tilak, *Indian J. Chem.*, **15B**, 411 (1977).
1898. H. V. Berde, V. N. Gogte, A. G. Namjoshi and B. D. Tilak, *Indian J. Chem.*, **10**, 9 (1972).
1899. B. M. Mikhailov, V. A. Dorokov and O. G. Boldyreva, *Izv. Akad. Nauk SSR Ser. Khim.*, **1973**, 2643.
1900. L. J. Sargent and L. F. Small, *J. Org. Chem.*, **19**, 1400 (1954).
1901. R. M. Acheson and R. G. Bolton, *J. Chem. Soc. Perkin Trans. 1*, **1975**, 650.
1902. N. P. Buu-Hoi, T. B. Loc and N. D. Xuong, *C. R. Acad. Sci.*, **244**, 477 (1957).
1903. R. M. Acheson and R. G. Bolton, *Tetrahedron Lett.*, **1973**, 2821.
1904. V. A. Stonik, V. I. Vysotskii and M. N. Tilichenko, *Khim. Geterotsikl. Soedin.*, **1972**, 673.
1905. B. L. Hollingsworth and V. Petrow, *J. Chem. Soc.*, **1948**, 1537.
1906. J. Kenner, W. H. Ritchie and F. S. Statham, *J. Chem. Soc.*, **1937**, 1169.
1907. M. Sekiya and T. Morimoto, *Chem. Pharm. Bull. (Tokyo)*, **23**, 1241 (1975).
1908. B. L. Hollingsworth and V. Petrow, *J. Chem. Soc.*, **1960**, 263.

1909. J. von Braun and H. Grube, *Ber.*, **55B**, 1710 (1922).
1910. J. Lindner, M. Djulerowa and A. Mayr, *Monatsh.*, **44**, 337 (1923).
1911. J. Lindner and M. Staufer, *Monatsh.*, **46**, 231 (1925).
1912. N. P. Buu-Hoi and P. Jacquignon, *J. Chem. Soc.*, **1951**, 2964.
1913. J. Lindner and B. Zaunbauer, *Monatsh.*, **72**, 213 (1939).
1914. J. Lindner and A. Siegel, *Monatsh.*, **46**, 225 (1925).
1915. R. Fielden, O. Meth-Cohn and H. Suschitzky, *J. Chem. Soc. Perkin Trans. 1*, **1973**, 702.
1916. P. Jacquignon and N. P. Buu-Hoi, *J. Org. Chem.*, **22**, 72 (1957).
1917. N. P. Buu-Hoi, P. Jacquignon and T. B. Loc, *J. Chem. Soc.*, **1958**, 738.
1918. N. P. Buu-Hoi, *J. Chem. Soc.*, **1949**, 2882.
1919. J. von Braun, *Ann.*, **451**, 1 (1927).
1920. K. R. Reddy, *Ph.D. Thesis*, University of Minnesota, 1972; *Diss. Abstr.*, **33**, 5215 (1973).
1921. W. E. Parham and K. B. Sloan, *Tetrahedron Lett.*, **1971**, 1947.
1922. W. E. Parham, K. B. Sloan and J. B. Biasotti, *Tetrahedron*, **27**, 5767 (1971).
1923. W. E. Parham, K. B. Sloan, K. R. Reddy and P. E. Olsen, *J. Org. Chem.*, **38**, 927 (1973).
1924. W. E. Parham, P. E. Olsen, K. R. Reddy and K. B. Sloan, *J. Org. Chem.*, **39**, 172 (1974).
1925. K. Funakoshi, Y. Kuchino, H. Shigyo, M. Sonoda and M. Hamana, *Chem. Pharm. Bull. (Toyko)*, **24**, 2356 (1976).
1926. W. Dymek, J. Moszew and M. Wojtas, *Ann. Univ. Mariae Curie-Skłodowska, Sect AA*, **8**, 57 (1953).
1927. H. Gilman and J. A. Beel, *J. Amer. Chem. Soc.*, **73**, 774 (1951).
1928. W. Borsche and O. Vorbach, *Ann.*, **537**, 22 (1938).
1929. M. Avramoff and Y. Springzak, *J. Org. Chem.*, **22**, 571 (1957).
1930. W. Borsche and W. Noll, *Ann.*, **522**, 127 (1937).
1931. A. R. Surrey and R. A. Cutler, *U.S. Pat.* 2,568,778 (1951).
1932. F. Zymalkowski and M. Kothari, *Arch. Pharm.*, **303**, 667 (1970).
1933. E. J. Aronoff, *Ph.D. Thesis*, Indiana University, 1954; *Diss. Abstr.*, **14**, 600 (1954).
1934. H. De Diesbach, A. Pugin, F. Morard, W. Nowaczinski and J. Dessibourg, *Helv. Chim. Acta*, **35**, 2322 (1952).
1935. C. E. Kaslow and E. Aronoff, *J. Org. Chem.*, **19**, 857 (1954).
1936. R. Fusco and F. Sannicolo, *Tetrahedron Lett.*, **1976**, 3991.
1937. E. G. Podrebarac and W. E. McEwen, *J. Org. Chem.*, **26**, 1165 (1961).
1938. K. Takagi, M. Hubert-Habart, A. Cheutin and R. Royer, *Bull. Soc. Chim. Fr.*, **1966**, 3136.
1939. S. Gabriel and R. Wolter, *Ber.*, **56B**, 2445 (1923).
1940. H. Yamanaka, H. Abe and T. Sakamato, *Chem. Pharm. Bull. (Tokyo)*, **25**, 3334 (1977).
1941. B. Heymann and W. Koenigs, *Ber.*, **21**, 2167 (1888).
1942. J. Moszew and H. Kossowska, *Zesz. Nauk. Uniw. Jagiellon. Pr. Chem.*, **7**, 91 (1962).
1943. K. Thomae GmbH, *Brit. Pat.* 735,683 (1945).
1944. J. Moszew and W. Zankowska-Jasińska, *Roczn. Chem.*, **29**, 541 (1955).
1945. J. Moszew and H. Kossowska, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.*, **8**, 419 (1960).
1946. W. H. Mills and A. T. Akers, *J. Chem. Soc.*, **127**, 2475 (1925).
1947. O. Fischer and A. Frankel, *Ber.*, **19**, 749 (1886).
1948. E. Noelting, *Ber.*, **24**, 3139 (1891).
1949. J. Howitz and W. Schwenk, *Ber.*, **38**, 1280 (1905).
1950. J. D. Baty, G. Jones and C. Moore, *J. Org. Chem.*, **34**, 3295 (1969).
1951. G. H. Keyes and L. G. S. Brooker, *U.S. Pat.* 2,652,396 (1953).
1952. A. M. Comey, *Ber.*, **23**, 1115 (1890).
1953. W. von Miller, *Ber.*, **21**, 1827 (1888).
1954. P. Cagniant and D. Cagniant, *Bull. Soc. Chim. Fr.*, **1954**, 1349.
1955. A. Meisters and T. Mole, *Aust. J. Chem.*, **26**, 1239 (1973).
1956. T. Kato and H. Yamanaka, *Chem. Pharm. Bull. (Tokyo)*, **12**, 18 (1964).
1957. V. E. Posazhennikova, O. N Chupakhin and I. Ya. Postovskii, *Khim. Geterotsikl. Soedin.*, **1970**, 1384.
1958. D. Kreysig, H. H. Stroh and G. Kempter, *Z. Chem.*, **9**, 187 (1969).
1959. R. Ida, K. Teramura, S. Tanimoto, M. Nomura, H. Suda and K. Matsuda, *Bull. Inst. Chem. Res. Kyoto Univ.*, **33**, 117 (1955).
1960. N. F. Ovchinnikov, *Tr. Novocherkassk. Politekh. Inst.*, No. 266, 138 (1972).
1961. I. N. Chernyuk, V. V. Shelest, M. Yu. Kornilov and G. T. Pilyugin, *Zhur. Obshch. Khim.*, **45**, 1559 (1975).

1962. H. De Koning, G. N. Mallo, A. Springer-Fiddler, K. E. C. Subramanian-Erhart and H. O. Huisman, *Rec. Trav. Chim.*, **92**, 683 (1973).
1963. B. I. Ardashev, V. V. Mezheritskii and V. F. Mischenko, *Khim. Geterotsikl. Soedin.*, **1968**, 128.
1964. J. B. Wommack Jnr., and D. E. Pearson, *J. Med. Chem.*, **13**, 383 (1970).
1965. S. R. Lander, V. Rogers and H. R. Sood, *J. Chem. Soc. Perkin Trans. 1*, **1976**, 2103.
1966. L. H. Klemm, D. R. McCoy and C. E. Klopfenstien, *J. Heterocycl. Chem.*, **8**, 383 (1971).
1967. P. Pfeiffer, E. Prahl, W. Fitz and W. Stoll, *J. Prakt. Chem.*, **109**, 41 (1925).
1968. G. Gasda, *Ber.*, **38**, 3699 (1905).
1969. F. Bergmann, *J. Amer. Chem. Soc.*, **60**, 2811 (1938).
1970. O. Doebner and J. Peters, *Ber.*, **22**, 3006 (1889).
1971. J. C. E. Simpson, *J. Chem. Soc.*, **1946**, 673.
1972. I. N. Zhmurova, O. M. Voitsekhovskaya, R. I. Yurchenko and A. V. Kirsanov, *Zh. Obshch. Khim.*, **46**, 232 (1976).
1973. A. Fozard and C. K. Bradsher, *J. Org. Chem.*, **31**, 3683 (1966).
1974. C. T. Bahner, E. S. Pace and R. Prevost, *J. Amer. Chem. Soc.*, **73**, 3407 (1951).
1975. R. F. Schuman and E. D. Amstutz, *Rec. Trav. Chim.*, **84**, 441 (1965).
1976. P. Pfeiffer, H. Rheinbolt and J. Wolf, *Ann.*, **441**, 265 (1925).
1977. E. Mueller, R. Maier and W. Diederen, *Ger. Pat.* 1,939,809 (1971).
1978. C. Schiele, D. Staudacher, D. Hendriks and G. Arnold, *Tetrahedron*, **24**, 5017 (1968).
1979. C. Schiele and H. D. Kalinowski, *Ann.*, **696**, 81 (1966).
1980. J. T. Leach and J. P. Phillips, *J. Org. Chem.*, **27**, 3309 (1962).
1981. H. Hirata, K. Imaeda, H. Tanaka and K. Fukuzumi, *Yukagaku*, **24**, 246 (1975).
1982. H. Hirata and K. Fukuzumi, *Nippon Kagaku Kaishi*, **1974**, 1929.
1983. G. Drefahl, K. Ponsold and E. Gerlach, *Chem. Ber.*, **93**, 481 (1960).
1984. R. I. Yurchenko, O. M. Voitsekhovskaya and I. N. Zhmurova, *Zh. Obshch. Khim.*, **46**, 1274 (1976).
1985. J. Schläger and W. Leeb, *Monatsh.*, **81**, 714 (1950).
1986. N. Marékov, *C. R. Acad. Bulg. Sci.*, **6**, 35 (1956).
1987. C. T. Bahner, L. M. Rives, E. B. Senter, W. Longmire, H. Kinder, D. T. Bales, F. Hannan, B. Pettyjohn, W. K. Easley, L. Free and H. Free, *J. Org. Chem.*, **27**, 2233 (1962).
1988. C. T. Bahner, D. Brotherton and M. K. Brotherton, *J. Med. Chem.*, **11**, 401 (1968).
1989. C. T. Bahner, W. Chapman, C. Cook, O. Crawford, C. Hannan, N. Hunt, L. M. Rives, W. Yee and W. Easley, *J. Org. Chem.*, **25**, 2053 (1960).
1990. A. N. Kost and A. K. Sheinkman, *Zh. Obshch. Khim.*, **33**, 2077 (1963).
1991. A. I. Kiprianov and T. K. Nikolaenko, *Ukr. Khim. Zh.*, **36**, 819 (1970).
1992. P. Cagniant and A. Deluzarche, *C. R. Acad. Sci.*, **227**, 1148 (1946).
1993. B. M. Michailov and G. S. Ter-Sarkisyan, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, **1960**, 1267.
1994. A. N. Nikitina, N. A. Ponomareva, G. S. Ter-Sarkisyan and L. A. Yanovskaya, *Opt. Spectrosk.*, **42**, 889 (1977).
1995. N. P. Buu-Hoi and G. Saint-Ruf, *Bull. Soc. Chim. Fr.*, **1967**, 955.
1996. W. von Miller and F. Kinkelin, *Ber.*, **18**, 3234 (1885).
1997. H. J. Friedrich, *Z. Naturforsch.*, **18B**, 635 (1963).
1998. M. Guia and R. Carpignano, *Gazz. Chim. Ital.*, **83**, 840 (1953).
1999. R. H. Poirer, R. D. Morin, A. M. McKim and A. E. Bearse, *J. Org. Chem.*, **26**, 4275 (1961).
2000. M. Yu. Kornilov, E. M. Ruban, E. V. Starinskaya and V. N. Fedchuk, *Ukr. Khim. Zhur.*, **40**, 503 (1974).
2001. P. Schmidt, M. Wilhelm, E. Eichenberger and E. Schmacher, *Swiss. Pat.* 396,909 (1966).
2002. N. Nakamura, Y. Utsui and Y. Ninomiya, *Yakugaku Zasshi*, **86**, 404 (1966).
2003. G. Asato, G. Berkelhammer and E. L. Moon, *J. Med. Chem.*, **12**, 374 (1969).
2004. G. Berkelhammer and G. Asato, *U.S. Pat.* 3,725,396 (1973).
2005. H. Häussermann, *Swiss. Pat.* 348,967 (1960).
2006. N. S. Kozlov, L. K. Slobodchikova and G. S. Shmanai, *Dokl. Akad. Nauk Beloruss. SSR*, **15**, 328 (1971).
2007. W. Kashiwara and I. Maenami, *Jap. Pat.* 68 00,516 (1968).
2008. C. H. Boehringer Sohn A.-G., *Ger. Pat.* 594,849 (1934).
2009. T. Joh and N. Hagihara, *Tetrahedron Lett.*, **1967**, 4199.

2010. O. Iwamoto, K. Suzuki, Y. Teras and M. Sokiya, *Chem. Pharm. Bull. (Tokyo)*, **24**, 2409 (1976).
2011. L. S. Povarov and B. M. Mikhailov, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, **1963**, 955.
2012. E. Murmann, *Monatsh.*, **25**, 621 (1904).
2013. O. Doebner and W. von Miller, *Ber.*, **16**, 1664 (1883).
2014. C. Goldschmidt, *Ber.*, **28**, 986 (1895).
2015. N. S. Kozlov, *Zh. Obshch. Khim.*, **8**, 413 (1938).
2016. R. J. W. Le Fèvre and J. Pearson, *J. Chem. Soc.*, **1932**, 2807.
2017. E. Grimaux, *C. R. Acad. Sci.*, **96**, 584 (1883).
2018. E. Bamberger and H. Weitnauer, *Ber.*, **55**, 3376 (1922).
2019. C. R. Hauser and M. J. Weiss, *J. Org. Chem.*, **14**, 310 (1949).
2020. E. E. Mikhlina, K. F. Turchin, A. D. Yanina, Yu. N. Sheinker and L. N. Yakhontov, *Khim. Geterotsikl. Soedin.*, **1973**, 839.
2021. G. Dienys, L. Cekuliene, S. Jokubaityte and P. Backus, *Khim. Geterotsikl. Soedin., Sb. Azotsoderzhashchie Geterotsikly*, **1967**, 260.
2022. J. Glinka, *Roczn. Chem.*, **39**, 885 (1965).
2023. G. I. Denis and P. Butskus, *Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhnol.*, **4**, 426 (1961).
2024. C. F. Koelsch and A. F. Steinhauer, *J. Org. Chem.*, **18**, 1516 (1953).
2025. K. Schofield and R. S. Theobald, *J. Chem. Soc.*, **1951**, 2992.
2026. J. Kenner and F. S. Statham, *J. Chem. Soc.*, **1935**, 299.
2027. P. Cagniant and P. Cagniant, *Bull. Soc. Chim. Fr.*, **1952**, 336.
2028. R. M. Summers, *Ph.D. Thesis*, Indiana University, 1955; *Diss. Abstr.*, **15**, 1499 (1955).
2029. W. La Coste, *Ber.*, **15**, 557 (1882).
2030. R. H. F. Manske, F. Leger and G. Gallagher, *Can. J. Res.*, **19B**, 318 (1941).
2031. C. E. Kaslow and R. M. Summers, *J. Org. Chem.*, **20**, 1738 (1955).
2032. F. H. Case and C. J. Buck, *J. Org. Chem.*, **21**, 697 (1956).
2033. D. H. Hey and C. W. Rees, *J. Chem. Soc.*, **1960**, 905.
2034. R. Möhlau and R. Berger, *Ber.*, **26**, 1994 (1893).
2035. N. P. Buu-Hoi and N. D. Xuong, *C. R. Acad. Sci.*, **247**, 654 (1958).
2036. E. Murmann, *Monatsh.*, **13**, 58 (1892).
2037. O. Neunhoeffer and H. Ulrich, *Chem. Ber.*, **88**, 1123 (1955).
2038. T. Miyadera and R. Tachikawa, *Tetrahedron*, **25**, 837 (1969).
2039. T. Miyadera and R. Tachikawa, *Tetrahedron*, **25**, 847 (1969).
2040. H. John, *J. Prakt. Chem.*, **139**, 97 (1934).
2041. H. John and E. Pietsch, *J. Prakt. Chem.*, **139**, 183 (1934).
2042. H. John and H. Ottawa, *J. Prakt. Chem.*, **133**, 13 (1932).
2043. J. Moir, *Trans. Roy. Soc. S. Africa*, **16**, 121 (1928).
2044. G. Jellinek, *Monatsh.*, **7**, 351 (1886).
2045. V. A. Petrow, M. W. Stack and W. R. Wragg, *J. Chem. Soc.*, **1948**, 316.
2046. W. Borsche and F. Sinn, *Ann.*, **532**, 146 (1937).
2047. C. E. Kaslow and H. Moe, *J. Org. Chem.*, **25**, 1512 (1960).
2048. H. Moe, *Ph.D. Thesis*, Indiana University, 1957; *Diss. Abstr.*, **17**, 2160 (1957).
2049. B. R. Brown and D. Ll. Hammick, *J. Chem. Soc.*, **1949**, 173.
2050. N. P. Buu-Hoi and P. Cagniant, *Rec. Trav. Chim.*, **62**, 713 (1943).
2051. P. V. Hai, N. P. Buu-Hoi and N. D. Xuong, *J. Org. Chem.*, **23**, 39 (1958).
2052. A. K. Sheinkman, A. N. Kost, A. N. Prilepskaya and Zh. V. Shiyan, *Zh. Org. Khim.*, **4**, 1286 (1968).
2053. M. Hartmann and H. Isler, *U.S. Pat.* 1,860,286 (1932).
2054. N. S. Kozlov and L. Y. Pinegina, *Zh. Obshch. Khim.*, **27**, 1965 (1957).
2055. A. K. Sheinkman, A. K. Tokarev and A. N. Prilepskaya, *Khim. Geterotsikl. Soedin.*, **1972**, 529.
2056. S. Kitaura, *Bull. Inst. Phys. Chem. Res. (Tokyo)*, **20**, 848 (1941).
2057. M. Jancevska and V. Prisaganec, *Croat. Chem. Acta*, **46**, 65 (1974).
2058. N. S. Kozlov and G. P. Korotyshova, *Vestsi Akad. Navuk B. SSR, Ser. Khim. Navuk*, **1974**, 65.
2059. G. I. Matyushecheva, A. I. Tolmachev, A. A. Shulezhko, L. M. Shulezhko and L. M. Yagupol'skii, *Zh. Obshch. Khim.*, **46**, 162 (1976).
2060. N. P. Buu-Hoi and P. Jacquignon, *Rec. Trav. Chim.*, **68**, 781 (1949).

2061. L. Avar, K. Hofer and M. Preiswerk, *Ger. Pat.* 2,304,270 (1973).
2062. N. S. Kozlov and L. Y. Pinegina, *Zh. Obshch. Khim.*, **26**, 247 (1956).
2063. S. Kitaura, *Bull. Inst. Phys. Chem. Res. (Tokyo)*, **20**, 967 (1941).
2064. J. P. Saxena, W. H. Stafford and W. L. Stafford, *J. Chem. Soc.*, **1959**, 1579.
2065. N. P. Buu-Hoi, M. Sy and N. D. Xuong, *Bull. Soc. Chim. Fr.*, **1956**, 629.
2066. M. Hamana, S. Takeo and H. Neda, *Chem. Pharm. Bull. (Tokyo)*, **25**, 1256 (1977).
2067. N. S. Kozlov and O. E. Kostromina, *Sb. Stat. Obshch. Khim.*, **2**, 934 (1953).
2068. L. Petit and N. P. Buu-Hoi, *J. Org. Chem.*, **26**, 3832 (1961).
2069. N. S. Kozlov and N. I. Panova, *Zh. Obshch. Khim.*, **24**, 317 (1954).
2070. C. G. Le Fèvre, R. J. W. Le Fèvre and J. Pearson, *J. Chem. Soc.*, **1934**, 137.
2071. V. I. Grigos, L. S. Povarov and B. M. Mikhailov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1965**, 2163.
2072. S. Yamada and I. Chibata, *Pharm. Bull. (Tokyo)*, **3**, 21 (1955).
2073. N. S. Kozlov and O. K. Koz'minykh, *Zh. Obshch. Khim.*, **27**, 3122 (1957).
2074. O. K. Koz'minykh, *Uch. Zap. Perm. Gos. Univ. im. A. M. Gor'kogo*, **15**, 111. (1958).
2075. N. P. Buu-Hoi and R. Royer, *Bull. Soc. Chim. Fr.*, **1947**, 820.
2076. N. Sharghi and I. Lalezari, *J. Chem. Eng. Data*, **10**, 196 (1965).
2077. H. John and E. Pietsch, *J. Prakt. Chem.*, **139**, 237 (1934).
2078. A. P. A. Rossi, *Belg. Pat.* 641,254 (1964).
2079. A. P. A. Rossi, L. H. Werner, W. L. Bencze and G. de Stevens, *U.S. Pat.* 3,332,951 (1967).
2080. B. Reichert and D. Iwanoff, *Arch. Pharm.*, **276**, 515 (1938).
2081. E. Besthorn and G. Jaeglé, *Ber.*, **27**, 907 (1894).
2082. W. Koenigs, *J. Prakt. Chem.*, **61**, 1 (1900).
2083. W. Koenigs, *Ber.*, **26**, 713 (1893).
2084. A. M. El-Abbady, M. A. Omara and N. G. Kandil, *Rev. Roum. Chim.*, **18**, 899 (1973).
2085. W. von Miller and F. Kinkelin, *Ber.*, **19**, 525 (1886)
2086. L. M. Roch, *Ann. Chim. (Paris)*, **6**, 105 (1961).
2087. H. John and F. Noziczka, *J. Prakt. Chem.*, **111**, 65 (1925).
2088. H. John, *Ber.*, **59B**, 387 (1926).
2089. R. D. Goeschke, *Ger. Pat.* 2,310,773 (1973).
2090. J. Haginiwa, Y. Higuchi and H. Ohtsuka, *Yakugaku Zasshi*, **96**, 209 (1976).
2091. N. S. Kozlov and O. E. Kostromina, *Sb. Stat. Obshch. Khim.*, **2**, 931 (1953).
2092. M. Montagne and M. Roch, *C. R. Acad. Sci.*, **213**, 620 (1941).
2093. H. John and M. E. Schmid, *J. Prakt. Chem.*, **121**, 177 (1929).
2094. G. P. Mueller and R. E. Stobaugh, *J. Amer. Chem. Soc.*, **72**, 1598 (1950).
2095. N. P. Buu-Hoi, N. Hoăn and N. D. Xuong, *J. Chem. Soc.*, **1951**, 3499.
2096. C. R. Hauser and J. G. Murray, *J. Amer. Chem. Soc.*, **77**, 3858 (1955).
2097. A. Makriyannis, J. S. Frazee and J. W. Wilson, *J. Med. Chem.*, **16**, 118 (1973).
2098. J. W. Wilson, J. S. Frazee and A. Makriyannis, *U.S. Clearinghouse Fed. Sci. Tech. Inf.*, AD 714,372 (1970).
2099. E. H. Sund, *Ph.D. Thesis*, University of Texas, 1960; *Diss. Abstr.*, **21**, 3638 (1961).
2100. E. H. Sund and H. R. Henze, *J. Chem. Eng. Data*, **15**, 578 (1970).
2101. N. S. Kozlov and B. I. Kiselev, *Uch. Zap. Perm. Gos. Pedagog. Inst.*, No. 2, 44 (1967).
2102. J. Moszew and Z. Urbanek, *Zesz. Nauk. Uniw. Jagiellon., Pr. Chem.*, **11**, 55 (1966).
2103. S. Goszczynski and A. I. Kucherenko, *Zhur. Org. Khim.*, **8**, 2586 (1972).
2104. E. E. Schweizer, C. S. Kim, C. S. Labaw and W. P. Murray, *J. Chem. Soc. Chem. Commun.*, **1973**, 7.
2105. E. E. Schweizer, S. D. Goff and W. P. Murray, *J. Org. Chem.*, **42**, 200 (1977).
2106. S. Goszczynski, *Roczn. Chem.*, **38**, 515 (1964).
2107. M. Hamana and H. Noda, *Chem. Pharm. Bull. (Tokyo)*, **14**, 762 (1966).
2108. C. Beyer, *Ber.*, **20**, 1767 (1887).
2109. B. I. Ardashev, *Dokl. Akad. Nauk SSSR*, **92**, 1175 (1952).
2110. E. A. Fehnel, *J. Heterocycl. Chem.*, **4**, 565 (1967).
2111. N. T. Cam-Van, B. K. Diep and N. P. Buu-Hoi, *Tetrahedron*, **20**, 2195 (1964).
2112. N. N. Quang, B. K. Diep and N. P. Buu-Hoi, *Rec. Trav. Chim.*, **83**, 1142 (1964).
2113. N. Hoăn and N. P. Buu-Hoi, *C. R. Acad. Sci.*, **224**, 1363 (1947).
2114. M. De Clerq and N. P. Buu-Hoi, *C. R. Acad. Sci.*, **227**, 1251 (1948).

2115. N. P. Buu-Hoi and P. Cagniant, *Rec. Trav. Chim.*, **64**, 214 (1945).
2116. W. J. Comstock and W. Koenigs, *Ber.*, **20**, 2674 (1887).
2117. B. K. Diep, N. P. Buu-Hoi and N. D. Xuong, *J. Chem. Soc.*, **1963**, 2784.
2118. T.-T. Vo-Thi and N. Hoãn, *C. R. Acad. Sci.*, **237**, 1016 (1953).
2119. N. P. Buu-Hoi and P. Cagniant, *Bull. Soc. Chim. Fr.*, **1946**, 123.
2120. N. P. Buu-Hoi, N. D. Xuong and D. Lavit, *J. Org. Chem.*, **18**, 910 (1953).
2121. N. P. Buu-Hoi and N. D. Xuong, *J. Chem. Soc.*, **1953**, 386.
2122. J. F. Miguel, P. Müller and N. P. Buu-Hoi, *Bull. Soc. Chim. Fr.*, **1956**, 633.
2123. S. A. Sultanov and S. Yu. Yunosov, *Khim. Prir. Soedin.*, **1969**, 131.
2124. S. A. Sultanov and S. Yu. Yunosov, *Khim. Prir. Soedin.*, **1969**, 195.
2125. G. P. Sidyakin, V. I. Pastukhova and S. Yu. Yunosov, *Uzbek. Khim. Zhur.*, **1962**, 56.
2126. G. P. Sidyakin, I. A. Bessonova, V. I. Pastukhova and S. Yu. Yunosov, *Zh. Obshch. Khim.*, **32**, 4091 (1962).
2127. N. S. Kozlov and O. E. Kostromina, *Sb. Stat. Obshch. Khim.*, **2**, 937 (1953).
2128. W. J. Comstock and W. Koenigs, *Ber.*, **18**, 2379 (1885).
2129. H. John and G. Weber, *J. Prakt. Chem.*, **111**, 85 (1925).
2130. P. Cagniant, *Bull. Soc. Chim. Fr.*, **1949**, 847.
2131. G. Dienys, J. Gureviciene, L. Cekvoliene and J. Steponavicius, *Liet. TSR Mokslu. Akad. Darb., Ser. B*, No. 1, 33 (1977).
2132. N. S. Kozlov, B. I. Kiselev and T. A. Skorokhodova, *Vest. Akad. Navuk B. SSR, Ser. Khim. Navuk*, No. 3, 57 (1970).
2133. C. T. Do, E. H. Kossoff, P. Jacquignon and M. Dufour, *Collect. Czech. Chem. Commun.*, **41**, 1212 (1976).
2134. N. P. Buu-Hoi, *Rec. Trav. Chim.*, **68**, 759 (1949).
2135. N. P. Buu-Hoi and J. F. Miquel, *J. Chem. Soc.*, **1953**, 3768.
2136. N. P. Buu-Hoi, *Fr. Pat.* 1,084,737 (1955).
2137. P. Cagniant, *C. R. Acad. Sci.*, **226**, 1133 (1948).
2138. R. Camps, *Ber.*, **32**, 3228 (1899).
2139. G. Kempter, D. Rehbaum and J. Schirmer, *J. Prakt. Chem.*, **319**, 573 (1977).
2140. O. Fischer, *Sitzungsber. Math.-Phys. Cl. Akad. Wiss. München*, **15**, 327 (1885).
2141. B. I. Ardashev and V. I. Minkin, *Zh. Obshch. Khim.*, **27**, 1261 (1957).
2142. R. B. Mitra and P. N. Khanna, *Indian J. Chem.*, **10**, 1195 (1972).
2143. T. van Schelvin, *Brit. Pat.* 388,078 (1933).
2144. Meister Lucius und Brüning Farbwerke, *Ger. Pat.* 19,766 (1882).
2145. C. Goldschmidt, *Chem.-Ztg.*, **27**, 279 (1903).
2146. W. Majert, *Ger. Pat.* 28,323 (1884).
2147. H. Baum, *Ger. Pat.* 27,948 (1884).
2148. T. Pavolini, F. Gambarin and E. Moretti, *Boll. Chim. Farm.*, **90**, 343 (1951).
2149. R. Camps, *Arch. Pharm.*, **239**, 591 (1901).
2150. G. Kempter, M. Mühlstädt and D. Heilmann, *Angew. Chem. Int. Ed. Engl.*, **5**, 248 (1966).
2151. G. Y. Paris, D. L. Garmaise, J. Komlossy and R. C. McCrae, *J. Med. Chem.*, **13**, 122 (1970).
2152. A. K. Sheinkman, A. N. Prilepskaya and A. N. Kost, *Khim. Geterotsikl. Soedin.*, **1970**, 1515.
2153. T. Kobayashi and R. Kikumoto, *Tetrahedron*, **18**, 813 (1962).
2154. Meister Lucius und Brüning Farbwerke, *Ger. Pat.* 80,501 (1895).
2155. H. John and E. Andraschko, *J. Prakt. Chem.*, **131**, 90 (1931).
2156. H. John and E. Andraschko, *J. Prakt. Chem.*, **133**, 114 (1932).
2157. M. De Clerq and N. P. Buu-Hoi, *C. R. Acad. Sci.*, **227**, 1377 (1948).
2158. D. Price and M. T. Bogert, *J. Amer. Chem. Soc.*, **56**, 2442 (1934).
2159. W. Koenigs, *Ber.*, **14**, 1852 (1881).
2160. N. P. Buu-Hoi, D. Lavit and N. D. Xuong, *J. Org. Chem.*, **19**, 1617 (1954).
2161. N. P. Buu-Hoi, M. Sy and J. Riche, *Bull. Soc. Chim. Fr.*, **1960**, 1493.
2162. A. Giacalone, *Gazz. Chim. Ital.*, **65**, 124 (1935).
2163. R. M. Acheson and D. F. Wisbet, *J. Chem. Soc. Perkin Trans. I*, **1973**, 1338.
2164. R. E. Pratt, W. J. Welstead, Jr., and R. E. Lutz, *J. Heterocycl. Chem.*, **7**, 1051 (1970).
2165. Y. Imai, E. F. Johnson, T. Katto, M. Kurihara and J. K. Stille, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 2233 (1975).
2166. M. Buddeberg, *Ber.*, **23**, 2066 (1890).
2167. W. Reid and E. Koenig, *Justus Liebigs Ann. Chem.*, **755**, 24 (1972).

2168. R. R. Schmidt, *Angew. Chem.*, **76**, 991 (1964).
2169. W. Borsche and F. Sinn, *Ann.*, **538**, 283 (1939).
2170. N. P. Buu-Hoi and R. Royer, *Bull. Soc. Chim. Fr.*, **1946**, 374.
2171. N. Hoān and N. P. Buu-Hoi, *C. R. Acad. Sci.*, **224**, 1228 (1947).
2172. J. Szmuszkovicz, E. M. Glenn, R. V. Heinzelman, J. B. Hester, Jr., and G. A. Youngdale, *J. Med. Chem.*, **9**, 527 (1966).
2173. N. P. Buu-Hoi, N. Hoān and R. Royer, *Bull. Soc. Chim. Fr.*, **1947**, 84.
2174. A. R. Forrester, M. Gill and R. H. Thomson, *J. Chem. Soc., Chem. Commun.*, **1976**, 677.
2175. G. W. J. Fleet and I. Fleming, *J. Chem. Soc. C*, **1969**, 1758.
2176. W. Steinkopf and H.-J. von Petersdorff, *Ann.*, **543**, 119 (1940).
2177. M. Wilk and J. Rochlitz, *Justus Liebigs Ann. Chem.*, **699**, 107 (1966).
2178. N. P. Buu-Hoi, N. Hoān and R. Royer, *Bull. Soc. Chim. Fr.*, **1950**, 489.
2179. N. P. Buu-Hoi, N. D. Xuong and K. van Thang, *Rec. Trav. Chim.*, **72**, 774 (1953).
2180. N. P. Buu-Hoi and M. Sy, *J. Org. Chem.*, **21**, 136 (1956).
2181. N. P. Buu-Hoi and R. Royer, *Rec. Trav. Chim.*, **70**, 825 (1951).
2182. N. P. Buu-Hoi, L. Petit and D. C. Thang, *Bull. Soc. Chim. Fr.*, **1960**, 335.
2183. N. P. Buu-Hoi and L. Petit, *J. Org. Chem.*, **24**, 39 (1959).
2184. N. P. Buu-Hoi, M. Sy and J. Riché, *J. Org. Chem.*, **22**, 668 (1957).
2185. N. P. Buu-Hoi, L. Petit and D. C. Thang, *J. Org. Chem.*, **29**, 762 (1964).
2186. R. D. Garrett and H. R. Henze, *J. Med. Chem.*, **9**, 976 (1966).
2187. E. K. Fields, *U.S. Pat.* 3,514,458 (1970).
2188. N. P. Buu-Hoi, N. D. Xuong and V. Q. Yen, *J. Org. Chem.*, **23**, 539 (1958).
2189. J. N. Rây, G. S. Ahluwalia and B. D. Kochmar, *J. Prakt. Chem.*, **136**, 117 (1933).
2190. W. Jenny, *Helv. Chim. Acta*, **34**, 539 (1951).
2191. N. P. Buu-Hoi, N. Hoān and D. Lavit, *J. Chem. Soc.*, **1953**, 485.
2192. R. D. Garrett, *Ph.D. Thesis*, University of Texas, 1960; *Diss. Abstr.*, **22**, 1826 (1961).
2193. N. P. Buu-Hoi and D. Lavit, *J. Org. Chem.*, **21**, 21 (1956).
2194. N. P. Buu-Hoi and D. Lavit, *J. Org. Chem.*, **21**, 1256 (1956).
2195. N. P. Buu-Hoi and D. Lavit, *J. Chem. Soc.*, **1956**, 1743.
2196. N. P. Buu-Hoi and J. Lecocq, *J. Chem. Soc.*, **1946**, 830.
2197. N. P. Buu-Hoi, D Lavit and J. Collard, *J. Org. Chem.*, **23**, 542 (1958).
2198. R. Royer, *Ann. Chim.*, Ser. 12, **1**, 395 (1946).
2199. N. P. Buu-Hoi, D. Lavit and J. Collard, *Croat. Chim. Acta*, **29**, 291 (1957).
2200. T. Kobayashi and R. Kikumoto, *Tetrahedron*, **21**, 1903 (1965).
2201. N. P. Buu-Hoi, N. Hoān and P. Jacquignon, *J. Chem. Soc.*, **1951**, 1381.
2202. P. Cagniant, *C. R. Acad. Sci.*, **226**, 1623 (1948).
2203. N. P. Buu-Hoi and R. Royer, *Bull. Soc. Chim. Fr.*, **1946**, 379.
2204. N. P. Buu-Hoi and P. Cagniant, *Rec. Trav. Chim.*, **62**, 519 (1943).
2205. N. P. Buu-Hoi and G. Saint-Ruf, *J. Org. Chem.*, **26**, 2996 (1961).
2206. N. P. Buu-Hoi, P. Mabille and D.-C. Thang, *Bull. Soc. Chim. Fr.*, **1968**, 981.
2207. N. P. Buu-Hoi and P. Cagniant, *Rec. Trav. Chim.*, **62**, 719 (1943).
2208. J. Garapon and J. K. Stille, *Macromolecules*, **10**, 627 (1977).
2209. J. Ropenga and S. Grudzinski, *Acta Pol. Pharm.*, **32**, 656 (1975).
2210. N. S. Kozlov, and G. S. Shmanai, *Vest. Akad. Navuk B. SSR, Ser. Khim. Navuk*, No. 4, 70 (1971).
2211. N. S. Kozlov, V. A. Serzhanina and G. S. Shmanai, *Vest. Akad. Navuk B. SSR, Ser. Khim. Navuk*, No. 1, 107 (1972).
2212. G. Kempter and G. Sarodnick, *Z. Chem.*, **8**, 179 (1968).
2213. N. P. Buu-Hoi and R. Royer, *Rec. Trav. Chim.*, **69**, 861 (1950).
2214. G. Kempter, H. Schaefer and G. Sarodnick, *Z. Chem.*, **9**, 186 (1969).
2215. H. Stetter and J. Krasselt, *J. Heterocycl. Chem.*, **14**, 573 (1977).
2216. T. Pozzo-Balbi, G. Romano and M. T. Bassi, *Ann. Chim. (Rome)*, **55**, 763 (1965).
2217. B. I. Ardashev and I. S. Malik, *Khim. Geterotsikl. Soedin.*, **1967**, 7.
2218. R. R. G. Haber and E. Schoenberger, *Brit. Pat.* 1,146,386 (1969).
2219. S. Yoshina, A. Tanaka, C.-H. Wu and H.-S. Kuo, *Yakugaku Zasshi*, **95**, 1418 (1975).
2220. W. Steinkopf, T. Barlag and H.-J. von Petersdorff, *Ann.*, **540**, 7 (1939).
2221. K. Tamao, S. Kodama, I. Nakajima, T. Nokatsuka, A. Minato and M. Kumada, *Hukusokan Kagaku Toronkai Koen Yoshishu, 8th*, **1975**, 174.

2222. I. Meshkauskaite and L. Urbonaite, *Tr. Nauchn.-Tekh. Konf. Stud. Vyssh. Uchebn. Zaved. Beloruss. SSR, Latv. SSR, Lit. SSR Est. SSR, 5th*, **1961**, 39.
2223. B. D. Tilak, T. Ravindranathan and K. N. Subbaswami, *Indian J. Chem.*, **6**, 422 (1968).
2224. M. Sy, N. P. Buu-Hoi and N. D. Xuong, *J. Chem. Soc.*, **1954**, 1975.
2225. N. P. Buu-Hoi and N. Hoăn, *Rec. Trav. Chim.*, **69**, 1455 (1950).
2226. P. Cagniant and P. Cagniant, *Bull. Soc. Chim. Fr.*, **1952**, 713.
2227. N. P. Buu-Hoi and N. Hoăn, *Rec. Trav. Chim.*, **68**, 5 (1949).
2228. J. Lamy, D. Lavit and N. P. Buu-Hoi, *J. Chem. Soc.*, **1958**, 4202.
2229. T. Kauffmann and A. Mitschker, *Tetrahedron Lett.*, **1973**, 4039.
2230. T. Kauffmann and A. Mitschker, *Tetrahedron Lett.*, **1977**, 393.
2231. N. P. Buu-Hoi and R. Royer, *C. R. Acad. Sci.*, **223**, 806 (1946).
2232. W. J. Gammans, *Ph.D. Thesis*, University of Texas, 1963; *Diss Abstr.*, **24**, 4994 (1964).
2233. P. Cagniant and P. Cagniant, *Bull. Soc. Chim. Fr.*, **1953**, 713.
2234. P. Cagniant and A. Deluzarche, *C. R. Acad. Sci.*, **225**, 455 (1947).
2235. N. P. Buu-Hoi and N. Hoăn, *Rec. Trav. Chim.*, **67**, 309 (1948).
2236. R. E. Atkinson and F. E. Hardy, *J. Chem. Soc. Perk. Trans. 2*, **1972**, 27.
2237. P. L. Trakhtenberg and A. E. Lipkin, *Khim. Geterotsikl. Soedin.*, **1974**, 61.
2238. M. Hamana and I. Kumadaki, *Chem. Pharm. Bull. (Tokyo)*, **19**, 1669 (1971).
2239. M. Colonna, P. Bruni and A. M. Guerra, *Gazz. Chim. Ital.*, **96**, 1410 (1966).
2240. M. Hamana and I. Kumadaki, *Chem. Pharm. Bull. (Tokyo)*, **18**, 1742 (1970).
2241. M. Hamana and I. Kumadaki, *Chem. Pharm. Bull. (Tokyo)*, **15**, 363 (1967).
2242. M. Hamana and I. Kumadaki, *Chem. Pharm. Bull. (Tokyo)*, **18**, 1822 (1970).
2243. CIBA Ltd., *Fr. Pat.* 1,489,340 (1967).
2244. H. J. Ziegler, H. Inion, G. Aussens, A. Christiaens, F. Chaillet and R. Charlier, *Chim. Ther.*, **6**, 159 (1971).
2245. M. Bisagni, N. P. Buu-Hoi and R. Royer, *J. Chem. Soc.*, **1955**, 3688.
2246. G. Chatelus and P. Cagniant, *C. R. Acad. Sci.*, **224**, 1777 (1947).
2247. G. Chatelus, *Ann Chim.*, Ser. 12, **4**, 505 (1949).
2248. N. P. Buu-Hoi, N. D. Xuong and N. V. Bac, *J. Chem. Soc.*, **1964**, 173.
2249. V. T. Suu, N. P. Buu-Hoi and N. D. Xuong, *Bull. Soc. Chim. Fr.*, **1962**, 1875.
2250. P. Cagniant, *C. R. Acad. Sci.*, **229**, 889 (1949).
2251. P. Cagniant and P. Cagniant, *Bull. Soc. Chim. Fr.*, **1953**, 62.
2252. P. Cagniant, P. Faller and D. Cagniant, *Bull. Soc. Chim. Fr.*, **1966**, 3055.
2253. P. Cagniant and D. Cagniant, *Bull. Soc. Chim. Fr.*, **1955**, 680.
2254. N. P. Buu-Hoi, *J. Org. Chem.*, **15**, 123 (1950).
2255. N. P. Buu-Hoi and R. Royer, *Rec. Trav. Chim.*, **66**, 533 (1947).
2256. N. P. Buu-Hoi and R. Royer, *Rec Trav. Chim.*, **67**, 175 (1948).
2257. C. Routier, N. P. Buu-Hoi and R. Royer, *J. Chem. Soc.*, **1956**, 4276.
2258. P. Cagniant and D. Cagniant, *Bull. Soc. Chim. Fr.*, **1955**, 931.
2259. W. Steinkopf and H. Engelman, *Ann.*, **564**, 205 (1941).
2260. N. P. Buu-Hoi and N. Hoăn, *J. Org. Chem.*, **17**, 643 (1952).
2261. E. G. Buryakovskaya, S. V. Tsukerman and V. F. Lavrushin, *Zh. Fiz. Khim.*, **43**, 863 (1969).
2262. CIBA Ltd., *Belg. Pat.* 612,971 (1962).
2263. L. H. Sarett, D. R. Hoff and D. W. Henry, *Brit. Pat.* 1,215,858 (1970).
2264. J. J. Baldwin and F. C. Novello, *Ger. Pat.* 2,061,489 (1971).
2265. J. J. Baldwin and F. C. Novello, *Fr. Pat.* 2,081,360 (1972).
2266. J. J. Baldwin, P. A. Kasinger, F. C. Novello, J. M. Sragué and D. E. Duggan, *J. Med. Chem.*, **18**, 895 (1975).
2267. J. J. Baldwin and F. C. Novello, *U.S. Pat.* 4,032,522 (1977).
2268. Yu. A. Rozin, V. E. Blokhin, Z. V. Pushkareva and M. E. Sukhova, *Khim. Geterotsikl. Soedin.*, **1972**, 681.
2269. Yu. A. Rozin, V. E. Blokhin, Z. V. Pushkareva, V. I. Elin and M. E. Sukhova, *Khim. Geterotsikl. Soedin.*, **1973**, 1105.
2270. P. P. E. Strzybny, T. van Es and O. G. Backeberg, *J. Org. Chem.*, **28**, 3381 (1963).
2271. K. Akagane, G. G. Allan, C. S. Chopra, T. Friberg, T. Mattila, S. Omuircheartaigh and J. B. Thomson, *Suom. Kemistil. B*, **45**, 223 (1972).
2272. T. Kauffmann, D. Tigler and A. Woltermann, *Tetrahedron Lett.*, **1977**, 741.
2273. M. Dadkhah and B. Prijs, *Helv. Chim. Acta*, **45**, 375 (1962).

2274. D. G. Ott, F. N. Hayes, E. Hansbury and V. N. Kerr, *J. Amer. Chem. Soc.*, **79**, 5448 (1957).
2275. H. Coates, A. H. Cook, I. M. Heilbron and F. B. Lewis, *J. Chem. Soc.*, **1943**, 419.
2276. A. Taurins and A. Blaga, *J. Heterocycl. Chem.*, **7**, 1137 (1970).
2277. V. I. Isagulyanto and N. M. Anufrieva, *Zh. Prikl. Khim.*, **46**, 1389 (1973).
2278. B. Miklaszewski and S. von Niementowski, *Ber.*, **34**, 2953 (1901).
2279. Merck & Co. Inc., *Neth. Pat.* 6,510,290 (1966).
2280. L. Hunter and J. A. Marriott, *J. Chem. Soc.*, **1941**, 777.
2281. S. von Niementowski, *Ber.*, **32**, 1465 (1899).
2282. T. N. Ghosh, *J. Indian Chem. Soc.*, **15**, 89 (1938).
2283. W. Borsche and W. Doeller, *Ann.*, **537**, 53 (1938).
2284. S. M. Jain and R. A. Pawar, *Indian J. Chem.*, **13**, 304 (1975).
2285. T. Hisano and M. Ichikawa, *Chem. Pharm. Bull. (Tokyo)*, **22**, 2051 (1974).
2286. T. Hisano, K. Muraoka and M. Ichikawa, *Yakugaku Zasshi*, **97**, 808 (1977).
2287. T. Hisano and M. Ichikawa, *Chem. Pharm. Bull. (Tokyo)*, **22**, 2051 (1974).
2288. M. T. Bogert and M. Meyer, *J. Amer. Chem. Soc.*, **44**, 1568 (1922).
2289. R. F. Hunter, *Chem. News*, **128**, 87 (1924).
2290. R. F. Hunter, *Chem. News*, **129**, 125 (1924).
2291. M. Meyer, *Chem. News*, **125**, 319 (1922).
2292. E. Barni and G. Di Modica, *Ann. Chim. (Rome)*, **63**, 373 (1973).
2293. R. A. Clarke, *U.S. Pat.* 3,152,132 (1964).
2294. I. I. Grandberg, *Zhur. Obshch. Khim.*, **31**, 2307 (1961).
2295. Yu. M. Yutilov and L. I. Kovaleva, *Russ. Pat.* 545,646 (1977).
2296. Yu. M. Yutilov and L. I. Kovaleva, *Khim. Geterotsikl. Soedin.*, **1977**, 553.
2297. B. Eistert and E. Endres, *Justus Liebigs Ann. Chem.*, **734**, 56 (1970).
2298. J. J. Baldwin and F. C. Novello, *Ger. Pat.* 2,147,794 (1972).
2299. E. J. Brown, *Aust. J. Chem.*, **28**, 2543 (1975).
2300. J. J. Baldwin and F. C. Novello, *U.S. Pat.* 4,011,218 (1977).
2301. I. Ya. Postovskii and N. N. Vereshchagina, *Zh. Obshch. Khim.*, **29**, 2139 (1959).
2302. G. Doleschall and K. Lempert, *Tetrahedron*, **30**, 3997 (1974).
2303. R. Huisgen, W. Mack and K. Bast, *Ger. Pat.* 1,170,958 (1964).
2304. C. Ainsworth, *J. Amer. Chem. Soc.*, **77**, 1148 (1955).
2305. K. Tonegawa, S. Seino and T. Fujino, *Jap. Pat.* 72 21,234 (1972).
2306. H. Moeller, *Ger. Pat.* 2,204,767 (1973).
2307. H. von Dobeneck, D. Wolkenstein, H. Deubel and H. Reinhard, *Chem. Ber.*, **102**, 3500 (1969).
2308. D. H. Hey and J. M. Williams, *J. Chem. Soc.*, **1950**, 1678.
2309. C. M. Harris, S. Kokot, H. R. H. Patil, E. Sinn and H. Wong, *Aust. J. Chem.*, **25**, 1631 (1972).
2310. J. Haginiwa, Y. Higuchi, T. Kawashima and T. Goto, *Yakugaku Zasshi*, **95**, 204 (1975).
2311. M. Strell and E. Kopp, *Chem. Ber.*, **91**, 2854 (1958).
2312. T. Tokuda, K. Matsumori and A. Ide, *Nippon Kagaku Zasshi*, **91**, 572 (1970).
2313. H. Coates, A. H. Cook, I. M. Heilbron, D. H. Hey, A. Lambert and F. B. Lewis, *J. Chem. Soc.*, **1943**, 401.
2314. F. R. Basford and F. L. Rose, *Brit. Pat.* 544,190 (1942).
2315. C. M. Harris, H. R. H. Patil and E. Sinn, *Inorg. Chem.*, **8**, 101 (1969).
2316. A. J. Nunn and K. Schofield, *J. Chem. Soc.*, **1952**, 583.
2317. E. Murmann, *Monatsh.*, **13**, 58 (1892).
2318. H. Coates, A. H. Cook, I. M. Heilbron, D. H. Hey, A. Lambert and F. B. Lewis, *J. Chem. Soc.*, **1943**, 406.
2319. F. R. Basford, H. Coates, I. Heilbron and A. H. Cook, *Brit. Pat.* 557,754 (1943).
2320. F. R. Basford, H. Coates, I. Heilbron and A. H. Cook, *U.S. Pat.* 2,416,563 (1947).
2321. A. H. Cook, I. M. Heilbron and L. Steger, *J. Chem. Soc.*, **1943**, 413.
2322. G. Kobayashi, Y. Matsuda, R. Natsuki and H. Yamaguchi, *Yakugaku Zasshi*, **91**, 934 (1971).
2323. R. Lepetit, *Gazz. Chim. Ital.*, **17**, 453 (1887).
2324. A. H. Cook, I. M. Heilbron and L. Steger, *Brit. Pat.* 567,846 (1945).
2325. M. M. Robison, W. G. Pierson, L. Dorfman, B. F. Lambert and R. A. Lucas, *J. Org. Chem.*, **31**, 3206 (1966).
2326. T. Kametani, K. Ogaswara and A. Kozuka, *Yakugaku Zasshi*, **87**, 1195 (1967).
2327. A. H. Cook, I. M. Heilbron, D. H. Hey, A. Lambert and A. Spinks, *J. Chem. Soc.*, **1943**, 404.

2328. I. M. Heilbron, D. H. Hey and A. Lambert, *Brit. Pat.* 558,010 (1943).
2329. A. Einhorn and P. Sherman, *Ann.*, **287**, 26 (1895).
2330. H. Weidel, *Monatsh.*, **8**, 120 (1887).
2331. G. R. Clemo and W. H. Perkin, Jr., *J. Chem. Soc.*, **125**, 1608 (1924).
2332. O. Mumm, H. Ludwig, D.-H. Lu and R. Radenhausen, *Ann.*, **514**, 34 (1934).
2333. O. W. Fischer, *Monatsh.*, **5**, 417 (1884).
2334. W. Roser, *Ber.*, **17**, 2767 (1884).
2335. A. Claus and P. Stegelitz, *Ber.*, **17**, 2380 (1884).
2336. S. von Niementowski and M. Seifert, *Ber.*, **38**, 762 (1905).
2337. F. R. Japp and C. C. Graham, *J. Chem. Soc.*, **39**, 174 (1881).
2338. J. Zimmermann and A. Müller, *Ber.*, **17**, 1965 (1884).
2339. W. Koenigs, *Ber.*, **12**, 97 (1879).
2340. A. L. Gershuns and R. I. Nazarova, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **14**, 1324 (1971).
2341. F. Kroehnke, H. Dickhaeuser and I. Vogt, *Ann.*, **644**, 93 (1961).
2342. T. Yamazaki, K. Matoba, M. Yajima, M. Nagata and R. N. Castle, *J. Heterocycl. Chem.*, **12**, 973 (1975).
2343. T. Kametani, H. Nemoto and S. Takano, *Yakugaku Zasshi*, **88**, 453 (1968).
2344. B. I. Ardashev and Y. M. Kozlenko, *Zh. Obshch. Khim.*, **26**, 498 (1956).
2345. R. F. Ruttan, *Trans. Roy. Soc. Can.*, **10**(III), 35 (1893).
2346. S. von Niementowski and M. Seifert, *Ber.*, **38**, 762 (1905).
2347. C. Schestopal, *Ber.*, **20**, 2506 (1887).
2348. E. E. Turner, *J. Chem. Soc.*, **107**, 1495 (1915).
2349. F. E. Arnold, *U.S. Pat.* 4,021,409 (1977).
2350. M. K. O'Rell, *U.S. Pat.* 3,944,553 (1976).
2351. J. K. Stille, R. G. Nelbe, II, and S. Norris, *Macromolecules*, **9**, 516 (1976).
2352. F. R. Crowne and J. G. Breckenridge, *Can. J. Chem.*, **32**, 641 (1954).
2353. S. Chakravorti, A. C. DasGupta, A. Raychaudhuri and U. P. Basu, *Indian J. Chem.*, **7**, 1010 (1969).
2354. M. Fujisawa, *Yakugaku Zasshi*, **65**, 2 (1945).
2355. P. Cagniant and A. Deluzarche, *C. R. Acad. Sci.*, **223**, 1012 (1946).
2356. A. K. Sheinkmann, S. G. Potashnikova and S. N. Baranov, *Zh. Org. Khim.*, **6**, 614 (1970).
2357. A. L. Gershuns and P. Ya. Pustovar, *Khim. Geterotsikl. Soedin.*, **1973**, 239.
2358. N. S. Kozlov, L. K. Slobodchikova and G. S. Shmanai, *Dokl. Akad. Nauk SSR, Ser. Khim.*, **187**, 803 (1969).
2359. P. Cagniant and D. Cagniant, *Bull. Soc. Chim. Fr.*, **1961**, 1560.
2360. G. C. Tsatsaronis and A. H. Kehayoglou, *J. Org. Chem.*, **35**, 438 (1970).
2361. W. Borsche and W. Doeller, *Ann.*, **557**, 39 (1938).
2362. E. Lescot, N. P. Buu-Hoi and N. D. Xuong, *J. Chem. Soc.*, **1956**, 2408.
2363. G. Vasiliu, E. Cohn and O. Maior, *An. Univ. Bucaresti Stiint Nat.*, **11**, 151 (1962).
2364. J. Servoin-Sidoine, M. Montaigne-Lepine and G. Saint-Ruf, *Bull. Soc. Chim. Fr.*, **1973**, 1460.
2365. F. H. Case, *J. Org. Chem.*, **30**, 931 (1965).
2366. C. M. Atkinson and H. D. Cossey, *J. Chem. Soc.*, **1962**, 1805.
2367. P. B. Russell and G. H. Hitchins, *J. Amer. Chem. Soc.*, **72**, 4922 (1950).
2368. J. T. Thurston and D. W. Kaiser, *U.S. Pat.* 2,535,968 (1950).
2369. P. Cagniant and P. Cagniant, *Bull. Soc. Chim. Fr.*, **1952**, 336.
2370. J. R. Watson, D. M. Klassen, H. W. Richardson and W. E. Hatfield, *Inorg. Chem.*, **16**, 1906 (1977).
2371. F. H. Case and T. J. Casper, *J. Amer. Chem. Soc.*, **78**, 5842 (1956).
2372. F. Kroehnke, E. Schmidt and W. Zecher, *Ber.*, **97**, 1163 (1964).
2373. H. Schlesinger, *Ger. Pat.* 1,099,846 (1961).
2374. P. Cagniant and A. Deluzarche, *C. R. Acad. Sci.*, **223**, 677 (1946).
2375. P. Cagniant, G. Jecko and D. Cagniant, *Bull. Soc. Chim. Fr.*, **1961**, 1931.

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CHAPTER 2

Reissert Compounds and Related *N*-Acyldihydroquinolines

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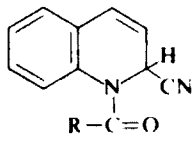
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I. Introduction

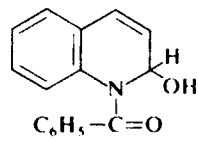
1-Acyl-1,2-dihydroquinaldonitriles (**1**) and related compounds in the isoquinoline series are generally referred to as Reissert compounds. These compounds, named after their discoverer Arnold Reissert,[1] are readily prepared and serve as valuable intermediates in the synthesis of a number of heterocyclic and non-heterocyclic compounds. The chemistry of Reissert compounds has been the subject of two reviews.[2,3] This chapter will be concerned primarily with the chemistry of the quinoline Reissert compounds but it will also cover other *N*-acyldihydroquinolines and related compounds.

II. Reissert Compounds of Quinoline

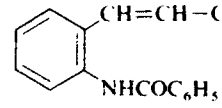
In 1905 Reissert[1] reported that reaction of quinoline and benzoyl chloride in an aqueous solution of sodium hydroxide gave a crystalline product, $C_{16}H_{13}NO_2$. Although structure (**2**) was originally assigned[1] to this product, it now appears that the tautomeric structure (**3**) must be considered.[4,5] At the same time it was observed[1] that the reaction



1



2



3

of benzoyl chloride with quinoline in an aqueous solution of potassium cyanide yielded a crystalline compound, $C_{17}H_{12}N_2O$. It was further observed that this compound underwent acid-catalysed cleavage to quinaldic acid, small amounts of derivatives of quinaldic acid and, remarkably, benzaldehyde. The structure (**1**, R = C_6H_5) was proposed for this interesting product.

1. Preparation

A. Preparation in Aqueous Media

Following the lead of Reissert,[1] most of the early preparations of Reissert compounds were carried out under aqueous conditions. The original preparation of 1-benzoyl-1,2-dihydroquinaldonitrile (**1**, R = C_6H_5) involved the gradual addition, with vigorous shaking, of 2 mol of benzoyl chloride to a suspension of 1 mol of quinoline in an aqueous solution of potassium cyanide. Application of efficient mechanical stirring increases the ease of operation but does not necessarily increase the yield of products.[6] Those Reissert compounds shown in Table 1 that were prepared by the aqueous method are so indicated.

The preparation of Reissert compounds by the aqueous method is limited to relatively unreactive acid halides. Aliphatic and reactive aroyl halides react too fast with water to permit the use of an aqueous medium. In addition, a significant number of quinolines do not form Reissert compounds when the aqueous method is used. The lack of solubility of starting material and product in water is a further disadvantage of the aqueous method of preparation.

In this, as well as in the other methods of preparation, the Reissert compound undoubtedly arises from addition of the cyanide ion to the 2-position of the acyl-quinolinium chloride which is formed by reaction of the quinoline and acid halide.

B. Preparation in Non-aqueous Media

A number of non-aqueous solvent systems have been investigated in order to prevent the hydrolysis of reactive acid chlorides in attempted preparations of Reissert compounds. No Reissert compound was obtained from quinoline, benzoyl chloride and potassium cyanide in ether, excess of quinoline, acetonitrile, benzonitrile, dioxan, acetone or chloroform.[7] A dimethylformamide–water mixture was found to be less satisfactory than water alone.[8] By use of liquid sulphur dioxide as a solvent Reissert compounds were obtained from quinoline and potassium cyanide with benzoyl and cinnamoyl chlorides but not with acetyl chloride.[7]

When quinoline, benzoyl chloride and hydrogen cyanide were reacted in anhydrous ether a small yield of compound (I, R = C_6H_5) was obtained[9] but acetyl chloride failed to react. Use of anhydrous benzene as a solvent, however, has proved to be a useful method.[10] With this solvent quinoline has been reacted with hydrogen cyanide and a variety of acyl halides to give compounds (I). This method, despite the necessity of using liquid hydrogen cyanide, is more general than the aqueous method. Reissert compounds prepared by this non-aqueous method are indicated in Table 1. In addition to the disadvantages associated with the use of liquid hydrogen cyanide this method suffers from the fact that half of the quinoline is tied up as the salt. This is a disadvantage when a substituted quinoline is available only in small amounts.

A Reissert compound has been prepared from quinoline using trimethylsilyl cyanide and a catalytic amount of aluminium chloride in methylene chloride.[11]

C. Preparation in Methylene Chloride–Water

The discovery of the methylene chloride–water solvent system for Reissert compound formation has added a valuable dimension to Reissert compound chemistry.[12–15] This method involves the addition of the acid halide neat or in methylene chloride to a mixture of the quinoline in methylene chloride and potassium cyanide in a minimum of water. Although this is a heterogeneous system, it has an advantage over the aqueous system in that all of the reactants and products are soluble in one phase or the other and that water is slightly soluble in methylene chloride. The small amount of water present is not sufficient to prevent the use of even reactive acid halides.[15] This solvent system appears to offer the method of choice for Reissert compound formation and its general advantages have been discussed.[13] Compounds prepared by this method are indicated in Table 1.

TABLE 1. Quinoline Reissert Compounds

Quinoline used	Acid chloride used	Yield[a]	Method[b]	Reference
Quinoline	Benzoyl	94	A	1, 6
		96	B	10
		87	C	7
		70	D	15
Quinoline	*o*-Chlorobenzoyl	80	B	10
Quinoline	*m*-Chlorobenzoyl	28	B	10
Quinoline	*p*-Chlorobenzoyl	26	A	16
		77	B	10
		20	D	15
Quinoline	*p*-Fluorobenzoyl	50	D	15
Quinoline	*o*-Methoxybenzoyl	66	B	10
Quinoline	Anisoyl	51	A	17
		88	B	10
		80	D	15
Quinoline	*p*-Toluyl	42	A	18
Quinoline	*o*-Nitrobenzoyl	80	B	19
Quinoline	*m*-Nitrobenzoyl	—	B	19
		12	D	15
Quinoline	*p*-Nitrobenzoyl	0	B	19
		3	D	15

[a] A dash indicates that the yield was not specified; a zero indicates that no Reissert compound was isolated.

[b] A = aqueous method; B = liquid hydrogen cyanide–anhydrous benzene method; C = liquid sulphur dioxide method; D = methylene chloride–water method.

TABLE I (*cont.*)

Quinoline used	Acid chloride used	Yield[a]	Method[b]	Reference
Quinoline	Veratroyl	36	A	17
Quinoline	3,4-Dinitrobenzoyl	0	B	19
Quinoline	3,5-Dinitrobenzoyl	0	B	19
Quinoline	2-Nitro-5-methoxybenzoyl	90	B	20
Quinoline	3,4,5-Trimethoxybenzoyl	Slight	A	17
		—	B	19
		65	D	15
Quinoline	2-Nitro-3,4,5-trimethoxybenzoyl	80	B	19
Quinoline	Phthaloyl	Trace	D	15
2-Chloroquinoline	Benzoyl	0	D	13
Quinaldine	Benzoyl	0	A	25
		0	D	13
3-Acetamidoquinoline	Benzoyl	15	A	13
		50	D	13
3-Acetylaminomethylquinoline	Benzoyl	76	A	26
3-Aminoquinoline[c]	Benzoyl	0	A	13
		68	D	13
3-Bromoquinoline	Benzoyl	0	A	13
		15	D	13
3-Hydroxyquinoline[d]	Benzoyl	58	D	13
2,3'-Biquinoline	Benzoyl	50	A	27
Lepidine	Benzoyl	32	A	28
		71	D	13
4-Hydroxyquinoline[d]	Benzoyl	0	A	13
		98	D	13
4-Chloroquinoline	Benzoyl	33	D	13
4-Methoxyquinoline	Benzoyl	82	D	13
5-Aminoquinoline[c]	Benzoyl	0	A	13, 25
		63	D	13
5-Nitroquinoline	Benzoyl	0	A	25
		19	D	13
5-Acetamidoquinoline	Benzoyl	0	A	25
5-Hydroxyquinoline[d]	Benzoyl	99	D	13
5-Carbomethoxyquinoline	Benzoyl	61	D	13
5-Chloroquinoline	Benzoyl	80	D	29
6-Nitroquinoline	Benzoyl	0	A	8, 13
		29	D	13
6-Dimethylaminoquinoline	Benzoyl	0	A	13, 25
		59	D	13
6-Bromoquinoline	Benzoyl	40	A	13
		48	D	13
Quinoline	Naphthoyl	63	D	14

[a] A dash indicates that the yield was not specified; a zero indicates that no Reissert compound was isolated.

[b] A = aqueous method; B = liquid hydrogen cyanide–anhydrous benzene method; C = liquid sulphur dioxide method; D = methylene chloride-water method.

[c] Isolated as the benzamide.

[d] Isolated as the benzoate.

TABLE I (*cont.*)

Quinoline used	Acid chloride used	Yield[a]	Method[b]	Reference
Quinoline	Chloroformylcyclopentadienylmanganese tricarbonyl	75	B	21
Quinoline	1-Methyl-2-chloroformylcyclopentadienylmanganese tricarbonyl	—	B	22
Quinoline	1-Methyl-3-chloroformylcyclopentadienylmanganese tricarbonyl	—	B	22
Quinoline	3-Methylisothiazole-4-carboxylic acid chloride	18	D	23
Quinoline	Acetyl	74	B	10
		0	C	7
		50	D	15
Quinoline	Propionyl	10	B	10
		12	D	15
Quinoline	Phenylacetyl	0	A	17
Quinoline	Cinnamoyl	34	A	17
		91	B	10
		77	C	7
		43	D	15
Quinoline	Butyryl	64	B	10
		25	D	15
Quinoline	Isobutyryl	28	B	10
		18	D	15
Quinoline	Valeryl	—	B	10
Quinoline	Isovaleryl	64	B	10
Quinoline	Pyruvoyl	0	D	15
Quinoline	Trimethylacryloyl	57	B	24
Quinoline	Heptanoyl	0	A	17
Quinoline	Cyclopropanecarbonyl	77	D	15
Quinoline	Cyclopentanecarbonyl	33	D	15
Quinoline	Adipoyl	Trace	D	15
3-Amino-4-methylquinoline[c]	Benzoyl	92	D	30
3-Amino-4,6,7-trimethylquinoline[c]	Benzoyl	80	D	30
6-Aminoquinoline[c]	Benzoyl	95	D	13
6-Hydroxyquinoline[d]	Benzoyl	99	D	13
6-Carbomethoxyquinoline	Benzoyl	49	D	13
6-Ethoxyquinoline	Benzoyl	87	A	31
6-Methoxyquinoline	Benzoyl	89	A	25
		89	D	13
6-Methylquinoline	Benzoyl	60	A	8
		99	D	13

[a] A dash indicates that the yield was not specified; a zero indicates that no Reissert compound was isolated.

[b] A = aqueous method; B = liquid hydrogen cyanide–anhydrous benzene method; C = liquid sulphur dioxide method; D = methylene chloride–water method.

[c] Isolated as the benzamide.

[d] Isolated as the benzoate.

TABLE I (*cont.*)

Quinoline used	Acid chloride used	Yield[a]	Method[b]	Reference
6-Chloroquinoline	Benzoyl	48	A	8
6,6'-Biquinoline	Benzoyl	—	A	32
7-Methoxyquinoline	Benzoyl	--	A	33
7-Nitroquinoline	Benzoyl	0	A	25
		17	D	13
7-Methylquinoline	Benzoyl	54	A	13
		64	D	13
7-Hydroxyquinoline[d]	Benzoyl	89	D	13
7-Chloroquinoline	Benzoyl	37	A	31
8-Nitroquinoline	Benzoyl	0	A	8
		0	D	13
8-Methylquinoline	Benzoyl	26	A	28
		0	D	13
8-Hydroxyquinoline	Benzoyl	0	A	25
		0	D	13
8-Methoxyquinoline	Benzoyl	0	A	25
8-Benzoyloxyquinoline	Benzoyl	0	A	25
8-Acetoxyquinoline	Benzoyl	0	A	25
8-Aminoquinoline	Benzoyl	0	D	13
8-Chloroquinoline	Benzoyl	0	D	13
2-Methyl-4-hydroxy-quinoline	Benzoyl	0	D	13
2-Methyl-4-amino-quinoline	Benzoyl	0	D	13
2-Methyl-6-methoxy-quinoline	Benzoyl	0	D	13
2,4-Dimethylquinoline	Benzoyl	0	D	13
2,6-Dimethylquinoline	Benzoyl	0	D	13
4,6-Dimethylquinoline	Benzoyl	0	A	13
		94	D	13
4-Hydroxy-7-chloro-quinoline[d]	Benzoyl	20	D	13
4,7-Dichloroquinoline	Benzoyl	0	A	13
		34	D	13
4-Chloro-6-methyl-quinoline	Benzoyl	87	D	13
Phenanthridine (3,4-benzoquinoline)	Benzoyl	94	B	34
		71	D	15
Phenanthridine	*p*-Methoxybenzoyl	60	D	15
Phenanthridine	Cinnamoyl	86	B	34
Phenanthridine	5-Phenyl-2,4-pentadienoyl	64	B	34
Phenanthridine	7-Phenyl-2,4,6-hepta-trienoyl	50	B	34
5,6-Benzoquinoline	Benzoyl	43	A	13, 36
		94	D	13
7,8-Benzoquinoline	Benzoyl	0	D	13
Quinine	Benzoyl	60	D	35

[a] A dash indicates that the yield was not specified; a zero indicates that no Reissert compound was isolated.

[b] A = aqueous method; B = liquid hydrogen cyanide–anhydrous benzene method; C = liquid sulphur dioxide method; D = methylene chloride–water method.

[d] Isolated as the benzoate.

D. Effect of Structure of the Quinoline

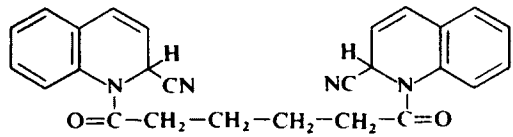
As can be seen from the examples in Table 1, Reissert compounds have been prepared from a wide variety of mono- and disubstituted quinolines. It is of significance that the preparation of a Reissert compound from a 2-substituted quinoline has never been reported, and with the exception of one report[28] of a Reissert compound from 8-methylquinoline Reissert compounds are not formed from 8-substituted quinolines. The lack of reactivity of 2- and 8-substituted quinolines has been attributed to steric effects.[2,3,13] Generally quinolines with electron-donating substituents give higher yields of Reissert compounds and this effect has been rationalized in two ways.[13]

As might be expected, in addition to Reissert compound formation, hydroxyquinolines were esterified and aminoquinolines were converted to the amides.[13] It is of interest that it has been reported[28,31,37] that several haloquinolines undergo dehalogenation with benzoyl chloride and potassium cyanide to yield 1-benzoyl-1,2-dihydroquinaldonitrile.

E. Effect of Structure of the Acyl Halide

Although the aqueous method of Reissert compound formation is restricted to the less reactive acid chlorides, a wide variety of acid chlorides have been used in the hydrogen cyanide method and in the more convenient methylene chloride–water solvent system. Table 1 indicates the variety of acid chlorides that have been used in the formation of Reissert compounds from quinolines. It is of interest that despite the presence of water in the methylene chloride–water solvent system it can be used successfully[15] with even aliphatic acid chlorides.

Although the yields are low, diacid chlorides can be reacted with 2 mol of quinoline to give bis-Reissert compounds such as compound (**4**), which was obtained from adipoyl chloride.[15]



4

Acid bromides and acid anhydrides may be used in place of the acid chlorides but the yields of Reissert compounds are generally lower with these reagents.[15]

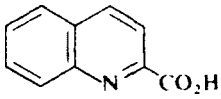
2. Chemical Properties and Reactions

A. Acid-catalysed Hydrolysis

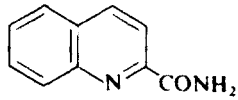
The early interest in the chemistry of Reissert compounds was centred on the acid-catalysed hydrolysis to aldehydes plus the corresponding heterocyclic carboxylic acid or acid derivative. The original[1] acid-catalysed hydrolysis of 1-benzoyl-1,2-dihydroquinaldonitrile (**1**, R = C_6H_5) resulted in the quantitative formation of benzaldehyde. In addition, quinaldic acid (**5**), quinaldamide (**6**) and benzoin quinaldate (**7**) were obtained.

Most of the Reissert compounds listed in Table 1 have been subjected to acid-catalysed hydrolysis to give aldehydes, generally in good yields. Acid-catalysed hydrolysis in mineral acid solution containing tritium oxide has been used to prepare tritium-

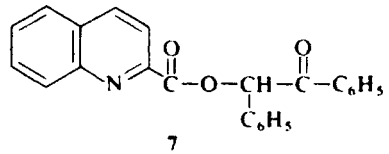
labelled benzaldehyde,[38] and a similar hydrolysis in deuterium oxide with deuterated acid gave deuterium-labelled benzaldehyde.[39]



5

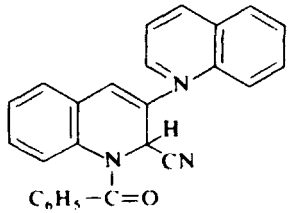


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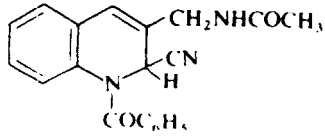


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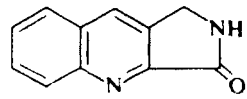
This acid-catalysed hydrolysis has also been of value in the synthesis of quinoline derivatives. Near quantitative yields of quinaldic acid (**5**) are obtained when compound (**1**, R = C_6H_5) is hydrolysed in a mixture of aqueous hydrobromic acid and acetic acid.[40] This method has subsequently been used to produce high yields of benzo(*f*)quinoline-3-carboxylic acid.[41] The 6-ethoxy analogues of compounds (**5**), (**6**) and (**7**) have been obtained from hydrolysis of 1-benzoyl-6-ethoxy-1,2-dihydroquinaldonitrile[42] with hydrochloric acid, and a similar hydrolysis of the biquinoline (**8**) gave 3-(2-quinolyl)quinaldic acid.[27] A series of Reissert compounds derived from substituted 3-aminoquinolines has been converted to the corresponding quinaldic acids by acid-catalysed hydrolysis.[30] Acid-catalysed hydrolysis of the amide (**8a**) occurs with cyclization to give pyrroloquinolone (**8b**).[26]



8

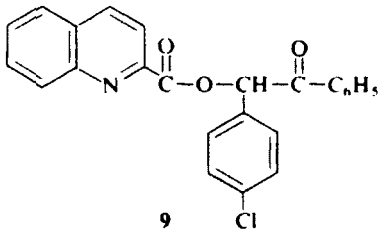


8a

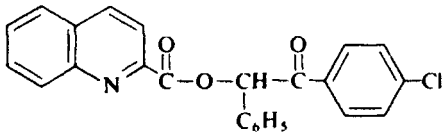


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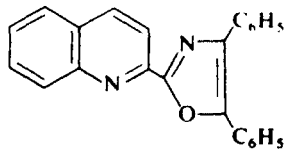
The yield of benzoin quinaldate (**7**) obtained on the acid-catalysed hydrolysis of (**1**, R = C_6H_5) is increased when the hydrolysis is carried out in the presence of an excess of benzaldehyde and substituted benzoin esters can be prepared by addition of a substituted benzaldehyde to the hydrolysis mixture.[16] Thus compound (**9**) was obtained when (**1**, R = C_6H_5) was treated with *p*-chlorobenzaldehyde and concentrated hydrochloric acid, whereas (**1**, R = *p*-ClC_6H_4) and benzaldehyde gave the isomer (**10**).[16] Treatment of the Reissert compound (**1**, R = C_6H_5) with anhydrous hydrogen chloride in benzaldehyde gave a mixture of benzoin quinaldate (**7**) and 2-(2-quinolyl)-4,5-diphenyloxazole (**11**).[43]



9

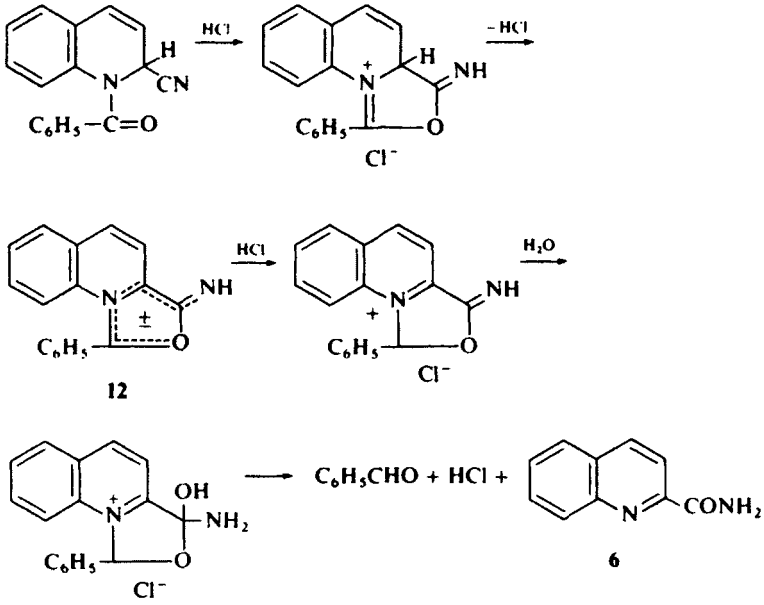


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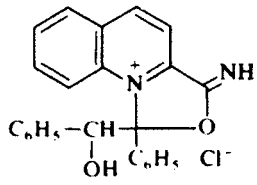
11

A mechanism has been proposed[43] for the acid-catalysed hydrolysis of Reissert compounds. This mechanism is shown in Scheme 1. Subsequent hydrolysis of the quinaldamide (**6**) yields quinaldic acid. Formation of benzoin quinaldate (**7**) may be rationalized by assuming that the conjugate acid of benzaldehyde adds to the intermediate (**12**) to give (**13**), which can then undergo rearrangement and hydrolysis to give compound (**7**).[43]

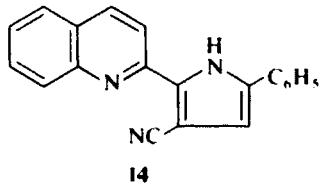


SCHEME 1

The acid-catalysed condensation of 1-benzoyl-1,2-dihydroquinaldonitrile (**1**, R = C_6H_5) with acrylonitrile gave 2-(2-quinolyl)-3-cyano-5-phenylpyrrole (**14**).[44]



13

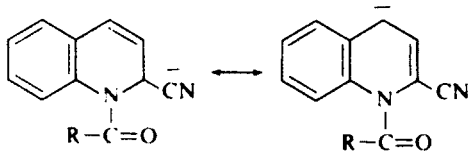


14

Treatment of 1-benzoyl-1,2-dihydroquinaldonitrile (**1**, R = C_6H_5) with phosphorus pentachloride[45,46] or thionyl chloride and sulphuryl chloride converts the Reissert compound to quinaldonitrile.

B. Reactions Involving the Formation of an Anion of the Reissert Compound

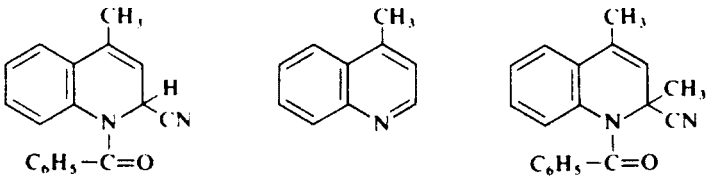
The acidic hydrogen bonded to the carbon alpha to the cyano group can be removed by a number of bases. Thus, treatment of compound (**1**) with a variety of bases gives, in solution, the anion (**15**). These anions of Reissert compounds can be used to good advantage in a number of reactions. It should be noted that these reactions have received much greater attention in the isoquinoline series[2,3,47] than in the quinoline series.



15a **15b**

a. Reactions with Alkyl and Aryl Halides It has been reported[48] that treatment of 1-benzoyl-1,2-dihydroquinaldonitrile (**1**, R = C_6H_5) with phenyllithium gave the conjugate base (**15**). Reaction of the base (**15**, R = C_6H_5) with methyl iodide and subsequent hydrolytic cleavage of the methylated derivative (**16**) gave lepidine (**17**).[48] No quinaldine was isolated in this reaction. Further reaction of compound (**16**) with phenyllithium and then methyl iodide gave the dimethyl derivative (**18**), which was hydrolysed to 2,4-dimethylquinoline.[48] An additional example of alkylation of the quinoline Reissert compound in the 4-position has appeared.[49] The crude Reissert compound (**18a**) formed from quinoline, potassium cyanide and 4-chlorobutanoyl chloride undergoes cyclization to give compound (**18b**) on treatment with sodium hydride in dimethylformamide.[50]

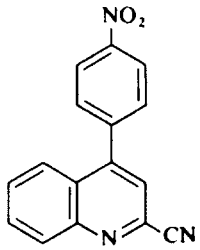
Generation of the anion (**15**) by treatment of compound (**1**, R = C_6H_5) with sodium hydride in dimethylformamide followed by reaction with *p*-fluoronitrobenzene gave 2-cyano-4-(*p*-nitrophenyl)quinoline (**19**).[51]



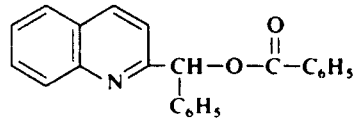
16 **17** **18**



18a **18b**

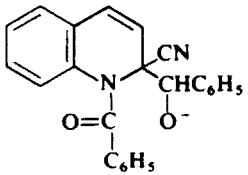


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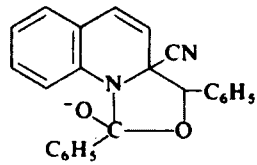


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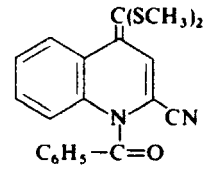
b. Reactions with Aldehydes and Ketones The anion (**15**) undergoes reaction with aldehydes to form esters of secondary alcohols containing the 2-quinolyl group bonded to the carbinol carbon.[52] In this manner benzaldehyde, 1-benzoyl-1,2-dihydroquinaldonitrile (**1**, R = C_6H_5) and phenyllithium gave the ester (**20**). This ester is undoubtedly formed through intermediates (**21**) and (**22**). Other aldehydes,[52] including formaldehyde,[53] also react to form esters. Anion (**15**) has also been reacted in a similar manner with acetophenone,[52] with the dialdehydes terephthalaldehyde and phthalaldehyde[54] and with ferrocene carboxaldehyde.[55]



21



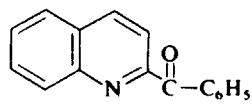
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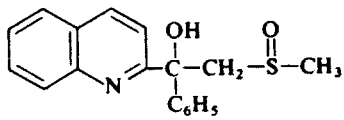
23

Reaction of the anion (**15**, R = C_6H_5) with carbon disulphide followed by the addition of methyl iodide[57] led to the formation of compound (**23**).

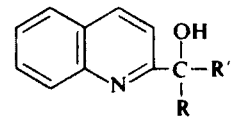
c. Rearrangement Reactions Treatment of (**1**, R = C_6H_5 or CH_3) with sodium hydride in refluxing xylene[48] or treatment of (**1**, R = Ar) with sodium hydride in dimethylformamide at room temperature[56,57] causes the anion to undergo rearrangement to give ketones of the type (**24**). The rearrangement of (**1**, R = C_6H_5) to (**24**, R = C_6H_5) also takes place with sodium hydride in dimethyl sulphoxide but in this case the anion of the solvent reacts with compound (**24**) to give (**25**) as the product.[57]



24



25

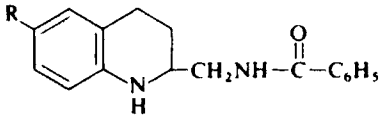


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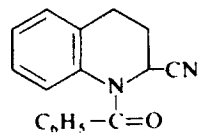
These base-catalysed rearrangements can also be catalysed by Grignard reagents.[18, 58, 59] In this case the products are tertiary alcohols (**26**) resulting from the interaction of the Grignard reagent with the rearrangement product. The mechanism of the rearrangement and condensation process has been studied[18, 59] and the rearrangement has been shown[18] to proceed by an intramolecular process.

C. Reductions

Catalytic hydrogenation of 1-benzoyl-1,2-dihydroquinaldonitrile (**1**, R = C_6H_5)[6] and 1-benzoyl-6-methoxy-1,2-dihydroquinaldonitrile[25] over a nickel catalyst and at relatively high temperature and pressure occurred with rearrangement to give the reduced compounds (**27**, R = H and OCH_3, respectively). Hydrogenation of several additional 6- and 7-substituted quinoline Reissert compounds in the presence of Raney nickel also led to compounds of the type (**27**).[60] When the hydrogenation of (**1**, R = C_6H_5) was carried out over a platinum catalyst at room temperature and 1 atm pressure the olefinic group was selectively reduced to give 1-benzoyl-1,2,3,4-tetrahydroquinaldonitrile (**28**).[61-63] This compound does not give benzaldehyde on acid-catalysed hydrolysis,[62] but gives tetrahydroquinaldic acid.[63]



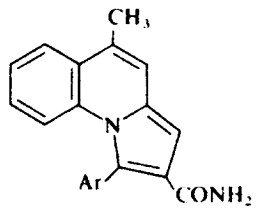
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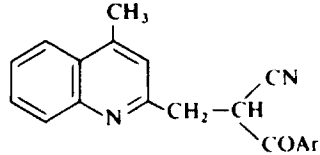
28

D. Other Reactions

Reaction of the Reissert compound of 4-methylquinoline with sodium hydride in dimethylformamide and acrylonitrile at 0 °C led to rearrangement to 4-methyl-2-benzoylquinoline, while reaction at −30 °C led to compounds (**28a**) and (**28b**).[49] Use of sodium amide in liquid ammonia gave an improved yield of these two compounds.



28a

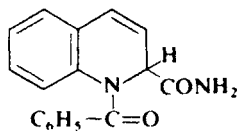


28b

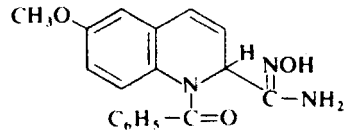
Treatment of 1-benzoyl-1,2-dihydroquinaldonitrile with 30% hydrogen peroxide in acetone with sodium bicarbonate gave 1-benzoyl-1,2-dihydroquinaldamide (**29**).[43] Air oxidation of the quinoline Reissert compound gave quinaldonitrile.[64]

Reaction of 1-benzoyl-6-methoxy-1,2-dihydroquinaldonitrile with hydroxylamine gave the amidoxime (**30**).[25] A similar reaction has been carried out with compound (**1**, R = C_6H_5).[65] An analogue of compound (**30**), lacking the methoxyl group has also been

prepared and undergoes acid-catalysed hydrolysis to give benzaldehyde.[66] Treatment of the Reissert compound (**1**, R = C_6H_5) with dry hydrogen chloride in chloroform and then ethanolic ammonia gave 2-amidinoquinoline.[67]

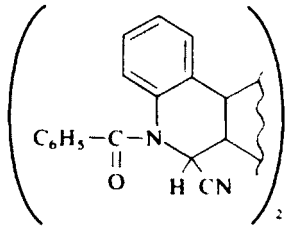


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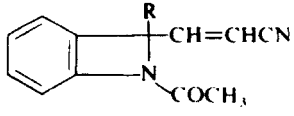


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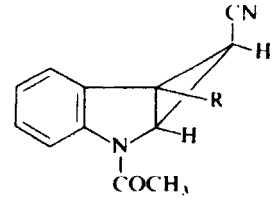
Photolysis of the quinoline Reissert compound (**1**, R = C_6H_5) showed a marked dependence on the wavelength of the ultraviolet source. A low yield of 2-cyanoquinoline was obtained by the action of a 2537-Å source with acetonitrile as the solvent, whereas a high-pressure source with benzene as the solvent gave a 41% yield of the dimer (**31**).[68] Photoisomerization of 1-acetyl-1,2-dihydroquinaldonitrile and the corresponding 4-methyl derivative gave compounds of type (**31a**) and (**31b**).[69]



31



31a, R = H, CH_3



31b, R = H, CH_3

3. Spectral Properties

Ultraviolet absorption spectra have been reported for a number of Reissert compounds[37,48,70] and support the structure (**1**) rather than a 1,4-dihydro structure.

Although the infrared spectra show absorption typical of an amide group, they completely lack absorption in the range 2200–2400 cm^{-1}. The reasons for this absence of absorption due to a cyano group have been discussed.[2]

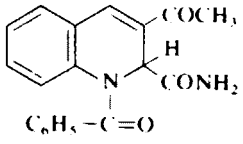
Several papers have appeared on the proton magnetic resonance spectra of isoquinoline Reissert compounds, but with the exception of a report with a few spectra[37] a similar study has not appeared for the quinoline series.

In the mass spectrum[71] of 1-benzoyl-1,2-dihydroquinaldonitrile the dominant ion was the benzoylium ion with the 2-cyanodihydroquinoline ion detected only to a small

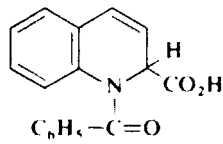
extent. The benzoylium ion was also the dominant ion in the spectrum of the benzo(*f*) analogue of (**1**, R = C_6H_5).

III. Other *N*-Acyldihydroquinolines

A number of analogues of 1-acyl-1,2-dihydroquinaldonitriles with groups other than cyano have been reported. Some of these have already been mentioned in the above section as products from reactions at the cyano group of Reissert compounds. Treatment of 1-benzoyl-1,2-dihydroquinaldamide (**29**) with phosphorus pentoxide gave 1-benzoyl-1,2-dihydroquinaldonitrile (**1**, R = C_6H_5) and reduction gave 1-benzoyl-1,2,3,4-tetrahydroquinaldamide;[43] 1-benzoyl-3-acetyl-1,2-dihydroquinaldamide (**32**) and the corresponding ester were both prepared by benzoylation of the appropriate amine.[43] Treatment of compounds (**29**) and (**32**) with concentrated hydrochloric acid failed to give any benzaldehyde, a reaction typical of Reissert compounds.

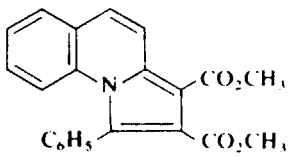


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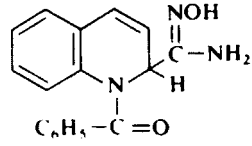


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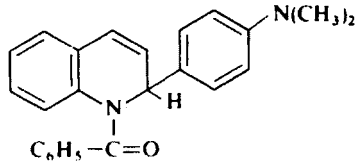
A selective hydrolysis of amide (**29**) to 1-benzoyl-1,2-dihydroquinaldic acid (**33**) has been accomplished on the surface of Amberlite IR-120 acid ion-exchange resin.[72] The acid (**33**) has been reduced by hydrogen over platinum oxide to the corresponding tetrahydro compound. The preparation of derivatives of the acid (**33**) has been reported.[73] Although treatment of compounds (**29**) and (**33**) with concentrated hydrochloric acid gave only benzoic acid, both gave benzaldehyde after a preliminary dehydration with polyphosphoric acid.[70] Reaction of the acid (**33**) with dimethyl acetylenedicarboxylate in acetic anhydride solution led to the isolation of the tricyclic compound (**33a**).[74] Compound (**33a**) is the product of a 1,3-dipolar addition to the intermediate formed in the hydrolysis of the acid (**33**). The hydrolysis of 1-benzoyl-2-carbomethoxy-3-acetyl-1,2-dihydroquinoline with hydrochloric acid at room temperature gave 1-benzoyl-3-acetyl-1,2-dihydroquinoline-2-carboxylic acid, whereas at 100 °C benzoic acid was obtained.[75]



33a



34

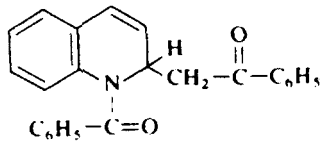


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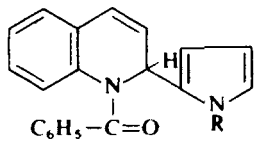
Hydrolysis of the amidoxime (**34**) led to the isolation of benzaldehyde, benzoic acid, quinaldic acid and quinoline.[65]

The reaction of quinoline, benzoyl chloride and dimethylaniline gave 1-benzoyl-2-(*p*-dimethylaminophenyl)-1,2-dihydroquinoline (**35**).[61,77] Alkaline hydrolysis of compound (**35**) gave benzoic acid and, after treatment of the amine fraction with nitrobenzene or picric acid, 2-(*p*-dimethylaminophenyl)quinoline.[61] Catalytic reduction of compound (**35**) gave the tetrahydro analogue.[61] All attempts to obtain benzaldehyde from compound (**35**) by acid hydrolysis failed. This reaction has been extended to the condensation of quinoline, various acyl halides and dialkylanilines to give analogues of compound (**35**).[77] Acid or alkaline hydrolysis of these analogues aromatized them to 2-(*p*-dialkylaminophenyl)quinolines.[77] Acetophenone,[68] pyrroles,[79] indoles[80] and a number of active methylene compounds[78,80] have also been used in this reaction to give analogues of the type (**36**)–(**39**), respectively.

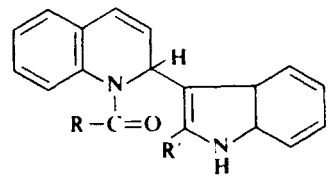
The reaction of quinoline, benzoyl chloride, and silver phenylacetylide led to the formation of the acetylene (**40**).[81] Reaction of quinoline, benzoyl chloride and sodium



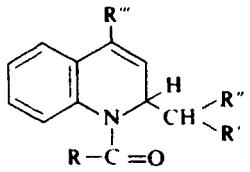
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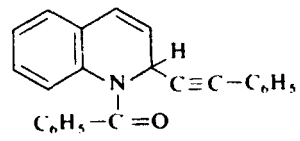
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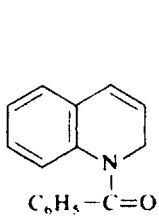


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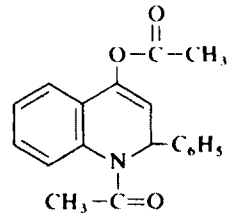
hydroxide had been reported[1] to give compound (**2**). However, as was noted earlier, it has subsequently been shown[5] that this compound has structure (**3**) (p. 354).

Crystalline 1-benzoyl-1,2-dihydroquinoline (**41**) has been prepared[82,116] by reaction of freshly purified 1,2-dihydroquinoline and benzoyl chloride. This compound (**41**) had been described as an oil by early workers. Hydrogenation of compound (**41**) gave 1-benzoyl-1,2,3,4-tetrahydroquinoline and acid-catalysed hydrolysis of compound (**41**) gave benzoic acid.[82] Although 1,2-dihydroquinoline undergoes disproportionation, the benzoyl derivative (**41**) and the 1-*p*-toluenesulphonyl derivative are stable.[83] *N*-benzoyl and *N*-acetyl derivatives have also been prepared from various substituted 1,2-dihydroquinolines.[84,85]

The *N*-acetyl-1,2-dihydroquinoline (**42**) is obtained when 1,2,3,4-tetrahydro-2-phenyl-4-quinolone is boiled with sodium acetate in acetic anhydride.[86]

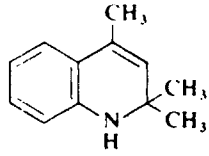


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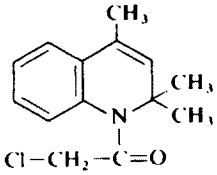


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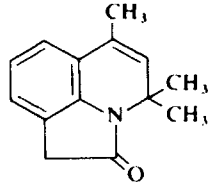
The *N*-acetyl and *N*-benzoyl derivatives of 2,2,4-trimethyl-1,2-dihydroquinoline (acetone anil) (**43**) and its analogues have received considerable attention.[87-93] Treatment of 1-chloroacetyl-1,2-dihydro-2,2,4-trimethylquinoline (**44**) with aluminium chloride in light petroleum gave compound (**45**), whereas with aluminium chloride in benzene compound (**44**) gave the tetrahydroquinoline (**46**).[94] Bromination of the *N*-acetyl derivative of compound (**43**) gave, depending on the proportion of bromine used,



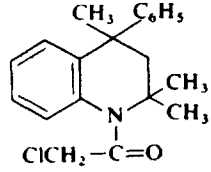
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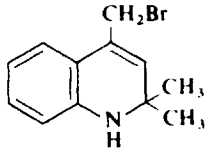
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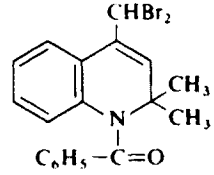
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46



47

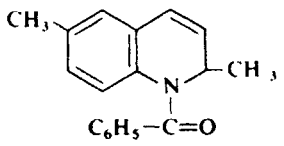


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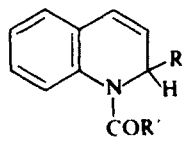
2,2-dimethyl-4-bromomethyl-1,2-dihydroquinoline (**47**), or the 6-bromo-, the 3,6-dibromo and the 3,6,8-tribromo analogues of compound (**47**).[95] The *N*-acetyl derivative of compound (**47**) reacted smoothly with a variety of nucleophiles with displacement of the bromine.[96] Reaction of the *N*-benzoyl derivative of compound (**43**) with *N*-bromosuccinimide gave, depending on the amount of reagent, the *N*-benzoyl derivative of

compound (**47**) and the dibromo compound (**48**).[97] These two products were shown to undergo a number of reactions typical of bromomethyl and dibromomethyl compounds, respectively.

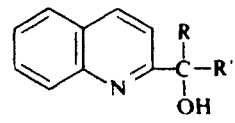
By heating 1-benzoyl-2,6-dimethyl-4-hydroxy-1,2,3,4-tetrahydroquinoline with potassium bisulphate at 180 °C, 1-benzoyl-2,6-dimethyl-1,2-dihydroquinoline (**49**) was obtained.[98] The 8-methyl analogue of compound (**49**) was prepared in an analogous manner. Catalytic hydrogenation of the dihydroquinoline (**49**) gave the corresponding tetrahydro compound,[98] whereas base hydrolysis gave 2,6-dimethylquinoline and benzoic acid.[98] On boiling, compound (**49**) disproportionated to give 2,6-dimethylquinoline and 1-benzoyl-2,6-dimethyl-1,2,3,4-tetrahydroquinoline,[98] and chlorination or bromination gave dihalo derivatives.[99]



49



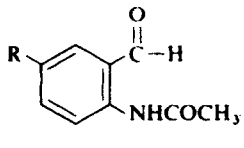
49a



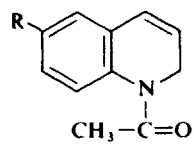
49b, R = R′ = C_6H_5;
R = C_6H_5,
R′ = 4-$CH_3C_6H_4$

With acid chlorides or esters, *N*-lithio-1,2-dihydroquinolines react to give the *N*-acylated derivatives (**49a**, R = C_6H_5), which can undergo rearrangement to the tertiary carbinols (**49b**) in the presence of organolithium compounds.[100]

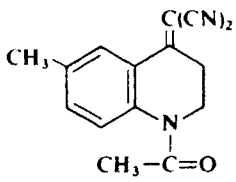
Reaction of compound (**50**) with sodium hydride and vinyltriphenylphosphonium bromide gave the *N*-acetyldihydroquinoline (**51**).[101] Reaction of the dinitrile (**52**) with polyphosphoric acid gave the *N*-acyldihydroquinoline (**53**).[102] The endo double bond appears to be favoured in the product because of the bulkier carboxamide groups.



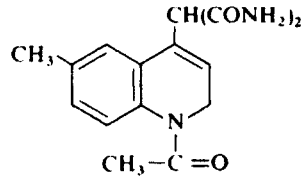
50



51



52



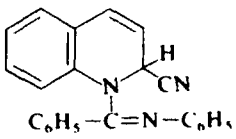
53

It is of interest that most of the *N*-acyl-1,2-dihydroquinolines without a cyano group in the 2-position do not exhibit the same chemistry as Reissert compounds.

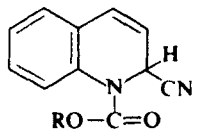
IV. Other Related 1,2-Dihydroquinolines

The compounds in this section, although not *N*-acyldihydroquinolines, contain related groups on the nitrogen atom.

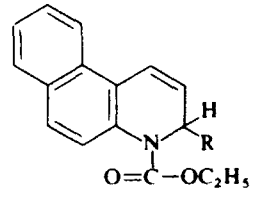
The hydrochloride of compound (**54**) was obtained by reaction of *N*-phenylbenzimidoyl chloride and hydrogen cyanide with quinoline.[103] Acid-catalysed hydrolysis of compound (**54**) gave benzaldehyde, aniline and quinaldic acid, whereas treatment with nitrobenzene gave quinaldonitrile. Reaction of quinoline with potassium cyanide and ethyl or methyl chloroformate gave compound (**55**).[104, 105] Benzo(*f*)quinoline gave an analogous compound (**56**).[106] Reaction of compound (**56**) with hydroxylamine gave[104] the amidoxime (**57**), benzo(*f*)quinaldamide, (**58**), and the isomer (**59**). Methylation of



54

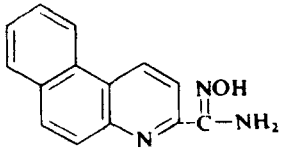


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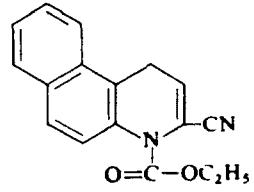


56, R = CN

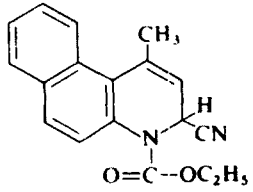
57, R = $-C(=NOH)-NH_2$



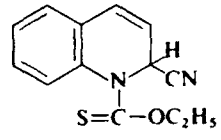
58



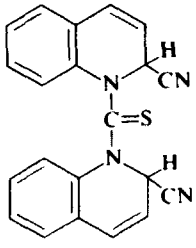
59



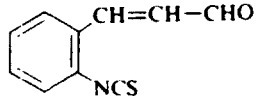
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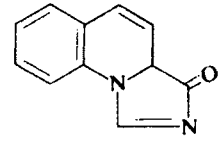
61



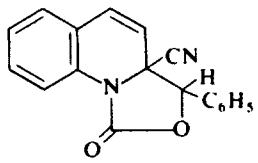
62



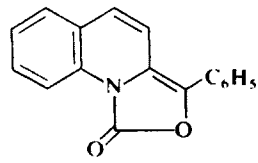
63



64



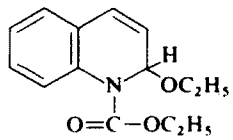
64a



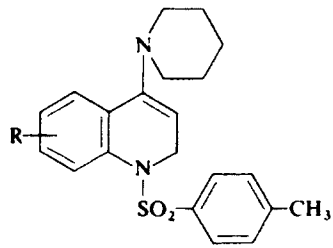
64b

either isomer (**56**) or (**59**) with methyl iodide in the presence of sodium hydride in dimethylformamide gave rise to the same methylated product (**60**). The thiocarbonyl adduct (**61**) has also been prepared.[107] The reaction of quinoline, potassium cyanide and thiophosgene failed to yield compound (**62**) but gave compounds (**63**) and (**64**).[107] Catalytic hydrogenation of compound (**55**) under mild conditions gave the corresponding tetrahydro analogue,[63] whereas on air oxidation it gave quinaldonitrile.[64] Compound (**55**) reacted with benzaldehyde and sodium hydride in dimethylformamide to give the oxazoloquinolones (**64a**) and (**64b**).[105] Several studies on the irradiation of compound (**55**) have been published.[108]

The *N*-ethoxycarbonyl derivative of 2-ethoxy-1,2-dihydroquinoline (**65**)[109] is of interest both as a non-equilibrium α-adrenergic blocking agent[109,110] and as a reagent for the formation of peptide linkages.[111] The compound (**65**) was obtained from ethoxycarbonylquinolinium chloride by treatment with sodium ethoxide.[108] Attack at the carbonyl group (giving quinoline and diethyl carbonate) could be minimized by use of ethanol and a hindered base, or by using sodium thiomethylate.



65



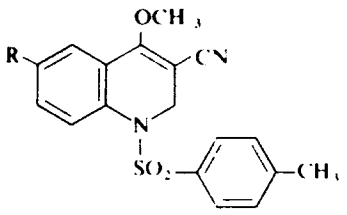
66

Reaction of 2,2,4-trimethyl-6-alkoxy-1,2-dihydroquinolines with isocyanates gives rise to a series of *N*-(dihydroquinolinyl)carboxanilides.[112,113]

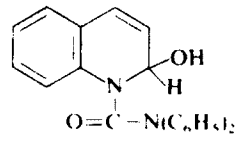
Enamines of the type (**66**) are formed from 1-(*p*-toluenesulphonyl)-2,3-dihydro-4-quinolones upon treatment with pyrrolidine.[114] The enamine (**66**, R = H) was alkylated with ethyl acrylate.

A variety of 1,2-dihydroquinolines have been converted into *N*-carbamoyl and *N*-sulphonyl derivatives.[84,85,88,101,115,116] Phosphorus pentachloride cyclization of the condensation product of tosylaniline with chloropropionic acid gave 1-tosyl-4-chloro-1,2-dihydroquinoline.[117] Tosyl derivatives of the type (**67**) were obtained from the alkylation of 4,5-dihydro-5-tolylsulphonyl-isoxazolo(3,2-*c*)quinolines.[118]

It has been reported[119] that quinoline and diphenylcarbamoyl chloride react to give a diphenylcarbamoylquinolinium chloride, which on treatment with sodium hydroxide gave compound (**68**), which was isolated as its methyl or ethyl ether.

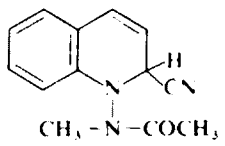


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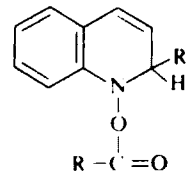


68

It is worth noting that some related systems have been proposed as intermediates in synthetic sequences. Structure (**69**) has been proposed[120] as an intermediate in the conversion of *N*-methylacetamidoquinolinium iodide to 2- and 4-cyanoquinoline. The reaction of quinoline, potassium cyanide and benzenesulphonyl chloride yields quinaldonitrile[121] and undoubtedly passes through 1-benzenesulphonyl-1,2-dihydroquinaldonitrile, although, in contrast to the isoquinoline series, this intermediate cannot be isolated. Although intermediates of the type (**70**) have not been isolated they appear to be involved in the conversion of quinoline-*N*-oxides to 2-substituted quinolines.



69



70

V. References

1. A Reissert, *Ber.*, **38**, 1603 (1905).
2. W. E. McEwen and R. L. Cobb, *Chem. Rev.*, **55**, 511 (1955).
3. F. D. Popp, *Adv. Heterocycl. Chem.*, **9**, 1 (1968).
4. A. Reissert, *Ber.*, **38**, 3415 (1905).
5. I. W. Elliott, *J. Org. Chem.*, **29**, 305 (1964).
6. H. Rupe, R. Paltzer and K. Engel, *Helv. Chim. Acta*, **20**, 209 (1937).
7. R. B. Woodward, *J. Amer. Chem. Soc.*, **62**, 1626 (1940).
8. I. W. Elliott, Jr., *J. Amer. Chem. Soc.*, **77**, 4408 (1955).
9. W. Dieckmann and H. Kammerer, *Ber.*, **40**, 3737 (1907).
10. J. M. Groscheintz and H. O. L. Fischer, *J. Amer. Chem. Soc.*, **63**, 2021 (1941).
11. S. Ruchirawat, N. Phadungkul, M. Chuankamnerdkarn and C. Thebtaranonth, *Heterocycles*, **6**, 43 (1977).
12. F. D. Popp and W. Blount, *Chem. Ind. (London)*, **1961**, 550.
13. F. D. Popp, W. Blount and P. Melvin, *J. Org. Chem.*, **26**, 4930 (1961).
14. F. D. Popp, W. Blount and A Soto, *Chem. Ind. (London)*, **1962**, 1022.
15. F. D. Popp and A. Soto, *J. Chem. Soc.*, **1963**, 1760.
16. W. E. McEwen and R. N. Hazlett, *J. Amer. Chem. Soc.*, **71**, 1949 (1949).
17. S. Sugasawa and T. Tsuda, *J. Pharm. Soc. Jap.*, **56**, 557 (1936); *Chem. Abstr.*, **32**, 5836 (1938).
18. A. P. Wolf, W. E. McEwen and R. H. Glazier, *J. Amer. Chem. Soc.*, **78**, 861 (1956).
19. G. L. Buchanan, J. W. Cook and J. D. Loudon, *J. Chem. Soc.*, **1944**, 325.
20. H. Shirai and N. Oda, *Chem. Pharm. Bull. (Tokyo)*, **8**, 744 (1960).
21. E. Cuingnet, D. Poulain and M. Tarterat-Adalberon, *Bull. Soc. Chim. Fr.*, **1969**, 514.

22. E. Cuingnet and M. Adalberon, *C. R. Acad. Sci.*, **258**, 3053 (1964).
23. D. Buttimore, D. H. Jones, R. Slack and K. R. H. Wooldridge, *J. Chem. Soc.*, **1963**, 2032.
24. R. Criegee, S. S. Bath and B. v. Bornhaupt, *Chem. Ber.*, **93**, 2891 (1960).
25. A. Gassmann and H. Rupe, *Helv. Chim. Acta*, **22**, 1241 (1939).
26. T. Sugasawa, T. Toyota, K. Sasakura and T. Hidaka, *Chem. Pharm. Bull. (Tokyo)*, **19**, 1971 (1971).
27. K. V. Ihnatowicz and St. Niementowski, *Ber.*, **52**, 186 (1919).
28. Y. Hamada, *Yakugaku Zasshi*, **80**, 1573 (1960); *Chem. Abstr.*, **55**, 10450 (1961).
29. Y. Hamada, I. Takeuchi and H. Matsuoka, *Chem. Pharm. Bull. (Tokyo)*, **18**, 1026 (1970).
30. C. K. Chu and T. J. Bardoes, *J. Heterocycl. Chem.*, **14**, 1053 (1977).
31. T. Takahashi, J. Okada and Y. Hamada, *Yakugaku Zasshi*, **77**, 1243 (1957); *Chem. Abstr.*, **52**, 6342 (1958).
32. K. Ueda, *J. Pharm. Soc. Jap.*, **57**, 825 (1937); *Chem. Abstr.*, **32**, 1265 (1938).
33. E. Späth and O. Brunner, *Ber.*, **57**, 1243 (1924).
34. G. Wittig, M. A. Jesaitis and M. Glos, *Ann.*, **577**, 1 (1952).
35. F. D. Popp, unpublished work.
36. M. Colonna and S. Fatutta, *Gazz. Chim. Ital.*, **83**, 622, footnote 19 (1953).
37. Y. Hamada, I. Takeuchi and H. Matsuoka, *Chem. Pharm. Bull. (Tokyo)*, **18**, 1026 (1970).
38. C. G. Swain, quoted in reference 2.
39. M. Wahrem, *Abhandl. Deut. Akad. Wiss. Berlin, Kl. Chem., Geol. Biol.*, **1964** (7), 687 (1963); *Chem. Abstr.*, **66**, 37577g (1967).
40. J. W. Davis, Jr., *J. Org. Chem.*, **24**, 1691 (1959).
41. F. D. Popp and W. R. Schleigh, *J. Heterocycl. Chem.*, **1**, 107 (1964).
42. T. Takahashi and Y. Hamada, *Yakugaku Zasshi*, **77**, 1244 (1957); *Chem. Abstr.*, **52**, 6342 (1958).
43. R. L. Cobb and W. E. McEwen, *J. Amer. Chem. Soc.*, **77**, 5042 (1955).
44. D. C. Glover, *Ph.D. Dissertation*, University of Massachusetts (1966); quoted in E. K. Evanguelidou and W. E. McEwen, *J. Org. Chem.*, **31**, 4110 (1966); see also *Chem. Abstr.*, **66**, 4386 (1967).
45. A. Kaufmann and P. Dandliker, *Ber.*, **46**, 2924 (1913).
46. F. M. Hamer, *J. Chem. Soc.*, **1939**, 1008.
47. F. D. Popp, *Heterocycles*, **1**, 165 (1973).
48. V. Boekelheide and J. Weinstock, *J. Amer. Chem. Soc.*, **74**, 660 (1952).
49. B. C. Uff, R. S. Budhram, M. F. Consterdine, J. K. Hicks, B. P. Slingsby and J. A. Pemblington, *J. Chem. Soc. Perkin Trans. I*, **1977**, 2018.
50. H. W. Gibson, D. K. Chesney and F. D. Popp, *J. Heterocycl. Chem.*, **9**, 541 (1972).
51. R. Piccirilli and F. D. Popp, *Can. J. Chem.*, **47**, 3261 (1969).
52. L. R. Walters, N. T. Iyer and W. E. McEwen, *J. Amer. Chem. Soc.*, **80**, 1177 (1958).
53. L. R. Walters, I. C. Mineo and R. S. Kripowicz, *J. Org. Chem.*, **29**, 980 (1964).
54. E. G. Podrebarac and W. E. McEwen, *J. Org. Chem.*, **26**, 1165 (1961).
55. F. D. Popp and E. B. Moynahan, *J. Heterocycl. Chem.*, **7**, 739 (1970).
56. F. D. Popp and J. M. Wefer, *J. Chem. Soc. Chem. Commun.*, **1966**, 207.
57. F. D. Popp and J. M. Wefer, *J. Heterocycl. Chem.*, **4**, 183 (1967).
58. W. E. McEwen, J. V. Kindall, R. N. Hazlett and R. H. Glazier, *J. Amer. Chem. Soc.*, **73**, 4591 (1951).
59. N. C. Rose and W. E. McEwen, *J. Org. Chem.*, **23**, 337 (1958).
60. W. B. Wright, *J. Med. Chem.*, **11**, 1161 (1968).
61. W. E. McEwen, R. H. Terss and I. W. Elliott, *J. Amer. Chem. Soc.*, **74**, 3605 (1952).
62. R. F. Collins, *J. Amer. Chem. Soc.*, **77**, 4921 (1955).
63. M. D. Rozwadowska, *Rocz. Chem.*, **51**, 2321 (1977).
64. M. D. Rozwadowska and D. Brozda, *Tetrahedron Lett.*, 589 (1978).
65. L. R. Walters, M. I. Siegel and R. C. Cook, *J. Heterocycl. Chem.*, **5**, 577 (1968).
66. L. R. Walters, R. C. Cook and E. A. McFadden, *J. Chem. Eng. Data*, **16**, 115 (1971).
67. R. F. Collins and T. Henshall, *J. Chem. Soc.*, **1956**, 1881.
68. P. T. Izzo and A. S. Kende, *Tetrahedron Lett.*, **1966**, 5731.
69. M. Ikeda, S. Matsugashita, F. Tabusa, H. Ishibashi and Y. Tamura, *J. Chem. Soc. Chem. Commun.*, **1975**, 575.
70. R. F. Collins and T. Henshall, *J. Amer. Chem. Soc.*, **80**, 159 (1958).

71. F. D. Popp, K. T. Potts and R. Armbruster, *Organic Mass Spectrom.*, **3**, 1075 (1970).
72. R. F. Collins, *Chem. Ind. (London)*, **1957**, 736.
73. L. R. Walters, *J. Chem. Eng. Data*, **10**, 79 (1965).
74. W. E. McEwen, I. C. Mineo, Y. H. Shen and G. Y. Han, *Tetrahedron Lett.*, **1968**, 5157.
75. R. B. Woodward and E. C. Kornfeld, *J. Amer. Chem. Soc.*, **70**, 2508 (1948).
76. A. N. Prilepskaya, A. K. Sheinkman and N. F. Kazarinova, *Metody Polucheniya Khim. Reaktivov: Preparatov*, No. 13, 19 (1965); *Chem. Abstr.*, **65**, 5437 (1966).
77. A. K. Sheinkman, A. N. Kost, A. N. Prilepskaya and Zh. V. Shiyan, *Zh. Org. Khim.*, **4**, 1286 (1968); *Chem. Abstr.*, **69**, 77092p (1968).
78. P. E. Wright and W. E. McEwen, *J. Amer. Chem. Soc.*, **76**, 4540 (1954).
79. A. K. Sheinkman, R. D. Bodnarchuk and A. N. Kost, *Russ. Pat.* 202,143 (1967); *Chem. Abstr.*, **69**, 2538 (1968).
80. H. von Dobeneck and W. Goltzsche, *Ber.*, **95**, 1484 (1962).
81. T. Agawa and S. I. Miller, *J. Amer. Chem. Soc.*, **83**, 449 (1961).
82. R. F. Collins, *J. Chem. Soc.*, **1954**, 3641.
83. R. F. Collins, *J. Chem. Soc.*, **1960**, 2053.
84. K. W. Rosenmund and F. Zymalkowski, *Chem. Ber.*, **86**, 37 (1953).
85. K. W. Rosenmund, F. Zymalkowski and N. Schwarte, *Chem. Ber.*, **87**, 1229 (1954).
86. C. Mannich and M. Dannehl, *Ber.*, **71**, 1899 (1938).
87. I. W. Elliott, Jr. and P. Yates, *J. Org. Chem.*, **26**, 1287 (1961).
88. W. H. Cliffe, *J. Chem. Soc.*, **1933**, 1327.
89. L. P. Zalukaev and R. P. Vorobeva, *Khim. Geterotsikl. Soedin.*, **1968**, 293; *Chem. Abstr.*, **69**, 6768 (1968).
90. B. A. Lugovik and Tr. Omskogo, *Vet. Inst.*, **18**, 248 (1960); *Chem. Abstr.*, **58**, 2433 (1963).
91. A. N. Kost, A. N. Kadenatsii, B. A. Lugovik, E. Kh. Zolotarev, L. G. Yudin and V. V. Lebeder, *Russ. Pat.* 159,529 (1963); *Chem. Abstr.*, **60**, 15082 (1964).
92. G. Reddelien and A. Thurm, *Ber.*, **65**, 1511 (1932).
93. W. H. Cliffe, D. Dodman and O. Meth-Cohn, *J. Chem. Soc. C*, **1966** 514.
94. B. A. Lugovik, L. G. Yudin and A. N. Kost, *Dokl. Akad. Nauk SSSR*, **170**, 340 (1966); *Chem. Abstr.*, **66**, 5224 (1967).
95. J. P. Brown and L. M. Jackman, *J. Chem. Soc.*, **1964**, 3132.
96. J. P. Brown, *J. Chem. Soc. C*, **1968**, 1071.
97. G. Kohl and H. Pracejus, *Ann.*, **694**, 128 (1966).
98. L. P. Zalukajevs and T. I. Zheltukhina, *Dokl. Akad. Nauk SSSR*, **153**, 592 (1963); *Chem. Abstr.*, **60**, 6820 (1964).
99. L. P. Zalukaev and T. I. Zheltukhina, *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.*, **9**, 681 (1966); *Chem. Abstr.*, **66**, 8020 (1967).
100. C. E. Crawforth and O. Meth-Cohn, *J. Chem. Soc. Chem. Commun.*, **1972**, 865.
101. E. E. Schweizer and L. D. Smucker, *J. Org. Chem.*, **31**, 3146 (1966).
102. E. Campaigne and C. D. Blanton, Jr., *J. Heterocycl. Chem.*, **7**, 1179 (1970).
103. P. Davis and W. E. McEwen, *J. Org. Chem.*, **26**, 815 (1961).
104. F. D. Popp, L. E. Katz, C. W. Klinowski and J. M. Wefer, *J. Org. Chem.*, **33**, 4447 (1968).
105. E. O. Snoke and F. D. Popp, *J. Heterocycl. Chem.*, **10**, 99 (1973).
106. L. E. Katz and F. D. Popp, *J. Heterocycl. Chem.*, **5**, 249 (1968).
107. R. Hull, *J. Chem. Soc. C*, **1968**, 1777.
108. M. Ikeda, H. Ishibashi, S. Matsugashita and Y. Tamura, *J. Chem. Soc. Chem. Commun.*, **1973**, 922; M. Ikeda, S. Matsugashita and Y. Tamura, *J. Chem. Soc. Chem. Commun.*, **1974**, 433; M. Ikeda, S. Matsugashita, F. Tabusa and Y. Tamura, *J. Chem. Soc. Perkin Trans. I*, **1976**, 2587; M. Ikeda, S. Matsugashita, F. Tabusa and Y. Tamura, *J. Chem. Soc. Perkin Trans. I*, **1977**, 1166; M. Ikeda, S. Matsugashita and Y. Tamura, *Heterocycles*, **9**, 281 (1978).
109. B. Belleau, R. Martel, G. Lacasse, M. Menard, N. L. Weinberg and Y. G. Perron, *J. Amer. Chem. Soc.*, **90**, 823 (1968).
110. R. R. Martel, R. Berman and B. Belleau, *Can. J. Physiol. Pharmacol.*, **47**, 909 (1969).
111. B. Belleau and G. Malek, *J. Amer. Chem. Soc.*, **90**, 1651 (1968).
112. D. J. Beaver and P. J. Stoffel, *U.S. Pat* 2,857,387 (1958); *Chem. Abstr.*, **53**, 5293 (1959).
113. D. J. Beaver, D. P. Roman and P. J. Stoffel, *J. Amer. Chem. Soc.*, **79**, 1236 (1957).
114. M. S. Atwal, L. Bauer, S. N. Dixit, J. E. Gearien and R. W. Morris, *J. Med. Chem.*, **8**, 566 (1965).

115. Monsanto Chemicals Ltd., *Fr. Pat.* 1,328,176 (1963); *Chem. Abstr.*, **59**, 12770 (1963).
116. J. F. Muren and A. Weissman, *J. Med. Chem.*, **14**, 49 (1951).
117. H. deDiesbach and H. Kramer, *Helv. Chim. Acta*, **28**, 1399 (1945).
118. W. N. Speckamp and H. O. Huisman, *Rec. Trav. Chim.*, **85**, 681 (1966).
119. J. Herzog and K. Budy, *Ber.*, **44**, 1584 (1911).
120. T. Okamoto, M. Hirobe and T. Yamazaki, *Chem. Pharm. Bull. (Tokyo)*, **14**, 512 (1966).
121. J. M. Wefer, A. Catala and F. D. Popp, *J. Org. Chem.*, **30**, 3075 (1965).

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CHAPTER 3

Quinoline *N*-Oxides

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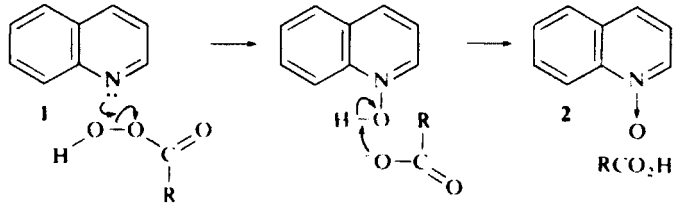
I. Introduction

The quinoline *N*-oxides were first obtained by cyclization of nitrobenzenes with an *ortho*-unsaturated chain, but were not recognized as such (see Section II). Meisenheimer first prepared quinoline *N*-oxide by oxidation of quinoline, using perbenzoic acid, in 1926,[1] and oxidation of the quinoline remains by far the most widely used method of synthesis. In this chapter synthesis by oxidation of quinolines or by cyclization of nitro compounds will be dealt with first. Many *N*-oxides have been prepared by interconversion and these will be tabulated as a particular class of reaction appears, in Section IV. Section III will deal with physical properties of the *N*-oxides. There are two major books on *N*-oxides which include quinoline *N*-oxides,[2,3] and a review.[4]

II. Synthesis of Quinoline *N*-Oxides

1. By Oxidation of Quinolines

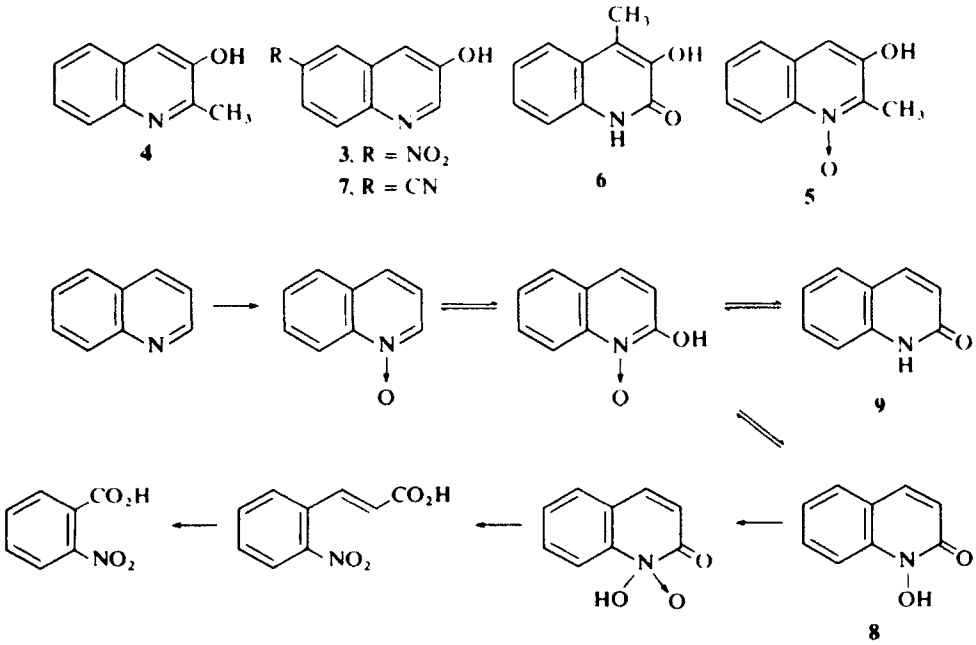
As mentioned above, Meisenheimer first reported[1] the oxidation of quinoline to its *N*-oxide. Relatively few quinoline *N*-oxides were prepared until the 1940s, although Bobranski used monoperphthalic acid (a mixture of phthalic anhydride and hydrogen peroxide),[5,6] and Clemo and McIlwain[7] used a mixture of acetic acid and hydrogen peroxide to oxidize a phenazine, thus establishing all of the common reagents. Ochiai, by far the most prolific worker in the field of *N*-oxides, studied the peroxide oxidation of pyridine,[8] established the necessity of an acid, preferably a carboxylic acid, and established the conditions which have been most commonly used. A mixture of glacial acetic acid with 30% hydrogen peroxide is most satisfactory, and only occasionally has it been necessary to use a stronger acid such as trifluoroacetic,[9] formic[10] or monochloroacetic acid;[11] in all these cases strongly electron-withdrawing groups were present on the quinoline. There seems no doubt about the mechanism, shown below for the conversion of quinoline (**1**) into quinoline *N*-oxide (**2**), but the only mechanistic study in the quinoline series appears to be a measurement of the kinetics of reaction between quinoline and perbenzoic acid in dioxan/water at 25 °C.[12]



For the lower temperature reaction, as well as perbenzoic or monoperphthalic acids, various workers have used *m*-chloroperbenzoic acid,[13] *p*-methoxycarbonylperbenzoic acid (used in suspension in chloroform and said to give a very fast reaction[8,56]) and maleic anhydride with hydrogen peroxide.[14] A mixture of hydrogen peroxide, *t*-butyl alcohol and tungstic acid gave a 70% yield of quinoline *N*-oxide,[15] and *t*-amyl hydroperoxide with molybdenum pentachloride gave 2-methoxycarbonylquinoline *N*-oxide.[16] Benzoyl peroxide in chloroform at 0 °C gave 90% of [2-^{14}C]quinoline *N*-oxide[17] and 3,5-dinitrobenzoylperoxide has been used in boiling benzene to produce quinoline *N*-oxide 3,5-dinitrobenzoate.[18]

There have been several reports of the formation of other oxidation products. Ochiai and his co-workers reported the formation of small amounts of 3-hydroxyquinolines,

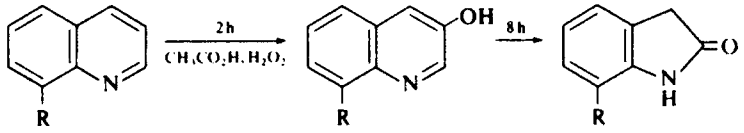
such as (**3**)[19] and (**4**)[20] during peracetic acid oxidations, when the *N*-oxide was the principal product; some 3-hydroxyquinaldine *N*-oxide (**5**) was also isolated,[20] while lepidine gave the 3-hydroxycarbostyril (**6**).[21] In the oxidation of 6-cyanoquinoline some 6-cyano-3-hydroxyquinoline (**7**) was formed.[22] An exhaustive study of the oxidation of quinoline *N*-oxide by hydrogen peroxide, with and without acetic acid, showed that it was possible to obtain 1-hydroxycarbostyril (**8**), carbostyril (**9**), 3-hydroxyquinoline and eventually *o*-nitrobenzoic acid.[23] The proposed route is shown in an abbreviated form in Scheme 1.



SCHEME 1

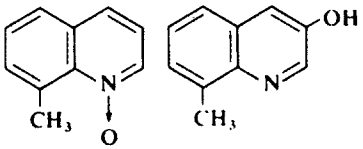
The formation of 3-hydroxyquinolines replaces *N*-oxide formation when a sterically obstructive group is present at position 8 of the quinoline.[19,24] Oxidation of the acid (**10**) or the ester (**11**) gave yields of 36% and 21% of the respective 3-hydroxy derivatives,[19] and oxidation of 8-nitroquinoline (**12**) gave 21% of 3-hydroxy-8-nitroquinoline. Prolonged oxidation of compounds (**10**)–(**12**) gave the oxindoles (**13**)–(**15**), but no such ring contraction products were obtained from 8-methylquinoline, which gave some *N*-oxide (**16**) (8%) and some 3-hydroxy-8-methylquinoline (**17**) (9%).[24] The formation of *N*-oxides from 8-substituted quinolines is obviously delicately balanced, since 8-fluoro (**18**)[25] and 8-hydroxyquinoline (**19**)[26] can be converted into the *N*-oxides, although the yield of 8-fluoro-*N*-oxide is lower than that of the other benzo-substituted fluoroquinolines (see p. 390, 391).

Peracetic acid oxidation of 2-phenylquinoline (**20**)[27] or of 2-phenylquinoline-4-carboxylic acid (**21**)[28] gave *N*-benzoylanthranilic acid (**22**). A thorough study of the peracetic acid oxidation of 8-hydroxyquinoline (**19**) showed that nicotinic acid *N*-oxide (**23**) could be formed;[29] oxidation of 2-methylaminoquinoline gave *cis*-(*o*-nitrophenyl)acrylonitrile (**24**),[30] possibly via the route shown in Scheme 2.

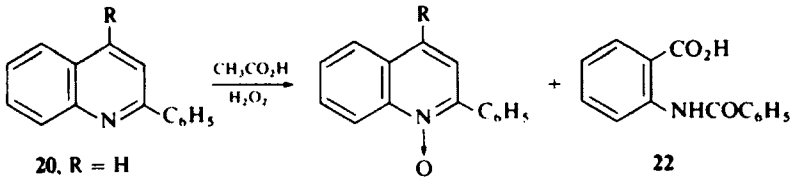


10, R = CO_2H 36%
11, R = $CO_2C_2H_5$ 21%
12, R = NO_2 21%
18, R = F
19, R = OH → *N*-oxides

13, R = CO_2H; 16%
14, R = $CO_2C_2H_5$; 17%
15, R = NO_2; 18%

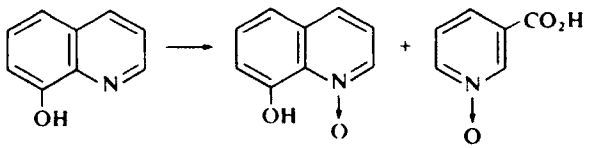


16 **17**

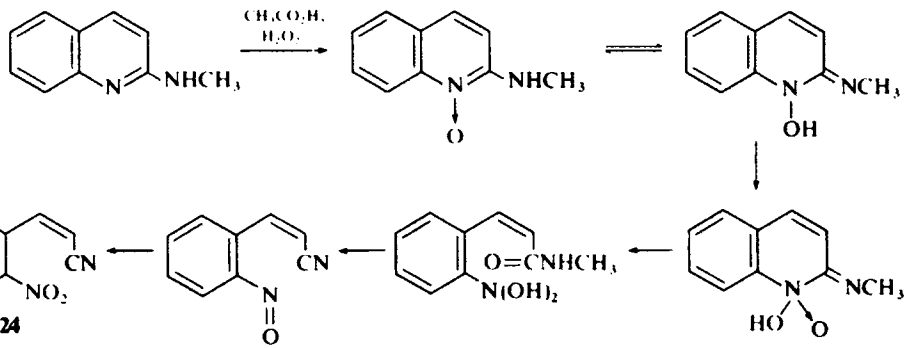


20, R = H
21, R = CO_2H

22



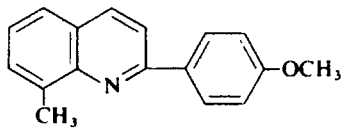
19 **23**



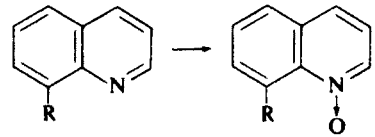
24

SCHEME 2

There are a number of cases where the presence of a methyl group in the 8-position (*peri* to the nitrogen lone pair) has been said to prevent oxidation to give the *N*-oxide. The difficulty with the 2-substituted compound (**25**)[31] is more easily understood than is the absence of *N*-oxide formation in 3,8-, 6,8- or 7,8-dimethylquinolines.[32] In some cases a combination of electron withdrawal and steric hindrance may prevent oxidation; peracetic acid[24] or monoperphthalic acid[33] oxidation of 8-nitroquinoline (**26**) failed, though 8-acetamidoquinoline (**27**) gave a 90% yield of *N*-oxide.[34]

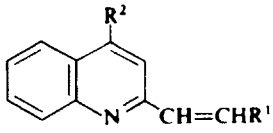


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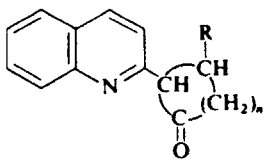


26, R = NO_2; 0%
27, R = $NHCOCH_3$; 90%

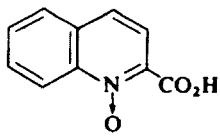
The range of substituents tolerant of the oxidizing conditions during *N*-oxide formation is surprisingly large. Oxidation of tetrahydroquinaldine *N*-oxide has been reported to give quinaldine *N*-oxide[823] or the tetrahydroquinaldine *N*-oxide.[82] Alkyl groups are normally unaffected, including those with double bonds if the double bond is deactivated [as in the arylvinylquinolines (**28**)–(**30**)[35-37]]. Prolonged oxidation of the 2-quinolylcycloalkanones (**31**) and (**32**) gave quinaldinic acid *N*-oxide (**33**).[38,39]



28, $R^1 = C_6H_5$, $R^2 = H$
29, R^1 = 5-nitrofuryl, $R^2 = H$
30, R^1 = 5-nitrofuryl, $R^2 = CH_3$



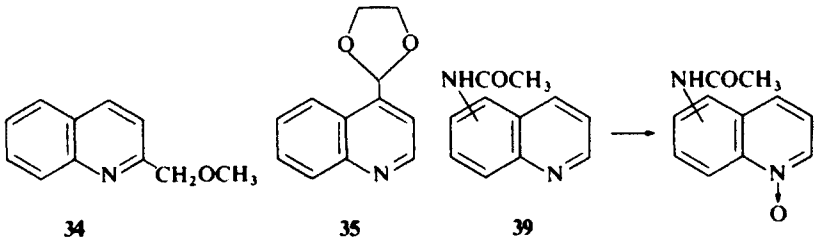
31, R = H, $n = 3$
32, R = $CO_2C_2H_5$, $n = 2$



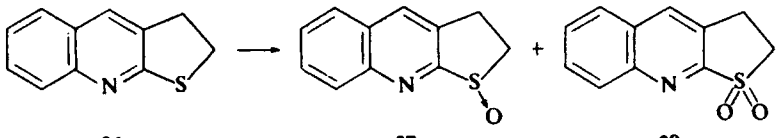
33

More easily oxidized groups, such as hydroxymethyl or aldehyde, must be protected; examples are provided by compounds (**34**)[40] and (**35**).[41] The cyclic sulphide (**36**) has been reported to be oxidized preferentially on sulphur, giving the sulphoxide (**37**) or dioxide (**38**).[42] Amino groups, whether on the quinoline ring or on side-chains, are particularly susceptible to oxidation and must be protected, usually by conversion into amides or carbamates. All the aminoquinolines except the 4-amino compound have been prepared in excellent yield by peracetic acid oxidation of the acetamides (**39**);[34] 7-chloro-4-aminoquinoline *N*-oxide (**41**) has been obtained through the diacetylamino derivative (**40**)[43] and 2-aminoquinoline *N*-oxide[44] and 8-aminoquinoline *N*-oxide[45] through the carbamates (**42**) and (**43**). Of particular interest was the preparation of 2-aminoquinoline *N*-oxide directly by using hydrogen peroxide, sodium tungstate and EDTA, which was necessary for reasonable yields;[46] 2-nitroquinoline was also formed.

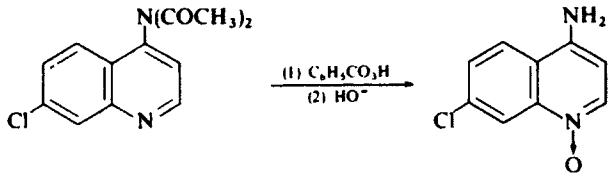
Tertiary amines present special problems as substituents. Dialkylamino substituents on side-chains are in general more rapidly oxidized than the heterocyclic nitrogen atom, as is shown by the case of 2-(*p*-dimethylaminostyryl)quinoline (**44**), which with perbenzoic acid gives the *N*-oxide (**45**).[35] The quinine alkaloids have been converted into



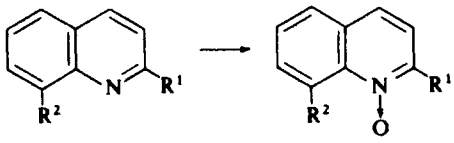
34 35 39



36 37 38

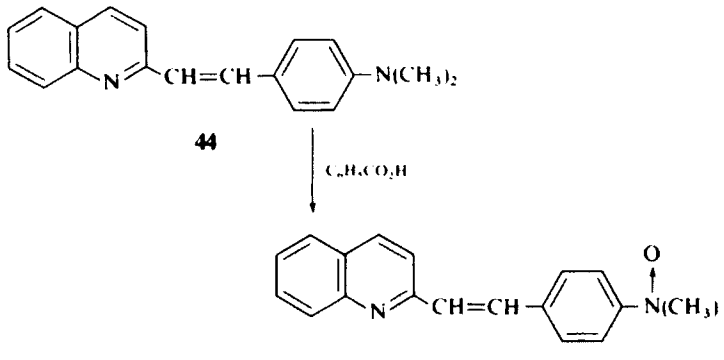


40 41

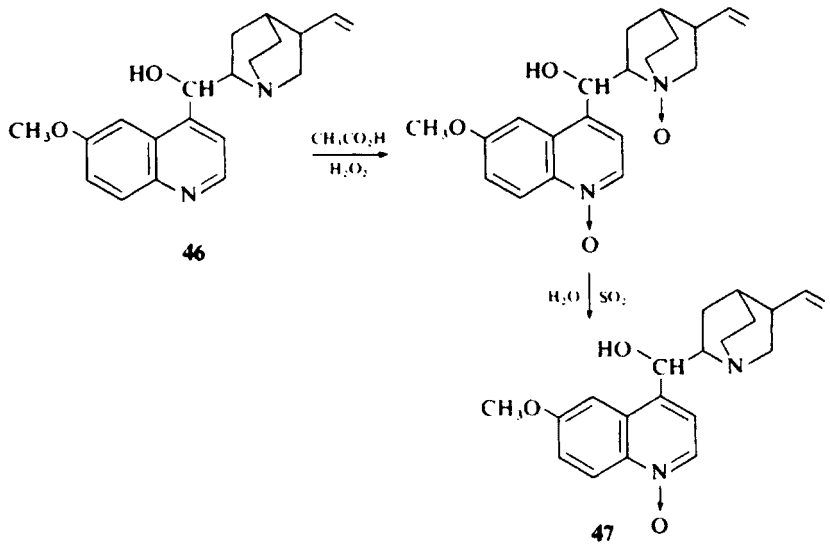


42, $R^1 = NHCO_2C_2H_5$, $R^2 = H$
43, $R^1 = H$, $R^2 = NHCO_2C_2H_5$

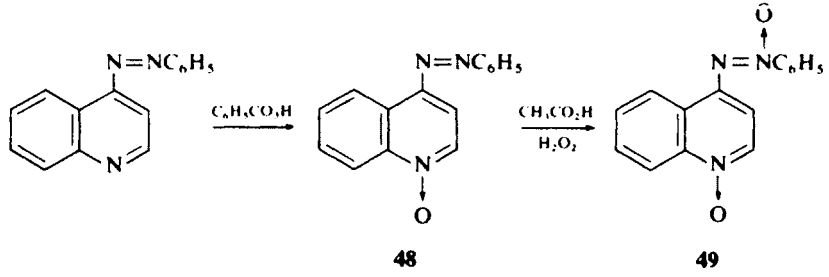
their *N*,*N*′-dioxides by peracetic acid, and then reduced by sulphur dioxide which preferentially attacks the quinuclidine *N*-oxide.[47-49] Quinine (**46**) thus gives the aryl *N*-oxide (**47**).[47]

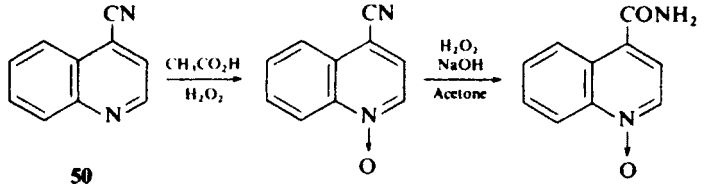


44 45



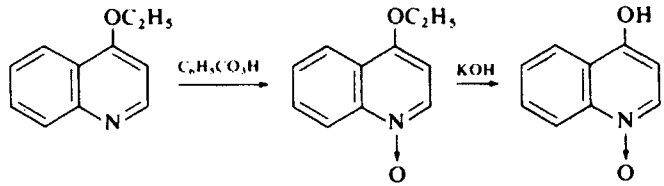
This sequence illustrates also the stability of the secondary alcohol group, and of the vinyl side-chain. Oxidation of 4-(phenylazo)quinoline with perbenzoic acid gave the *N*-oxide (**48**), which was further oxidized to 4-(phenylazoxy)quinoline (**49**) by peracetic acid.[50] Nitrogen-containing functional groups which are stable to the oxidation conditions are azides,[51,11] sulphonamides[40] and nitriles,[52,53,22] although nitriles are



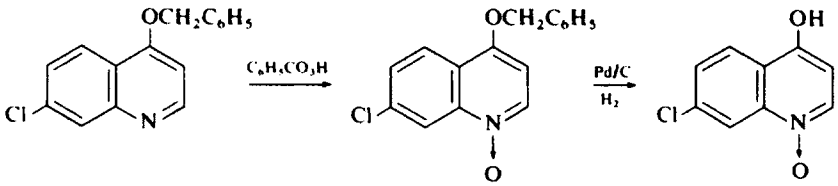


readily converted into amides by alkaline hydrogen peroxide, as shown for 4-cyanoquinoline (**50**).[52]

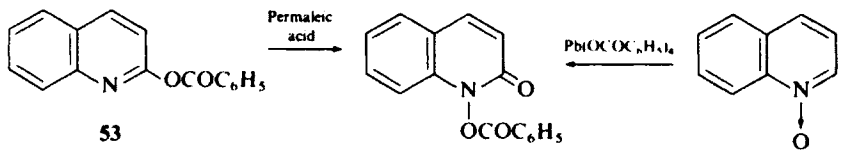
Nuclear hydroxyl groups are generally stable towards oxidizing agents, although in most cases which have been reported their ethers have been oxidized. Subsequent cleavage was either by hydrolysis,[54] as in example (**51**), or by catalytic reduction if a benzyl protecting group was used, as in example (**52**).[55] Halogen substituents are also generally stable; there are examples of *N*-oxides formed from all four types of halogenoquinoline, including 5-iodoquinoline.[56] For the more reactive 2- and 4-halogenoquinolines it is probably safer to minimize hydrolysis by using perbenzoic acid[57-59] or permaleic acid.[14] Bromomethyl-[60] or chloromethylquinolines[40] and 2-dibromomethylquinoline[60] have been oxidized by peracetic acid in satisfactory yield.



51



52



53 **54**

Oxidation of 2-benzyloxyquinoline (**53**) gave *N*-benzoyloxycarbostyril (**54**),[61] also obtained by the action of lead tetrabenzoate on quinoline *N*-oxide, presumably by rearrangement of 2-benzoyloxyquinoline *N*-oxide. Quinoline *N*-oxides prepared by oxidation are grouped in Table 1.

TABLE 1. Quinoline *N*-Oxides Prepared by Direct Oxidation of Quinolines. Substituted quinolines are arranged in the following main groups: alkyl- and arylquinolines; halogeno- and nitroquinolines; quinoline ketones; hydroxyquinolines (including thiols); quinolinecarboxylic acids; and aminoquinolines (including azidoquinolines). Multi-substituted quinolines will appear in the latest group possible; thus, a methylnitrohydroxyquinoline would appear with the hydroxyquinolines. Within main groups alkyl appear before aryl groups, all monosubstituted derivatives before any disubstituted derivatives, and isomers in order of ring numbering.

Quinoline substituent	Oxidizing agent	Temperature (°C)	Yield (%)	References	M.p. or B.p. (°C) and derivatives
None	Perbenzoic acid	Room	100	1, 64	62 ($2H_2O$);[1] 65–67;[62] 68.5–69.5[63] m.p.; 171–172/4 mmHg;[65] picrate m.p. 143[1,64] HCl m.p. 131–132;[1,64]
	3,5-Dinitrobenzoyl peroxide	Boiling benzene	—	18	3,5-dinitrobenzoate m.p. 145;[18] tartrate m.p. 121 (needles), 138 (plates);[66] α-bromo-*d*-camphorsulphonate m.p. 125[66]
	H_2O_2, *t*-C_4H_9OH, tungstic acid	60–65	70	15	
	Phthalic anhydride perhydrol	< 15	70	62, 805	
	PA (30%)[a]	Water-bath	Almost quant.	65, 67–72	
	t-Amylhydroperoxide, $MoCl_5$		Quant.	73, 16, 74	
2-^{14}C-	Benzoyl peroxide/$CHCl_3$	0	90	17	152–153/3 mmHg
5,6,7,8-Tetrahydro	PA (30%)	68–71	87	75, 63	151–153/3 mmHg;[75] 117–119/0.4 mmHg;[63] 68.5–69.5 m.p.
5,6,7,8-$^3H_4$	Benzoyl peroxide			76	
2-Methyl	PA (30%)	75–80	70	20, 77–79	77–78 m.p.[80,81] Picrate 173–174;[81] hydrochloride 202[80]
	Perbenzoic	Cold	V.good	81	Hydriodide 167;[80] platinichloride 201[80]
	H_2O_2, sodium tungstate EDTA	60–65	48	46	
2-Methyl-5,6,7,8-tetrahydro	PA (30%)	75–80	76.6	82	82–84 m.p.; 142–144/0.2 mmHg; picrate 99–99.5

[a] PA(%) = H_2O_2/AcOH using % H_2O_2.

2-Methyldecahydro	PA (30%)	70	61	83	258–259 m.p. (H_2O)[83]
2-Ethyl	PA (30%)	50–60	70	84, 85	75 m.p. ($2H_2O$);[84] 192–194/14 mmHg[85]
2-*n*-Heptyl	Perbenzoic acid	Cold	55	43	37–38 m.p.
2-Bromomethyl	Monoperphthalic acid	Cold	14	60	137.5–138 m.p.
2-Dibromomethyl	PA (30%)	—	67	60	108–109 m.p.
2-Chloromethyl	PA (30%)	65–75	31	40	125–126 m.p.
2-Trifluoromethyl	CF_3CO_2H, H_2O_2	Water-bath	51	9	100–101 m.p.
2-Hydroxymethyl[b]	Perphthalic acid	—	90	40	131 m.p.
2-(β-Carboxyethyl)	PA (30%)	60–80	68	40	162 m.p.
2-$(EtO_2C)_2CH(NHAc)CH_2$	PA (30%)	70	—	86	183–187 m.p.
2-Styryl	Perbenzoic acid	—	—	35	127–128 m.p.
2-β-(5-Nitrofuryl)vinyl	Perbenzoic acid	—	—	36	211–212 m.p.
	Pa (30%)	65–70	60	87–89, 37	210 (dec.) m.p.,[88] 215–216 m.p.[37]
1,2-Bis(2-Quinolyl)-ethylene	Pa (30%)	Water-bath	—	90	243 (dec.) m.p.
2-Phenyl	Monoperphthalic acid	Room	10–12	91	141 m.p. Hydrochloride 150; picrate 187
	PA (30%)	60–70	—	92, 27, 93	131–141 m.p.;[92] 144 m.p.[27]
5,6,7,8-Tetrahydro-2-phenyl	PA (30%)	70–80	68	63	144–145 m.p.
2-(*o*-Methoxyphenyl)	Perbenzoic acid	0–5	—	64	178–178.5 m.p.; picrate 133–134
2-(*p*-Methoxyphenyl)	PA (30%)	80	62.5	94	130 m.p.
2-(*p*-Nitrophenyl)	PA (30%)	80	66	94	225–226 m.p.
2-(2,4,6-Trimethylphenyl)	Perbenzoic acid	3–5	90	95	139–140 m.p.
2-(2-Quinolyl)	Monoperphthalic acid (1 equiv.)	Room	—	96	170 m.p.
	O_2, $KOBu^t$[c]	70	10	96	
2-(1-Oxido-2-quinolyl)	Monoperphthalic acid	Room	—	96	248–250 m.p.
	PA (30%)	70–80	85	97, 98	246.5–248 m.p.;[97] 257[98]
3-Methyl	PA (30%)	65–70	—	32, 99	81–83 m.p.[32]
3-Ethyl	PA (30%)	65–70	—	99	83–84 m.p.[99]
5,6,7,8-Tetrahydro-3-methyl	PA (30%)	80	—	100	—
3-Trifluoromethyl	Trifluoroperacetic acid	Water-bath	81	9, 101	116–118 m.p.[9]

[b] Oxidation performed on 2-acetoxymethylquinoline with subsequent hydrolysis.
[c] Quinoline *N*-oxide was used.

TABLE 1 (*cont.*)

Quinoline substituent	Oxidizing agent	Temperature (°C)	Yield (%)	References	M.p. or B.p. (°C) and derivatives
3-(Dicarbethoxymethyl)	*m*-Chloroperbenzoic acid	—	—	13	—
3-Phenyl	PA (30%)	65–70	38	102	123–124 m.p.
3-(*p*-Nitrophenyl)	PA (30%)	65–70	25	102	258.5–259.5 m.p.
4-Methyl	Monoperphthalic acid	—	—	103	121 m.p.
	PA (30%)	90	70	21, 104	113–115 m.p.;[21] picrate 179–181;[21] benzoate 76–78;[105] chloroacetate 89–90;[105] 3,5-dichlorobenzoate 129;[105] 3,5-dinitrobenzoate 157–158[105]
4-[6-(1-Oxido-4-quinolyl)hexan-1-yl]	Perbenzoic *or* PA			106	184–186 m.p.
4-(2-Pyridylmethyl)	PA (30%)	80–85	73[d] 82[e]	107	173–173.5 m.p. *NN'*-dioxide 234–236 (dec.)
4-(2-Quinolylmethyl)	PA (30%)	70–80	70	108	196–197 m.p.
4-(3-Ethylquinuclidin-8-ylmethanol)	PA (30%)	70–80	—	48, 49	237–238.5 m.p. (dihydrocinchonine)[48]
	Monoperphthalic acid	Room	—	109	208–209 m.p. (dihydrocinchonidine);[49] dihydrocinchonidine di-*N*-oxide 208–209
4-(3-Vinylquinuclidin-8-ylmethanol)	Monoperphthalic acid	Room	—	109	223.5–224.5 m.p. (cinchonine); cinchonine di-*N*-oxide 171.5–172; 228 m.p. (cinchonidine); cinchonidine di-*N*-oxide 198
4-(β-Phenylvinyl)	Perbenzoic acid	—	—	35	175–176 m.p.
4-(*p*-Dimethylaminophenylvinyl)	PA (30%); then SO_2	50–55	30	110	208–209 m.p.
4-(5-Nitrofuran-2-ylvinyl)	PA (30%)	70–80	—	88, 89	221–222 (dec.) m.p.[89]
4-Phenyl	Monoperphthalic acid	Room	96	91	122 m.p.[91]
	PA (30%)	60–70	—	92	Picrate 230
5-Methyl	PA (30%)	65–70	50	111	115–116 m.p. (H_2O)

[d] From 4-(2-pyridylmethyl)quinoline.
[e] From 2-pyridyl(1-oxidoquinolin-4-yl)acetonitrile.

6-Methyl	PA (30%)	70	81	112, 103, 113, 62	51.5–52.0 m.p.;[112] 75 m.p.;[103] 172–175/3 mmHg
6-Methyl	H_2O_2, sodium tungstate, EDTA	60–65	93	46	Picrate 178–178.5
6-R[f]	Monoperphthalic acid	—	—	114	223–226 m.p.; diacetyl 220–222; free amine 234–235; dichloroacetyl derivative m.p. 205 (dec.)
8-Methyl	PA (30%)	70	8	24	57–59 m.p.
8-Methyl	H_2O_2, sodium tungstate, EDTA	60–65	10.6	46	
Di- and Polysubstituted					
2,3-Dimethyl	PA (30%)	—	70	115	130–131 m.p.
2,4-Dimethyl	PA (30%)	—	74	115, 116	118–120 m.p.
2,6-Dimethyl	PA (30%)	Boil	67	117	82.5–82.8 m.p.
2,7-Dimethyl	PA (30%)	Boil	78	117	73.6–73.9 m.p.
3,6-Dimethyl	PA (30%)	—	66	32	69–71 m.p.
3,7-Dimethyl	PA (30%)	—	63	32	131–132 m.p.
6,7-Dimethyl	PA (30%)	—	48	32	165–167 m.p.
2,3-Cyclobutano 2,3-Cyclohexano	*m*-Chloroperbenzoic acid	0–5	84	118	177–179 m.p.
2,4-Decacyclophano	PA (30%)	80	—	119	125–127 m.p.
3,4-Dihydro-3,3-dimethyl-1*H*-pyrano[4,3-*b*]	PA (30%)	—	—	120	90–91 m.p.; picrate 131–133
2,3,4-Trimethyl	PA (30%)	—	95	115	168–170 m.p.
2-Methyl-4-(β-5-nitro-furylvinyl	PA (30%)	70	—	37	226–227 m.p.
2-Ethyl-4-(β-5-nitro-furylvinyl)	PA (30%)	70	—	37	173.5–174.5 m.p.
2-Acetoxymethyl-4-(β-5-nitrofurylvinyl)	PA (30%)	70	—	37	188–189.5 m.p.
2-Methyl-4-phenyl	Monoperphthalic acid	Room	98	91, 121	138–139 m.p.;[121] hydrochloride 166;[91] picrate 136–138[91]
2-(β-5-Nitrofurylvinyl) 4-methyl	PA (30%)	70	—	37	210–212 m.p.
2-Phenyl-3-methyl	PA (30%)	Boiling point	75	95	170–171 m.p.

[f] R = $HOCH_2(Cl_2CHCONAc)CH(OH)$—.

TABLE I (*cont.*)

Quinoline substituent	Oxidizing agent	Temperature (°C)	Yield (%)	References	M.p. or B.p. (°C) and derivatives
2-(*m*-Chlorophenyl-6-methyl	Perbenzoic acid	Cold	76	122	132–134 m.p.
2-(*p*-Methoxyphenyl)-6-methyl	Perbenzoic acid	Cold	88	31	163 m.p.
2-(*p*-Methylphenyl)-6-methyl	Perbenzoic acid	Cold	58	122	188–189 m.p.
2-(*p*-Chlorophenyl)-7-methyl	Perbenzoic acid	Cold	54	122	198–199 m.p.
2-(*p*-Methoxyphenyl)-7-methyl	Perbenzoic acid	Cold	75	31	145 m.p.
2,4-Diphenyl	PA (30%)	70–80	—	92	116–118 m.p.
5,6,7,8-Tetrahydro-2,4-diphenyl	PA (30%)	—	—	123	—
2,6-Dimethyl-4-(β-5-nitrofurylvinyl)	PA (30%)	70	—	37	227–229 m.p.
2,7-Dimethyl-4-(β-5-nitrofurylvinyl)	PA (30%)	70	—	37	217–218.5 m.p.
2-Ethyl-6-methyl-4-(β-5-nitrofurylvinyl)	PA (30%)	70	—	37	158.5–159.5 m.p.
2-Methyl-6-ethyl-4-(β-5-nitrofurylvinyl)	PA (30%)	70	—	37	194–195 m.p.
Halogenoquinolines					
2-Chloro	Permaleic acid	Room	41–51	14	90–93 m.p.;[14] 105–107 m.p. (H_2O)[11]
	Chloroacetic acid, H_2O_2	—	25	11	
2-Bromo	Permaleic acid	Room	55–58	14	141–142 m.p.[14]
3-Fluoro	PA (30%)	70–80	94	25, 124	118 m.p.;[25] picrate 130[25]
3-Chloro	PA (30%)	70	80	125	103–104 m.p.
3-Bromo	PA (30%)	75	30	126, 807	96–101 m.p.; picrate 218–219; hydrochloride 194–196
5-Fluoro	PA (30%)	70–80	60	25	176 m.p.; picrate 136
5-Chloro	PA (30%)	—	—	127	134–136 m.p.
5-Iodo	PA (30%)	—	90	56	159–161 m.p.

6-Fluoro	PA (30%)	70–80	30	25	100 m.p.
6-Chloro	Perphthalic acid	15	—	805	126.5 m.p.; dihydrate 55–59
7-Fluoro	PA (30%)	70–80	63	25	67 m.p.
8-Fluoro	Monoperphthalic acid	0	10.5	25	64 m.p.; picrate 128
4,7-Dichloro	Perbenzoic acid	—	42	57, 58	165–166 m.p.
2-Chloro-4-methyl	Permaleic acid	Room	60–70	14	154–156 m.p.
2-Bromo-4-methyl	Permaleic acid	Room	55–58	14	141–142 m.p.
2-Methyl-4-chloro	Perbenzoic acid	Room	50[g]	59	135 m.p.; picrate 145.5; hydrochloride 173–174
4-Chloro-3-(2-chloro ethyl)-2-methyl	Monoperphthalic acid	Cool	—	42	108–109 m.p.
3-Chloro-2,4-deca-cyclophano	PA (30%)	80	—	119	159–160 m.p.
7-Chloro-2-methy-4-(β-5-nitrofurylvinyl)	PA (30%)	70	—	37	293 (dec.) m.p.
4,7-Dichloro-2-methyl	PA (30%)	—	—	128	286 m.p.
Nitroquinolines					
3-Nitro	Monoperphthalic acid	Ice-cold	10[h]	129	192–193 m.p.
5-Nitro	Monoperphthalic acid	—	79	33	155–157 m.p.
6-Nitro	Monoperphthalic acid	Room	67.5	103, 130, 805	221 (dec.) m.p.[131]
	H_2O_2, sodium tungstate, EDTA	60–65	15	46	
	Perbenzoic acid	Room	—	131	
6-Nitro- *and* 3-hydroxy-6-nitro	PA (30%)[i]	85	32–41	132, 133, 19	3-Hydroxy-6-nitroquinoline-*N*-oxide, m.p. 285[19]
7-Nitro	Monoperphthalic acid	Ice-cold	35	91, 129	174–175 m.p.[129] Monoperoxyphthalate 109 (dec.)
	PA (30%)	75–80	55	134	
8-Nitro	PA (30%)	70	None	24, 33	
2-Methyl-6-nitro	PA (20%)	60–70	65	135	118–119 m.p.
2-Methyl-8-nitro	PA (20%)	60–70	10	135	225–227 m.p.
7-Methyl-8-nitro	PA	70	75	136	246 m.p.

[g] Yield of crude picrate.
[h] On unrecovered 3-nitroquinoline.
[i] Added pyridine or pyridine-*N*-oxide as catalyst was said to be necessary.[19]

TABLE 1 (*cont.*)

Quinoline substituent	Oxidizing agent	Temperature (°C)	Yield (%)	References	M.p. or B.p. (°C) and derivatives
7,8-Dimethyl-5-nitro	PA (30%)	70	20	131	186–187 m.p.
Cyclopentano[*b*]-5-nitro	Monoperphthalic acid	Cold	—	137	185–185.5 m.p.
Cyclopentano[*b*]-8-nitro	Monoperphthalic acid	Cold	—	137	162–163 m.p.
Cyclohexano[*b*]-8-nitro	Monoperphthalic acid	Cold	—	137	149–151 m.p.
Cyclohexano[*c*]-5-nitro	Monoperphthalic acid	Cold	—	137	176–178 m.p.
5-Nitro-3-(*p*-nitrophenyl)	PA (30%)	65–70	50	102	263–265 m.p.
3-Bromo-5-nitro	PA (20%)	70	80	138	149–150 m.p.
Aldehydes and Ketones					
4-(Dioxolan-2-yl)	PA	—	—	41	—
4-Acetyl	PA (30%)	60–70	45	139, 140	103 m.p.
4-Benzoyl[j]	PA (33%)	70	73	141, 140	105–107 (dec.) m.p.
Hydroxyl- and Thiol-substituted Quinolines and Ethers					
2-Hydroxy	Perbenzoic acid	Room	3	55, 142	189–191 m.p.
2-Ethoxy	PA	56	35	143, 144	71–73 m.p. (H_2O); picrate 124–125[143]
5-Methoxy	PA (20%)	60–70	70	145	106–107 m.p.
5-Tosyloxy	PA	—	—	127	141–142 m.p.
6-Methoxy	PA (30%)	50	90	146, 103, 62	91–92 m.p.;[62k]
	Monoperphthalic acid	15	—	805	picrate 175–176[147]
6-Ethoxy	PA	Water-bath	—	148	51 m.p.
7-Methoxy	PA	—	—	127	78–80 m.p.
7-(*p*-Tosyloxy)	PA	—	—	127	157–158.5 m.p.
8-Hydroxy	Perbenzoic acid	0	—	149, 28	138–139.5 m.p.
	Monoperphthalic acid	—	—	150, 151	
	PA (30%)[l]	80	45	29, 152, 26, 150	
8-Methoxy	Perbenzoic acid	0	—	149	Picrate 133–134
8-Ethoxy	Perbenzoic acid	0	22	149	61–62 m.p.;[28] hydrochloride
	PA (30%) + acetic anhydride	45–50	61	28	158;[28] picrate 137–139[149]

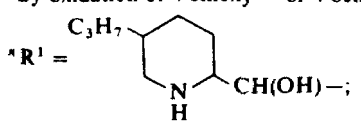
[j] From 4-quinolylphenylacetonitrile.

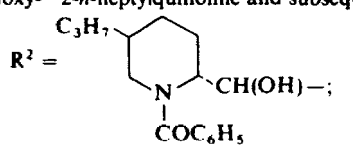
[k] *Chem. Abstr.* gives m.p. 186–187 °C in ref. 146.

[l] Said to go in 'better' yield (40%) by use of more dilute H_2O_2.[29]

8-Propoxy	Perbenzoic acid	0	25	149	Hydrochloride 132–134
8-Isopropoxy	Perbenzoic acid	0	12	149	Hydrochloride 135–136 (dec.)
8-Butoxy	Perbenzoic acid	0	13	149	Hydrochloride 120–121.5; picrate 119–120
8-Isoamyloxy	Perbenzoic acid	0	16	149	Hydrochloride 114–115.5; picrate 115–116
8-*n*-Hexyloxy	Perbenzoic acid	0	37	149	Hydrochloride 107–108; picrate 101.5–102.5
8-*n*-Heptyloxy	Perbenzoic acid	0	41	149	45–46.5 m.p.; hydrochloride 109–110; picrate 88.5–89
8-*n*-Octyloxy	Perbenzoic acid	0	38	149	Hydrochloride 117.5–118.5; picrate 98–99
8-*n*-Nonyloxy	Perbenzoic acid	0	—	149	Hydrochloride 114.5–116; picrate 98–100
8-*n*-Decyloxy	Perbenzoic acid	0	42	149	52–54 m.p.; hydrochloride 115.5–117; picrate 105.5–106.5
8-*n*-Undecyloxy	Perbenzoic acid	0	22	149	Hydrochloride 118.5–120; picrate 102–103
6,7-Methylenedioxy	PA	70	54	153	179–180 m.p.
2-Ethoxy-4-methyl	PA	50	35	154	61 m.p.; picrate 144–145
2-*n*-Heptyl-4-hydroxy[m]	Perbenzoic acid	Cold	—	54, 43	158–160 m.p.[54]
6-*n*-Heptyl-4-hydroxy	Perbenzoic acid	Cold	—	43	183 m.p.
7-Chloro-4-hydroxy-2-methyl	PA	80	75	806	278–280 m.p.
6-Methoxy-2-methyl	PA (30%)	—	76	115	118 m.p.;[103] 154–156 m.p.;[115]
	Monoperphthalic acid	Cold	—	103	Hydrochloride 195 (dec.);[103] picrate 144–146[103]
6-Methoxy-4-methyl	Monoperphthalic acid	Cold	—	103	146 m.p.; hydrochloride 209; picrate 168
6-Methoxy-4-R[1][n]	PA (30%)	60–63	18	155	128–129 m.p.
6-Methoxy-4-R[2][n]	PA (30%)	60–63	60	155	198 m.p.
6-Methoxy-4-R[3][n]	PA (30%)	60–63	85	155	182 m.p.; debenzylated product m.p. 140

[m] By oxidation of 4-ethoxy-[54] or 4-benzyloxy-[43]2-*n*-heptylquinoline and subsequent hydrolysis.

[n] R[1] = 

R[2] = 

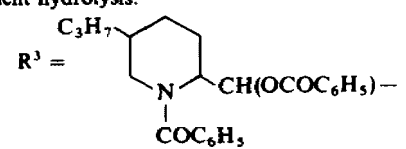
R[3] = 

TABLE 1 (*cont.*)

Quinoline substituent	Oxidizing agent	Temperature (°C)	Yield (%)	References	M.p. or B.p. (°C) and derivatives
6-Methoxy-4-(3-ethyl-quinuclidin-8-ylmethanol	PA (30%) Monoperphthalic acid	— Room	— —	156, 47 109	Dihydroquinine methiodide 260–262, monothiocyanate 224–226; dihydroquinine *NN'*-dioxide monothiocyanate 225–227, dihydrobromide 182–184;[156] dihydroquinidine 188; dihydroquinidine *NN'*-dioxide monothiocyanate 188–189 (dec.)[109]
6-Methoxy-4-(3-vinyl-quinuclidin-8-ylmethanol)	PA (30%)	—	—	156, 47	Quinine monothiocyanate 225–227; monohydriodide 197–199; methiodide 255–257;[156] quinine *NN'*-dioxide m.p. 178–179;[109] monothiocyanate 210–212; dihydrobromide 159–161; dihydrochloride 210–212;[156] quinidine-*N*-oxide m.p. 176–178; *NN'*-dioxide thiocyanate 191–192 (dec.)[109]
6-Methoxy-2-phenyl	Perbenzoic acid	0–5	55–65	64	170–171 m.p.
6-Methoxy-2-(*m*-chlorophenyl)	Perbenzoic acid	0–5	67	64	153–154 m.p.
6-Methoxy-2-(*p*-chlorophenyl)	Perbenzoic acid	0–5	73	64	166–168 m.p.; picrate 171–172
6-Acetoxy-2-methyl-4-(β-5-nitrofurylvinyl)	PA (30%)	70	—	37	176 m.p.
6-Methoxy-2-methyl-4-(β-5-nitrofurylvinyl)	PA (30%)	70	—	37	207–208 m.p.
7-Ethoxy-2-methyl-4-(β-5-nitrofurylvinyl)	PA (30%)	70	—	37	201–202 m.p.
2,5,7-Trimethyl-8-hydroxy	PA/CH_2Cl_2	Room	61	157	126–126.5 m.p.
7-Chloro-2-hydroxy	Perbenzoic acid	—	—	142	190–192 m.p.
4-Benzyloxy-7-chloro	Perbenzoic acid	—	65	55	163 m.p.
7-Chloro-4-hydroxy-2-methyl	PA (30%)	80	74.5	158	278–280 (dec.)
5-Chloro-8-hydroxy	Perbenzoic acid	0	—	149	169–170 m.p.

3-Hydroxy-6-nitro[o]	PA (30%)	80	27	19	285 m.p.
Carboxylic Acids and Derivatives: Nitriles; Amides					
2-Carboxylic acid	PA	100	55	52, 159	172–173 m.p.;[159] hydrazide 191;[52] amide m.p. 217[160]
2-Methoxycarbonyl[p]	*t*-Amyl hydroperoxide, $MoCl_5$		90	16, 73, 74	89–90 m.p.
2-(*N*-Phenyl-*N*-methyl-carboxamido)	PA	60	—	161	153–154 m.p.
2-Cyano	PA (30%)	60–70	90	160, 53, 162	169–170 m.p.[53]
3-Cyano	PA	—	10	22	171–172 m.p.
4-Carboxylic acid[q]	PA (30%)	Boiled	—	95, 27, 93	261 m.p.;[27] methyl ester 156;[52] hydrazide 204;[52] amide 243[52]
4-Cyano	PA (30%)	80–95	76	53, 163, 22, 52	189–190 m.p.[22]
5-Methoxycarbonyl	PA (30%)	80	77.5	873	83–87 m.p.; picrate 158–161
6-Carboxylic acid	PA (30%)	75–80	70	40	305–307 m.p.
6-Cyano	PA	—	24	22	201–202 m.p.
2,4-Dicarboxylic acid	Performic acid	—	32	10	272–273 m.p.
2-Cyano-5-methoxycarbonyl	PA (30%)	85	90.5	873	189–191 m.p.
4-Methyl-2-carboxylic acid[r]	PA	—	—	164	174–175 m.p.
2-Cyano-4-methyl	PA	100	80	164, 162	179–181 m.p.
4-Phenyl-2-carboxylic acid	H_2O_2/acetone	Room	—	91	Acetone peroxide complex m.p. 129
2,3-Dimethyl-4-carboxylic acid	PA	—	25	165	229 m.p.
2-Phenyl-4-carboxylic acid	PA	Boiling or room	75	28, 165, 166	260 m.p.;[165] methyl ester[166] 122–123; ethyl ester 88–90;[166] propyl ester 80[166]
4-Chloro-2-cyano	PA (30%)	70	80	160, 162	114–115 m.p.; amide 221
6-Chloro-2-cyano	PA	—	76	167	257 m.p.; amide 286
2-Cyano-4-methoxy	PA	100	62	162	—

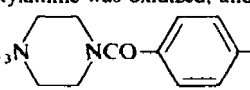
[o] From 6-nitroquinoline in 1% yield.[19]
[p] Also prepared by reaction of acid with diazomethane.[52]
[q] Also by hydrolysis (HNO_2/H_2SO_4) of amide.[52]
[r] From 2-(cyclohexa -2-on-1-yl)-4-methylquinoline.

TABLE 1 (*cont.*)

Quinoline substituent	Oxidizing agent	Temperature (°C)	Yield (%)	References	M.p. or B.p. (°C) and derivatives
2-Cyano-4-ethoxy	PA	100	60	162	—
2-Cyano-6-ethoxy	PA	—	70	167	160 m.p.; amide 212
3-Methoxy-4-carboxamide[a]	PA (30%)	70–75	49	168	243–244 m.p.
4-Cyano-3-methoxy	PA	75	75	168, 169	236–237 m.p.[169]
Amines and Derivatives					
2-Amino	10% H_2O_2, Na tungstate, EDTA	60–65	66	46	
2-Acetamido	PA (30%)	70	72	34	199–200 m.p.;[34] free amine[34] 168–169;[34] amine picrate 196–205[170]
2-Ethoxycarbonylamino	PA (30%)	70	91	170, 44	102–104 m.p.;[44] picrate 157–157.5[170]
3-Acetamido	PA (30%)	70	85	34, 171	285–286.5 m.p.;[34] free amine 189–190[34]
5-Acetamido	PA (30%)	70	72	34	231–231.5 m.p.; free amine 201–202.5
6-Acetamido	PA (30%)	70	80	34	203–205 m.p.; free amine 125–127
7-Acetamido	PA (30%)	70	79	34	261 m.p.; free amine 240–242
8-Acetamido	PA (30%)	70	90	34	191 m.p.; free amine 112
8-Ethoxycarbonylamino	PA (30%)	60–70	66	45	128–129 m.p.
4-Amino-2-*n*-heptyl[f]	Perbenzoic acid	0	40	43	176–177 m.p.
4-Amino-6-*n*-heptyl[f]	Perbenzoic acid	0	—	43	211–212 m.p.
5-Acetamido-2-(β-5-nitrofurylvinyl)	PA (30%)	65–70	—	88	251 (dec.) m.p.
7-Trifluoromethyl-4-R^1[e]	—	—	—	172	—
7-Chloro-4-diacetylamino	Perbenzoic acid	0	55	43	137–138 m.p.
7-Chloro-4-R^1[e]	—	—	—	172	—
7-Chloro-4-R^2[g]	Perbenzoic acid	Room	19	58, 57	162–165 m.p. (dec.)
8-Acetamido-6-methoxy	Monoperphthalic acid	—	30	33	118–120 m.p.

[a] Also by hydrolysis of 3-methoxy-4-cyanoquinoline.[168]

[f] The diacetylamine was oxidized, and the amide group subsequently hydrolysed.

[e] R^1 =  ; by oxidation of 7-X-4-(*p*-$CNCH_2O_2CC_6H_4NH$), then treatment with *N*-methylpiperazine.

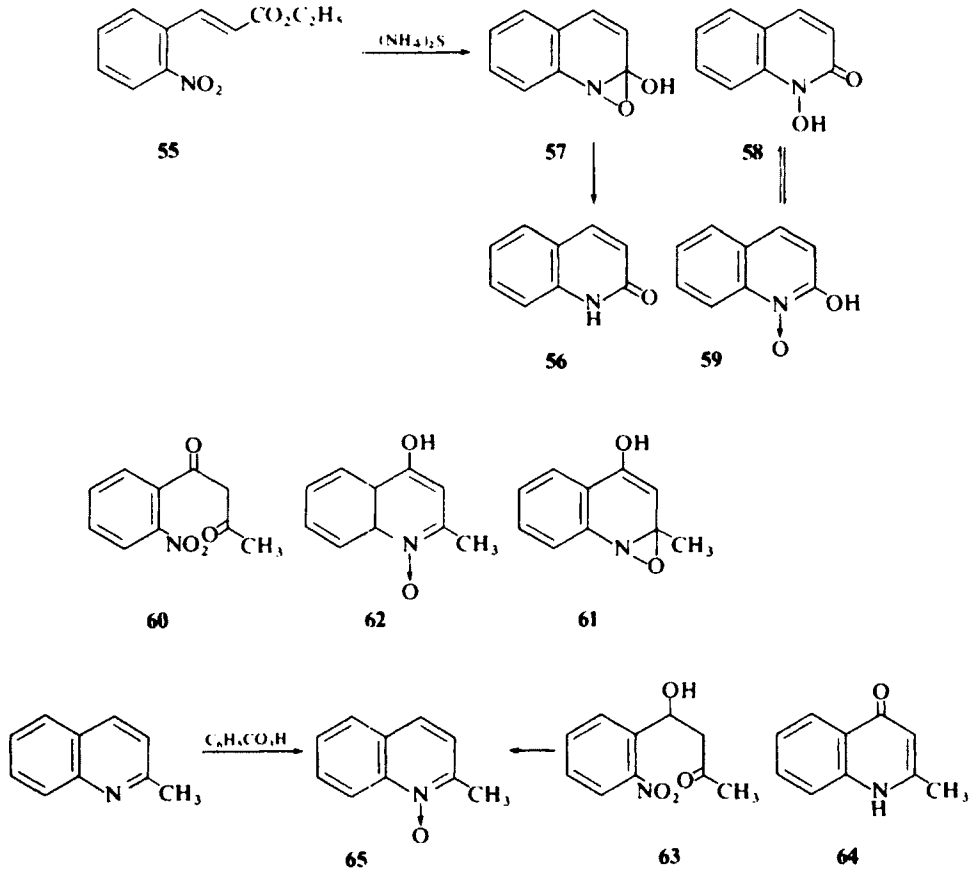
[g] R^2 = 3-$Et_2N(O)CH_2$-4-$HOC_6H_3NCH_3$.

Miscellaneous					
3-Azido	PA (30%)	70–80	90	11	136–137 (dec.) m.p.
4-Azido	PA (30%)	60–70	33	51	141–142 m.p. (explodes); picrolonate 168; hydrochloride 179 (dec.)
5-Azido	PA (30%)	60–70	84	11	157–158 m.p.
6-Aminosulphonyl	PA (30%)	70–75	—	40	219–220 m.p.
4-Phenylazo	Perbenzoic acid	0–5	~100	50	168–169 m.p.
4-Phenylazoxy	PA	—	—	50	181–182 m.p.
4-(*p*-Bromophenylazo)	PA	—	—	50	173–174 m.p.
4-(*p*-Chlorophenylazo)	PA	—	—	50	176–177 m.p.
4-(2,4-Dibromophenylazo)	PA	—	—	50	218 m.p.
4-(2,4-Dichlorophenylazo)	PA	—	—	50	230–231 m.p.

2. By Cyclization of 2-Nitrophenyl Derivatives

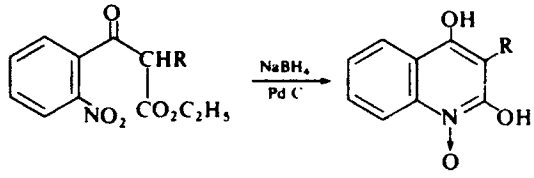
A. Reductive Cyclizations

Reductive cyclization pre-dates direct oxidation as a route to quinoline *N*-oxides. Friedlander and Ostermaier reported in 1881 that ammonium sulphide reduction of ethyl *o*-nitrocinnamate (**55**) gave a compound which on further reduction gave carbostyril (**56**).[173] Von Niementowski suggested that this compound was the oxaziridine (**57**), but it was actually 1-hydroxycarbostyril (**58**) or the tautomeric 2-hydroxyquinoline 1-oxide (**59**). Gabriel and Gerhard suggested[174] an oxaziridine structure (**61**) for the reduction product from *o*-nitrobenzoylacetone (**60**), but this was corrected by McCluskey[175] to 2-methyl-4-hydroxyquinoline *N*-oxide (**62**). Heller and Sourlis[80] recorded the reduction of 4-(*o*-nitrophenyl)butan-4-ol-2-one (**63**) to 2-methyl-4-quinolone (**64**), but Meisenheimer and Stotz[81] showed the reduction product to be identical with quinaldine *N*-oxide (**65**) prepared by perbenzoic acid oxidation of quinaldine.

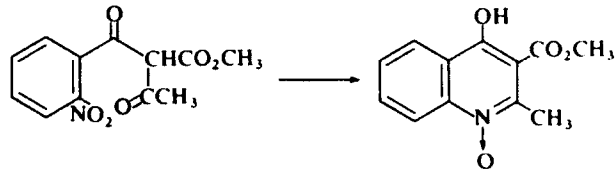


In general, reduction of *o*-nitrophenylbutan-3-ones gives the corresponding *N*-oxide, whereas reduction of an *o*-nitrocinnamate gives the 2-hydroxyquinoline *N*-oxide. Straightforward examples of these reactions are provided by the syntheses of compounds

(**62**) and (**65**) above and of compound (**66**)–(**69**),[176] where the reducing agent was sodium borohydride and palladium/charcoal in methanol. In the case of compound (**69**) cyclization to the ketone function was preferred to cyclization on the ester.

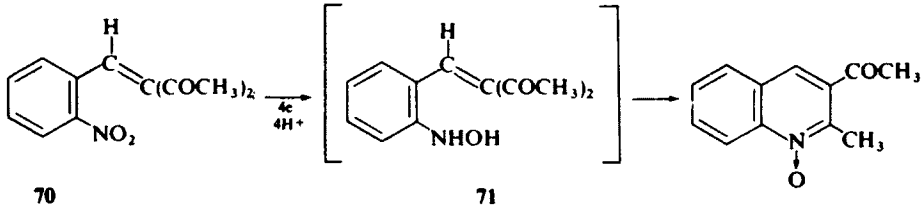


66, R = H
67, R = CN
68, R = $CO_2C_2H_5$



69

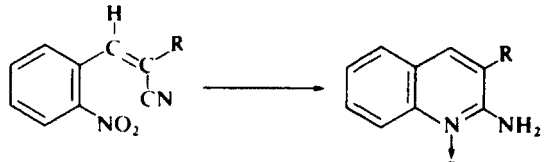
Other reducing agents used include tin(II) chloride and hydrochloric acid,[175,174] palladium/charcoal and cyclohexene;[177] controlled electrochemical reduction of compound (**70**) was said[178] to proceed via the intermediate hydroxylamine (**71**), using four electrons and four protons with elimination of one molecule of water.



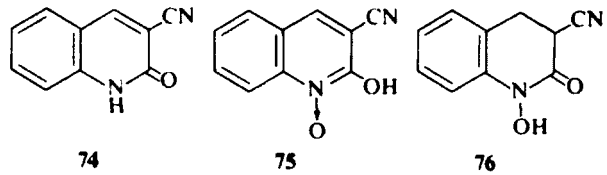
70 **71**

When the side-chain contains an appropriately placed nitrile the 2-aminoquinoline *N*-oxide is generally formed, as in the electrochemical reduction of *o*-nitrobenzylidene cyanoacetate (**72**)[178] or the reduction by zinc and acetic acid of the corresponding cyanoacetamide (**73**).[179–181] In both cases catalytic hydrogenation follows the same course.[180,182] In the case of compound (**72**), reduction by sodium borohydride with palladium/charcoal in methanol gave a mixture of the 3-cyano-2-quinolone (**74**), the *N*-oxide (**75**) and, under some conditions, the dihydro derivative (**76**).[182]

The direction of cyclization may depend on the stereochemistry about the double bond in compounds of type (**72**) and (**73**) where the smaller nitrile group would normally be adjacent to the *o*-nitrophenyl group, but Coutts noted[182] that *trans–cis* isomerization had occurred when 3-cyano-2-quinolone was formed.



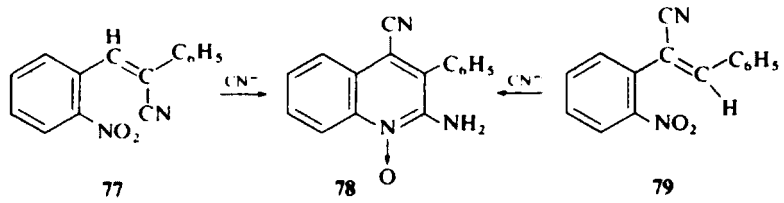
72. R = $CO_2C_2H_5$
73. R = $CONH_2$



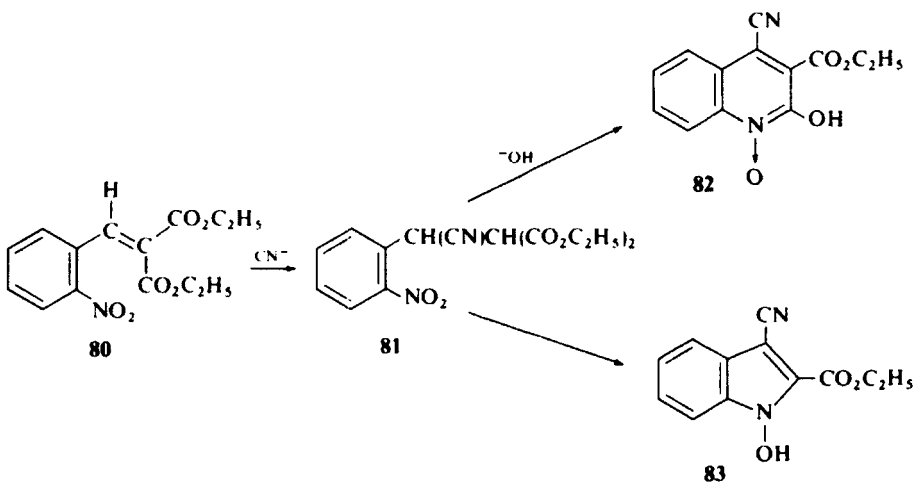
74 75 76

B. Cyclization by Non-reductive Methods

These reactions have been reviewed,[183] and are dealt with briefly here. Brand and Loehr[184] treated the *o*-nitrocinnamonitrile (**77**) with potassium cyanide and obtained a compound formulated as $C_{17}H_{13}ON_3$, which was shown by Loudon and Tennant[185] to be the *N*-oxide (**78**). The cyclization is obviously initiated by addition of cyanide ion to



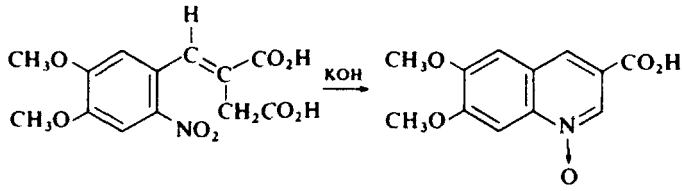
77 78 79



80 81 82 83

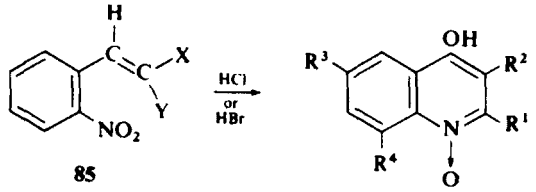
the α,β-unsaturated nitrile, and this was confirmed when the same product (**78**) was obtained from the isomeric nitrile (**79**).

In a similar manner *o*-nitrobenzylidene malonate (**80**) adds cyanide to give compound (**81**), which can be cyclized to the *N*-oxide (**82**).[186] Both cyclizations can lead to indoles instead of quinolines, as shown by the conversion of compound (**81**) into compound (**83**). The reaction has been studied in detail by Sword,[187] who suggested that quinoline formation was favoured when strongly electron-withdrawing groups are present. The cyanide group may be hydrolysed to a carboxamide (see Table 2 for examples). A more conventional cyclization of the aldol type is that of *o*-nitroveratrylidenesuccinic acid, by aqueous potassium hydroxide, to give the quinoline *N*-oxide (**84**).[188,189]

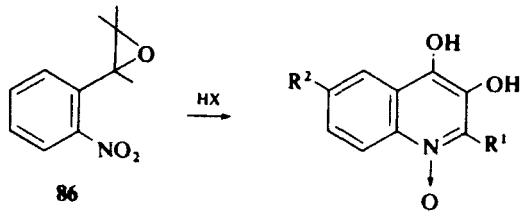


84

The other major cyclization mode is initiated by anhydrous hydrogen chloride or hydrogen bromide on an *o*-nitrobenzylidene derivative (**85**).[190,191] When hydrogen chloride is used, a 6-chloroquinoline *N*-oxide may be formed, though substitution is not observed with hydrogen bromide, or when quinol is added to the solution with hydrogen chloride. With hydrogen chloride, when the 6-position is blocked, the 8-position undergoes substitution. Closely related is the cyclization of epoxides of general type (**86**) by hydrogen chloride.[192,193]



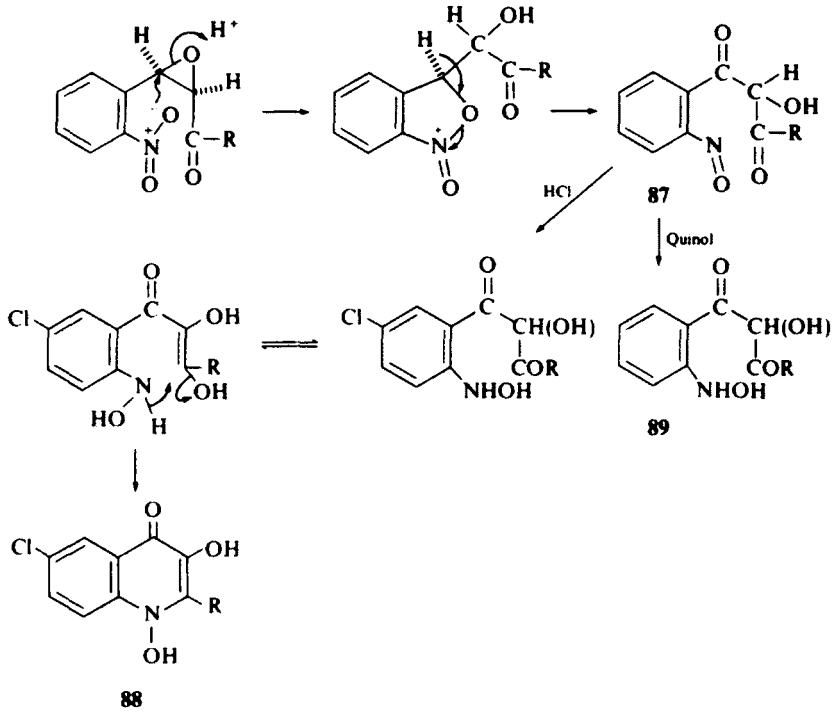
85



86

A detailed mechanism has been suggested for the cyclization of the epoxides, involving an intermediate nitroso compound (**87**) which can react with hydrogen chloride to give

the 6-(or 8-)chloro compound (**88**), but which with quinol gives the hydroxylamine (**89**). A steric effect was noted, with high yields in the compounds where *o*-nitrophenyl and acyl groups were in a *cis* arrangement.



N-Oxides prepared by cyclization of nitro compounds are listed in Table 2.

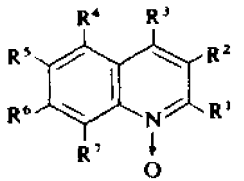
3. By Ring Expansion

A few quinoline *N*-oxides have been prepared from anthranils or oxindoles. Taylor and Bartulin[204] treated anthranil with active methylene compounds and isolated either 2-aminoquinoline *N*-oxides, such as (**90**)–(**92**) or 2-hydroxyquinoline *N*-oxides (*N*-hydroxy-2-quinolones) such as (**93**) and (**94**). The suggested mechanism (Scheme 3) passes through an intermediate (**95**) such as is postulated for the cyclization of nitro compounds (p. 401).

Treatment of 3-carboxymethylanthranil (**96**) with 10% hydrochloric acid gave 1,4-dihydroxy-2-quinolone (**97**),[200] whereas an *N*-oxide was postulated as intermediate in the production of tetrahydroacridine (**98**) from anthranil and cyclohexanone.[205]

The oxindole derivatives (**99**) and (**100**) gave, with alcohols and triethylamine, aminoquinoline *N*-oxides (**101**)–(**103**).[206]

TABLE 2. Quinoline *N*-Oxides Prepared by Cyclization of Nitro Compounds



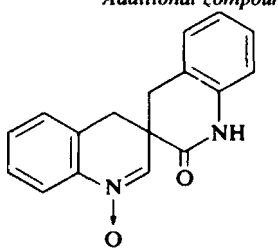
R^1	R^2	R^3	R^4	R^5	R^6	R^7	Cyclizing agent	Yield (%)	References	M.p. (°C) and derivatives
CH_3	—	—	—	—	—	—	Zn/acetic acid	—	80, 81, 94	77–78 m.p.;[81] hydrochloride 202;[80] hydriodide 167;[80] platinichloride 201;[80] picrate 173–174[81]
OH	—	—	—	—	—	—	$(NH_4)_2S$	—	173, 195	190.5 m.p.;[173] ethyl ether 73
OH	CH_3	—	—	—	—	—	$(NH_4)_2S$	—	154	182 m.p.
CH_3	—	OH	—	—	—	—	$SnCl_2$ or HI, P	—	175	247 m.p.;[175] *chloroplatinate* 229–230;[175] picrate 171;[175] *monobenzoyl* 236;[175] dibenzoyl 171[175]
							$NaBH_4$; Pd,C	86	176	
							Pd,C; cyclohexene	61	177	
n-C_7H_{15}	—	OH	—	—	—	—	$SnCl_2$, acetic acid, HCl	35	54	158–160 m.p.
n-C_9H_{19}	—	OH	—	—	—	—	$SnCl_2$, acetic acid, HCl	35	54	148–149 m.p.
n-$C_{11}H_{23}$	—	OH	—	—	—	—	$SnCl_2$, acetic acid, HCl	65	54	148.5–149.5 m.p.
C_6H_5	—	OH	—	—	—	—	$SnCl_2$ or HI, P	65	196	249.5 m.p.
OH	—	OH	—	—	—	—	$NaBH_4$; Pd,C	61	176	275–276 m.p.
OH	n-C_3H_7	OH	—	—	—	—	NH_2NH_2/Pd,C	68	99	115–116 m.p.
OH	i-C_3H_7	OH	—	—	—	—	NH_2NH_2/Pd,C	89	99	142–143 m.p.
OH	n-C_4H_9	OH	—	—	—	—	NH_2NH_2/Pd,C	43	99	107–108 m.p.
OH	i-C_4H_9	OH	—	—	—	—	NH_2NH_2/Pd,C	54	99	158–159 m.p.
CH_3	OH	OH	—	—	—	—	HCl, ether, quinol	—	193	204–210 m.p.
CH_3	OH	OH	—	Cl	—	—	HCl, ether	—	193	235 m.p.
C_6H_5	OH	OH	—	—	—	—	HCl, ether, quinol	—	193, 197	175–180 m.p.

TABLE 2 (*cont.*)

R^1	R^2	R^3	R^4	R^5	R^6	R^7	Cyclizing agent	Yield (%)	References	M.p. (°C) and derivatives
C_6H_5	OH	OH	—	Cl	—	—	HCl, ether	—	193, 197	264 m.p.;[197] 270 m.p.;[193] hydrochloride 264.[197]
CH_3	$COCH_3$	—	—	—	—	—	Electrochemical reduction	69	178	147–148 m.p.
CH_3	$COCH_3$	OH	—	Cl	—	—	HCl, ether	—	190	286 (dec.) m.p.; 1-acetyl 166; 1-methyl ether 172
OH	CO_2H	—	—	—	—	—	Electrochemical reduction	—	198	259–261 m.p.[182]
OH	$CO_2C_2H_5$	—	—	—	—	—	$NaBH_4$; Pd,C	—	182	167–169 m.p.; 3,4-dihydro 135–137
OH	CN	—	—	—	—	—	$NaBH_4$; Pd,C	—	182	234–238 m.p.
CH_3	CO_2CH_3	OH	—	—	—	—	$NaBH_4$; Pd,C	98	176	192–193 m.p.
CH_3	$CO_2C_2H_5$	OH	—	—	—	—	$SnCl_2$, HCl	100	175	174 m.p.;[175] chloroplatinate 203; free acid 209 (dec.); hydrobromide 140[191]
							HCl, ether, quinol	90	191	
CH_3	$CO_2C_2H_5$	OH	—	Cl	—	—	HCl, ether	45	190, 191	226 (dec.) m.p.; free acid 236; diacetyl 155; free acid monoacetyl 190; hydrobromide 135[191]
CH_3	$CO_2C_2H_5$	OH	—	Br	—	—	HBr, ether	70	191	Hydrobromide 140; acetoxy 211
CH_3	$CO_2C_2H_5$	OH	—	Cl	—	Cl	HCl, ether	60	191	233 m.p.; free acid 258
CH_3	$CO_2C_2H_5$	OH	—	Br	—	Cl	HCl, ether	55	191	193 m.p.; acetoxy 137
n-C_7H_{15}	CO_2H	OH	—	—	—	—	$SnCl_2$, HCl	low	54	173 m.p.
$C_2H_5O_2C$-CH_2	$CO_2C_2H_5$	OH	—	Cl	—	—	HCl, ether	—	190	202 (dec.) m.p.
	CO_2H	—	—	OCH_3	OCH_3	—	20% KOH	87	188, 189	282–283 (dec.) m.p.;[189] methyl ester 211–212;[189] ethyl ester 214–215[189]
OH	$CO_2C_2H_5$	OH	—	—	—	—	$NaBH_4$; Pd,C	59	176	168–169 m.p.
OH	CN	OH	—	—	—	—	$NaBH_4$; Pd,C	99	176	228–229 (dec.) m.p.
C_6H_5	—	CN	—	—	—	—	KCN, C_2H_5OH	—	187	149 m.p.
CH_3	$COCH_3$	$CONH_2$	—	—	—	—	KCN, C_2H_5OH	41	187	260 m.p.; free acid 219 (dec.); methyl ester 152

C_6H_5	COC_6H_5	$CONH_2$	—	—	—	—	KCN, C_2H_5OH	—	187	270 m.p.; free acid 251 (dec.); methyl ester 169 (dec.)
C_6H_5	$CH_2COC_6H_5$	$CONH_2$	—	—	—	—	$NaOC_2H_5$, C_2H_5OH	56	187	224 (dec.) m.p.; free acid 266 (dec.); methyl ester 165
CH_3	$CO_2C_2H_5$	CN	—	—	—	—	KCN, C_2H_5OH	3[a]	187	132 m.p.; 3,4-dicarboxylic imide 257 (dec.)
NH_2	C_6H_5	—	—	—	—	—	Pd, H_2	—	199	184–185 m.p.
NH_2	—	OH	—	—	—	—	Zn, ammonia	—	200	276 (dec.) m.p.; 4-methyl ether 192 (hydrochloride 214)
OH	NH_2	—	—	—	—	—	$NaBH_4$; Pd,C	—	201	190–192 m.p.; hydrochloride 238–240; diacetyl 233–235
NH_2	CO_2H	—	—	—	—	—	$NaBH_4$; Pd,C	—	182	323–325 m.p.
							Zn dust, acetic acid	80	180	
NH_2	$CO_2C_2H_5$	—	—	—	—	—	Pd,H_2	—	199	141–142 m.p.
NH_2	$CONH_2$	—	—	—	—	—	H_2, Pt O_2	55	180	303 m.p.[180]
							Zn dust, acetic acid	50	179–181	
NH_2	C_6H_5	CN	—	—	—	—	KCN,NH_4Cl	—	190	236 m.p.; acetyl 238
NH_2	CN	OH	—	—	—	—	Electrochemical reduction	75	202[b]	—
NH_2	CO_2CH_3	OH	—	—	—	—	Cyclohexene; Pd,C	51	177	Hydrochloride 230–232
NH_2	$CO_2C_2H_5$	OH	—	—	—	—	Cyclohexene; Pd,C	43	177	189–190 m.p.; hydrochloride 261–262

Additional compounds

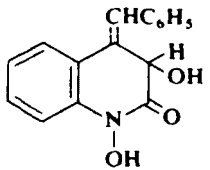
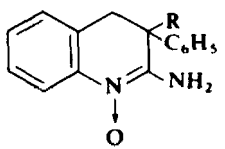


From $(o\text{-}NO_2C_6H_4CH_2)_2C(COCH_3)CO_2C_2H_5$ by $SnCl_2$/AcOH/HCl reduction;[203] m.p. 184 °C

[a] +68% of the dicarboxylic acid imide.

[b] Many other compounds, substituted on the benzene ring, were also prepared.

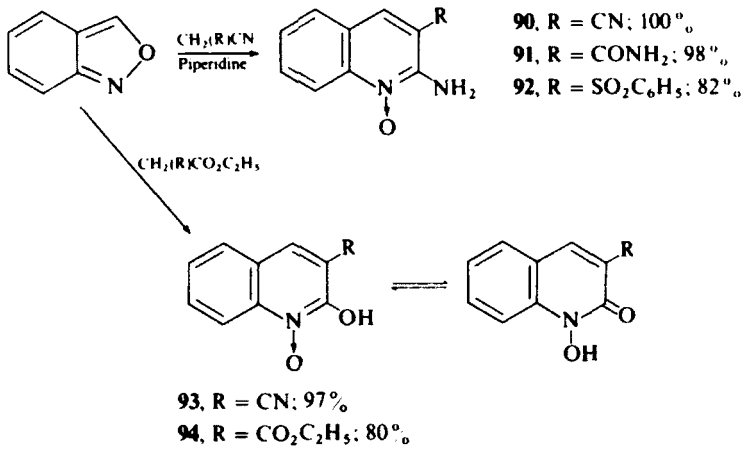
TABLE 2 (*cont.*)

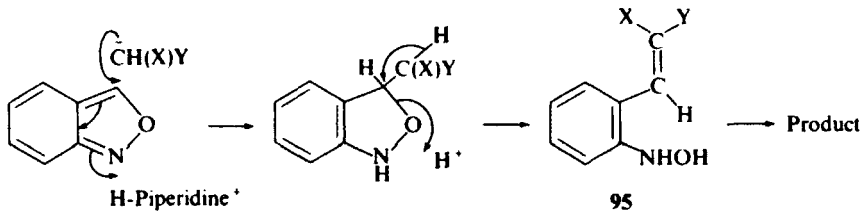
R^1	R^2	R^3	R^4	R^5	R^6	R^7	Cyclizing agent	Yield (%)	References	M.p. (°C) and derivatives
										
										

From $C_6H_5CH{=}C(C_6H_5)COCO_2C_2H_5$ by Pd/C, $NaBH_4$ reduction:[201] m.p. 244–245 °C

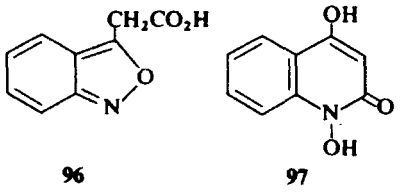
From C_6H_5-C(R)(CN)$CH_2C_6H_4NO_2$-*o* by Sn or Fe/dil. HCl *or* Pd/C/H_2.[814]

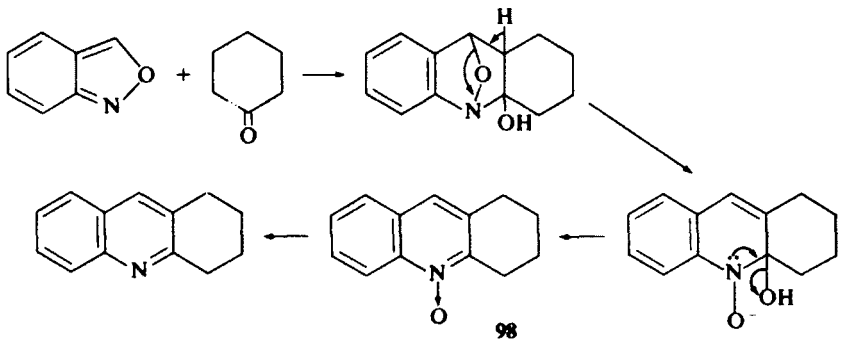
R	CH_3	C_2H_5	i-C_3H_7	C_6H_5	$C_6H_5CH_2$
%	68	60	50	80	60
M.p.(°C)	213–214	224–225	232–233	218–219	234–235

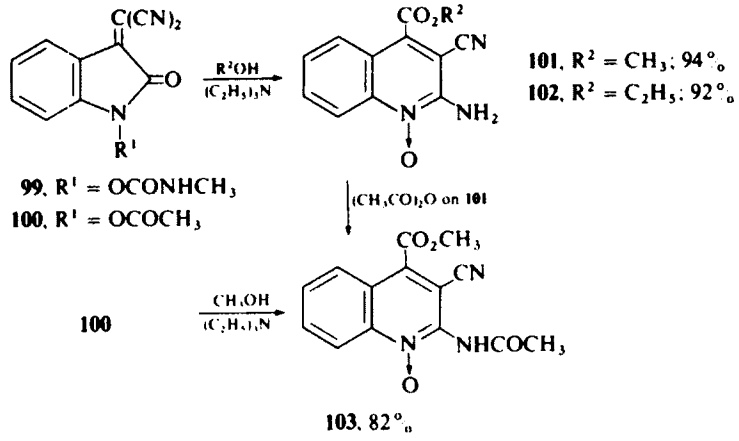

CH2(R)CN
Piperidine
CH2(R)CO2C2H5
90, R = CN; 100%
91, R = CONH2; 98%
92, R = SO2C6H5; 82%
93, R = CN; 97%
94, R = CO2C2H5; 80%


CH(X)Y
H-Piperidine+
H+
Product
95

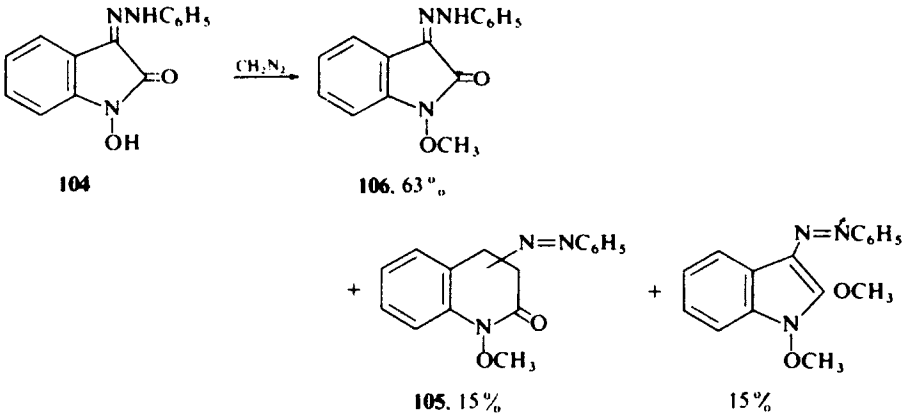
SCHEME 3


96
97


98



The related phenylhydrazone (**104**) reacted with diazomethane to give some 3,4-dihydro-1-methoxy-*x*-phenylazo-2-quinolone (**105**) (the position of the azo group was not established); the major product was the methyl ether (**106**).[207] Oxides prepared by ring expansion are collected in Table 3.



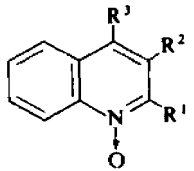
III. Properties and Reactions

1. Physical Properties

A. Electronic Spectra

Quinoline *N*-oxide and simple alkyl quinoline *N*-oxides show two main bands in the electronic spectrum, one around 230 nm and one which varies from 313 to 351 nm depending on the solvent. The spectra in ethanol and in heptane are shown in Fig. 1, where they are compared with the spectrum of quinoline and of the isoelectronic α-naphthoate anion.[208] The shorter wavelength band is clearly of a π–π^* transition, but

TABLE 3. Quinoline *N*-Oxides Prepared by Ring Expansion



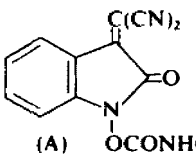
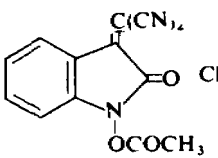
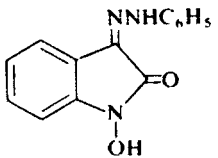
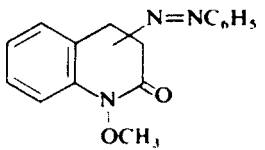
Starting material	Reagent	R^1	R^2	R^3	Yield (%)	References	M.p. (°C) and derivatives
3-Carboxymethyl anthranil	HCl, H_2O	OH	—	OH	—	200	276 (dec.) m.p.; dimethyl ether ether 124; 1-methyl ether 264
Anthranil	$CH_2(CO_2C_2H_5)_2$, piperidine	OH	$CO_2C_2H_5$	—	80	204	
Anthranil	$CH_2(CN)CO_2C_2H_5$, piperidine	OH	CN	—	97	204	
Anthranil	$CH_2(CN)CONH_2$, piperidine	NH_2	$CONH_2$	—	98	204	
Anthranil	$CH_2(CN)_2$, piperidine	NH_2	CN	—	100	204	
Anthranil	$CH_2(CN)SO_2C_6H_5$, piperidine	NH_2	$SO_2C_6H_5$	—	82	204	
 (A)	CH_3OH,$(C_2H_5)_3N$	NH_2	CN	CO_2CH_3	94	206	233 m.p.
(A)	C_2H_5OH,$(C_2H_5)_3N$	NH_2	CN	$CO_2C_2H_5$	92	206	197 m.p.
	CH_3OH,$(C_2H_5)_3N$	NH $COCH_3$	CN	CO_2CH_3	82	206	189 m.p.

TABLE 3 (*cont.*)

Starting material	Reagent	R^1	R^2	R^3	Yield (%)	References	M.p. (°C) and derivatives
	CH_2N_2				15	207	157 m.p.

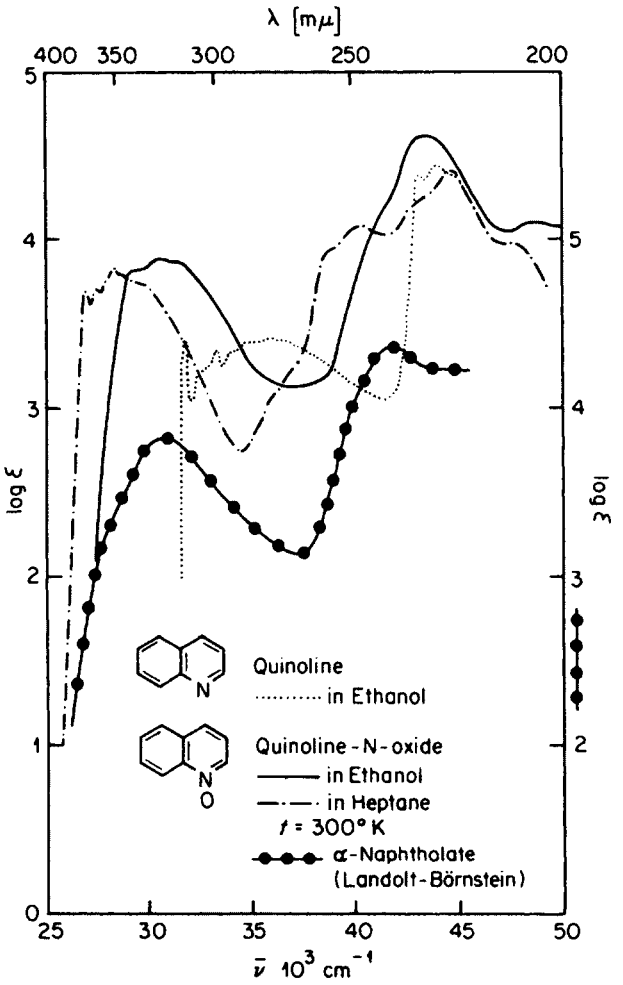


Fig. 1. U-v spectra of quinoline (. . . .) and quinoline *n*-oxide (- and -. -.). Reproduced, by permission, from B. Ziolkowsky and F. Dörr, *Ber. Bunsenges. Phys. Chem.* **69**, 448 (1965)

there has been disagreement over the longer wavelength absorption. The considerable hypsochromic change in wavelength of the absorption maximum (from 351 nm in cyclohexane to 313 nm in water[209]) has been taken as evidence of a $p(o_1p_2)$–π^* transition,[210] but a detailed study of absorption, fluorescence, phosphorescence and

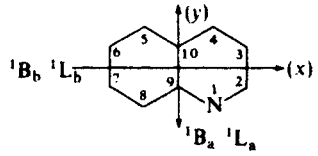
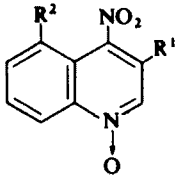


Fig. 2. Polarization diagram of aza-naphthalene, based on Platt's Free Electron Model[211]

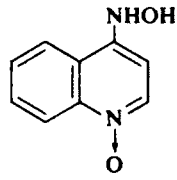
degree-of-polarization spectra[208] have provided 'no certain evidence of a longwave n–π* absorption of the lone pair electrons of oxygen'. The shortwave band was assigned as ^1B_b on Platt's nomenclature (Fig. 2) and the longer wavelength as $^1L_a + {}^1L_b$.[211]

Ochiai (ref. 2, p. 145), following Kubota and Miyazaki[222] and references cited by them, separates each type of substituent into two groups, depending on the position, group I being 1, 4, 5 and 8 and group II 2, 3, 6 and 7, and suggests that the bands affected most are respectively ^1B_a and ^1L_a, or ^1B_b and ^1L_b. This suggestion has been further examined for 4-substituted quinoline *N*-oxides, particularly for those known to be carcinogenic.[211] The size of the ε values was said to indicate that all bands were π–π*, and the hypsochromic effect in solvents of increasing polarity was due chiefly to hydrogen bonding between the oxygen atom and hydroxylic solvents. From simple LCAO–MO calculations of the energy levels of molecular orbitals in the *N*-oxides[211] and from correlation with oxidation–reduction potentials in non-aqueous media,[212] the ^1L_b band has been assigned to a one-electron transfer from the HOMO to LUMO, the ^1L_a band to a transfer from the second highest occupied MO to the LUMO and the ^1B_b band to a transfer from HOMO to the second highest unoccupied MO. The singlet–triplet absorption spectrum of quinoline *N*-oxide has been observed by high-pressure oxygen perturbation, producing a new band at *ca.* 550 nm; from the transition energy for this transformation and a value for $^1L_a \leftarrow N$ a singlet–triplet energy was calculated.[213] The lowest triplet state was assigned as a π–π* transition of a ^3L_a (CT) nature. The same authors[213] reported that a satisfactory phosphorescence spectrum for quinoline *N*-oxide could not be obtained. Most measurements in rigid glasses giving rise to a mixture of the phosphorescence of the *N*-oxide and of its photochemical reaction product (the phosphorescence described by Ziolkowsky and Dörr[208] was identified as that of a photoproduct). Fluorescence has been observed for quinoline *N*-oxide in a weak band at 470 nm in neutral and weakly acidic solutions at room temperature[214] The fluorescence band shows a hypsochromic shift at lower temperatures; the calculated pK_a^* (first excited singlet state) is about 10^3 times lower than in the ground state (*ca.* −3).[214] The lifetime of the emitting triplet state for the protonated molecule was estimated as 0.2 s. Other reports of measurement of ultraviolet absorption of quinoline *N*-oxide are available.[210,211,215–219] Acidic solutions of quinoline *N*-oxide show absorptions very similar to those of aqueous solutions, and approximating to that of quinoline itself.[216] Ezumi and co-workers have determined the electronic spectrum of the quinoline *N*-oxide anion radical;[220,827] the anion radicals were obtained by controlled-potential electrolysis[827] or by γ-irradiation in a methyltetrahydrofuran glass at 77 K; five well developed peaks were observed and calculated transition energies (LP–SCFMO–CI and CNDO/S) were given.[220] Other, substituted, quinoline *N*-oxides where some discussion of the electronic absorption has been made are the seven monomethylquinoline derivatives,[209] 2-phenylquinoline *N*-oxide,[93,221] a number of substituted quinaldine derivatives,[115] 4-cysteinylquinoline *N*-oxide and 4-thioglycolylquinoline *N*-oxide,[20] and a wide range including aminoquinoline *N*-oxides.[222] In the last case many fluorescent bands were recorded in polar and in non-polar solvents.[222] A great deal of interest has centred on the potent carcinogen 4-nitroquinoline *N*-oxide (**107**)[211,223] and related compounds. A detailed comparison between the absorption and phosphorescence spectra of 3-nitro- and of 4-nitroquinoline *N*-oxides has been reported, with assignment of the main configuration for each absorption.[224] A blue shift was observed when a 3- or a 5-substituent was present [compounds (**108**) and (**109**)] due to twisting of the nitro group out of the plane of the ring.[223] Changes in the electronic absorption spectrum of 4-nitroquinoline *N*-oxide in the presence of phenols and alcohols showed both hydrogen bonding[225] and charge-transfer effects.[226,227,828] A similar study has been made of interactions between 4-nitroquinoline *N*-oxide and methyl-substituted benzenes or anilines.[228,828] The biological significance of 4-nitroquinoline *N*-oxide as a charge-

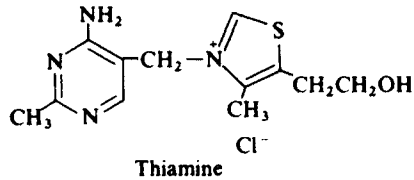
transfer species has been discussed.[229] The role of 4-nitroquinoline *N*-oxide and 4-hydroxyaminoquinoline *N*-oxide (**110**) as charge-transfer acceptors, and in hydrogen bonding with proteins, DNA and RNA, has been studied by difference spectra in an attempt to understand the binding which is important in carcinogenesis.[230-234,829] The studies on proteins included model studies on amino acids;[231,235,236] the complex of 4-hydroxyaminoquinoline *N*-oxide (**110**) with DNA and RNA showed fluorescence similar to, but not identical with, that of compound (**110**). The fluorescence of acidic solutions of calf thymus DNA deoxyadenosine and deoxyguanosine was quenched by some nitroquinoline *N*-oxides, although the quenching was not paralleled by carcinogenesis.[237] On the other hand, the visible difference spectra of interaction between DNA and deoxyribonucleosides with various quinoline *N*-oxides, again due to charge transfer with the basic moieties of the DNA, could be correlated with carcinogenic activity.[233,238] Charge-transfer complexes were also observed between 4-nitroquinoline *N*-oxide and thiamine (**111**) (and models for the thiazolium or pyrimidine sections)[239] and between 4-nitroquinoline *N*-oxide and nicotinamide;[240] in both series the quinoline *N*-oxide was the acceptor. Difference spectra due to interaction between 4-nitroquinoline *N*-oxide and bases from DNA in aqueous medium showed 1 : 1 complexes to be formed, with charge transfer from base to *N*-oxide.[241] In another study difference spectra were measured for 4-nitroquinoline *N*-oxide and 4-hydroxyaminoquinoline *N*-oxide; 1 : 2 complexes were said to be formed with the DNA bases.[830]



107, $R^1 = R^2 = H$
108, $R^1 = CH_3$, $R^2 = H$
109, $R^1 = H$, $R^2 = CH_3$



110

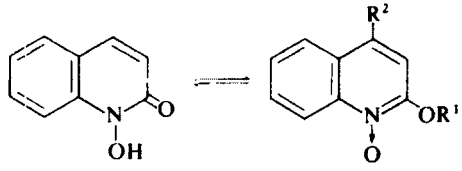


Thiamine

111

Circular dichroism spectra have been determined for 4-nitroquinoline *N*-oxide bound to native calf thymus DNA; the quinoline was said to be bonded with its molecular plane parallel to the bases in the DNA.[831] The ultraviolet absorption of the tautomeric 1-hydroxy-2-quinolone (**112**) and 2-hydroxyquinoline *N*-oxide (**113**) has been compared with that of the ether (**114**)[154] and this, with other evidence, favours the quinolone form (**112**). On the other hand, Ochiai[2] and Ochiai and Hayashi,[242] in a similar study with the 4-hydroxyquinoline *N*-oxide (**115**), favoured the enol betaine form (**116**) (for infrared evidence, see p. 415).

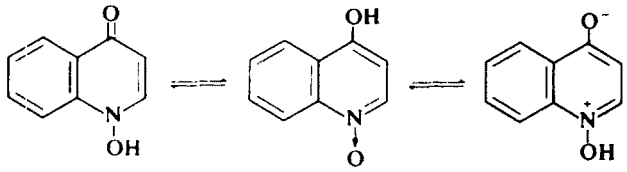
Ultraviolet absorption has been used to determine the dissociation constant of quinoline *N*-oxide, which at 0.70 ± 0.07 is much smaller than those of aliphatic tertiary amines;[243] the ionization constants for 4-aminoquinoline *N*-oxide have also been determined.[244] Fluorimetric detection of 4-aminoquinoline *N*-oxide[245] and colorimetric determination[246] of 4-aminoquinoline *N*-oxide and 4-hydroxyaminoquinoline *N*-oxide have been reported. There is a report of the visible absorption of a number of quinoline *N*-oxides in solution with potassium amide in liquid ammonia; the band positions were said to approach those of the parent heterocycles but with increased intensity.[247]



112

113, $R^1 = R^2 = H$

114, $R^1 = C_2H_5$, $R^2 = CH_3$



115 116

B. Infrared Spectra

Most infrared studies involving quinoline *N*-oxides have been concerned with complexes, particularly with metal complexes; the latter are gathered in Table 27.

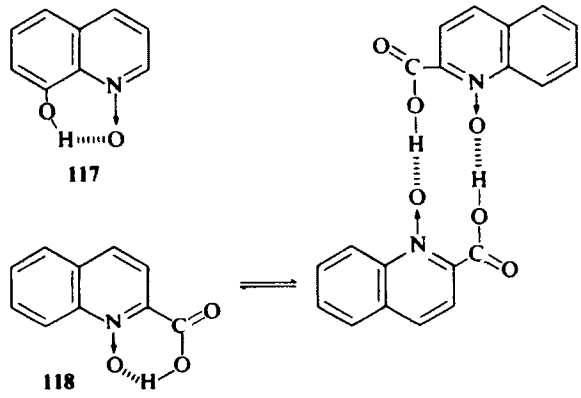
Assignments of the principal bands in the spectrum of quinoline *N*-oxide and a number of substituted quinoline *N*-oxides have been made for the region 4000–700 cm^{-1} by Shindo[248] and by Ghersetti *et al.*[249] The latter authors also reported on the far-infrared region (400–40 cm^{-1}).[250] The principal interest in Shindo's paper is in the assignment of bands for the N—O stretch in the region 1000–1600 cm^{-1}, where detailed comparisons were made with the parent quinolines. It was found that all *N*-oxides showed three to five strong absorptions in the region 1190–1350 cm^{-1} which were absent or weak in the parent quinolines. The narrower range of 1220–1260 cm^{-1} and 1300–1340 cm^{-1} was specified as most characteristic. No very satisfactory correlations in frequency shift with substitution were made, and the discussion of the use of C—H deformation in determining substitution pattern has been partly superceded by the advent of nuclear magnetic resonance spectra. The strong bands at 1308 and 1245 cm^{-1} showed no large frequency shift in the presence of methanol, but the formation of a hydrogen bond was established by an examination of the intermolecular hydrogen bonding shift of the methanol O—H frequency.[248] There was a larger methanol shift of the band at 1184 cm^{-1} in the $^2H_7$-quinoline *N*-oxide (this is the equivalent of the 1233 cm^{-1} band in the $^1H_7$-quinoline *N*-oxide).[249] In the far-infrared region (Table 4)

TABLE 4. Far-infrared Absorption Bands of Quinoline *N*-Oxide and $^2H_7$-Quinoline *N*-Oxide[250]

$^1H_7$	380w	368vw	318s	268m	220w	184	158s,b	80m,b
$^2H_7$	370m,s		304s	250w		170sh	148s,b	70w,b

two major bands at 158 and 318 cm^{-1} were assigned[250] to an out-of-plane bending and to an in-plane bending vibration, both of the N—O bond, since both were sensitive to hydrogen bonding (with phenol). So far as the substituted quinoline *N*-oxides were concerned the only ones lacking the band near 160 cm^{-1} were those carrying 3-substituents.

There are other reports of the infrared spectrum of quinoline *N*-oxide.[251-253] The infrared spectra of 2-methyl- and 4-methylquinolines in liquid ammonia with potassium amide showed an absorption at 3066 cm^{-1} for the $—CH_2^-$ group, 15 cm^{-1} lower than that of the parent bases, reflecting the increase in electron density due to the lower electron acceptor character of the N—O group.[254] Szafran and Dziembowska have reported infrared studies on a number of 2-cyanoquinoline *N*-oxides.[837] Kaneko has used the infrared spectrum of 2- and of 4-hydroxyquinoline *N*-oxide to support the *N*-hydroxycarbostyril (**112**) and the betaine (**116**) structures, respectively.[838] In the region of 3660 and 3400 cm^{-1} no hydroxyl absorption was observed for 8-hydroxyquinoline (**117**); absorption at 2857–2440 cm^{-1} independent of concentration was taken as evidence of a strong intramolecular hydrogen bond.[26] Earlier reports of dimer formation in solid quinaldinic acid *N*-oxide (**118**)[255,256] have been followed by reports of strong intramolecular hydrogen bonding in a variety of 4-substituted quinaldinic acid *N*-oxides,[257] and in the corresponding amides.[258] Szafran and co-workers have published many reports of hydrogen-bonded salts of quinoline *N*-oxides with a variety of carboxylic acids,[105,259-263,842] sulphonic acids,[264,841] and inorganic acids.[265,266] Hydrogen bonding interactions between quinoline *N*-oxides and phenols have been studied by infrared spectroscopy.[250,248,267,227]



117

118

C. Nuclear Magnetic Resonance Spectra and Electron Spin Resonance

The ^{1}H-nmr spectrum of quinoline *N*-oxide has been determined at 60 MHz,[268,269,854] 100 MHz[270] and 220 MHz.[270] The last two spectra, with assignments, are shown in Fig. 3, and the shifts and coupling constants are recorded for the neutral and protonated forms in Table 5.

A comparison with the ^{1}H-nmr spectrum of quinoline itself (Vol. 1, p. 11) shows substantial shift differences for H2 (0.38 p.p.m. upfield in the *N*-oxide), H4 (0.37 p.p.m. upfield in the *N*-oxide) and H8 (0.63 p.p.m. downfield in the *N*-oxide), which can be readily interpreted on the basis of increased electron density (H2 and H4) and magnetic anisotropy of the polar N—O group (H8). In the protonated forms only the signal for H4 retains a reasonable difference in shift. The coupling constants are very similar for quinoline and the *N*-oxide, the largest difference being for $J_{2,3}$ in the unprotonated forms. Hamm and Von Philipsborn[270] also reported the shifts and coupling constants for 4-methoxy-, 6-methyl- and 8-methylquinoline. The 8-methyl group is substantially deshielded by the *N*-oxide, as has been observed elsewhere.[24] The conclusion was drawn[270] that the major part of the shielding by the *N*-oxide group originates from the

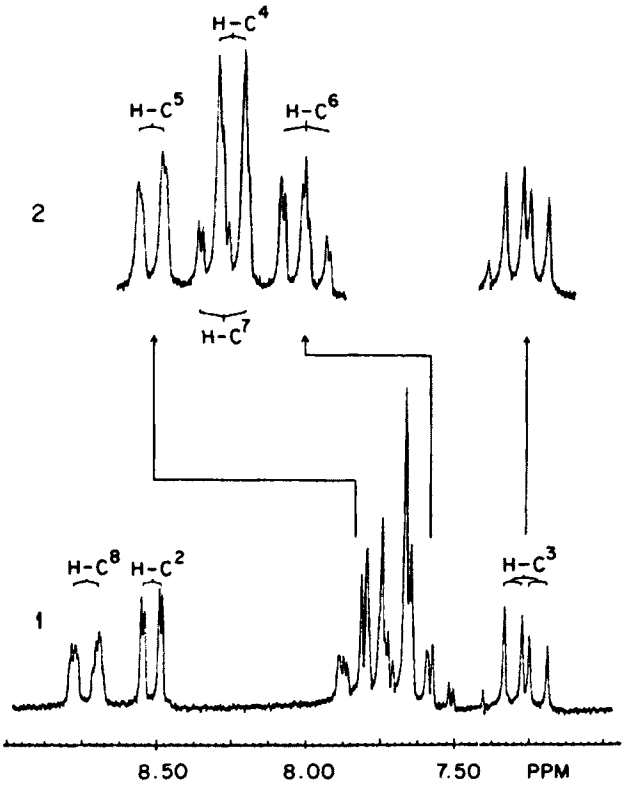


Fig. 3. ^{1}H-nmr spectra of quinoline *N*-oxide. *1.* 100 MHz, *2.* 220 MHz. Reproduced, by permission, from P. Hamm and W. Von Philipsborn, *Helv. Chim. Acta*, **54**, 2365 (1971)

TABLE 5. ^{1}H-nmr Shifts and Coupling Constants for Quinoline *N*-Oxide[270]

Solvent	δ values						
	H2	H3	H4	H5	H6	H7	H8
0.9 M, $CDCl_3$	8.53	7.27	7.72	7.85	7.62	7.74	8.76
0.9 M, $CDCl_3$ + CF_3CO_2H	9.02	7.64	8.37	8.06	7.80	7.97	8.67

	J (Hz)								
	2,3–	2,4–	3,4–	5,6–	5,7–	5,8–	6,7–	6,8–	7,8–
0.9 M, $CDCl_3$	+6.0	+1.1	+8.5	8.3	1.3	—	7.0	1.2	8.9
0.9 M, $CDCl_3$ + CF_3CO_2H	6.0	1.1	8.4	7.9	2.0	~0.8	7.3	1.4	8.2

electric dipole; the single bond structure and the double bond structure for the N—O bond were thought to be of approximately equal importance. A study of shift differences shown by protons adjacent to methyl groups has been used to estimate double bond

character, which was greater for the 3,4- than for the 2,3-bond.[832] An almost equally detailed study has been made of the nitroquinoline *N*-oxides at 60 MHz[269] and 100 MHz.[117] In the 100-MHz study, Eu(fod)$_3$ shift reagent was used, complexing strongly with the *N*-oxide function but not with the nitro groups, and thus producing large shifts in the signals for H2 and H8. Shifts for equimolar quantities of Eu(dpm)$_3$ or Pr(dpm)$_3$ with quinoline *N*-oxide are shown in Table 5A.[271]

TABLE 5A. Chemical Shifts[a] in the Quinoline *N*-Oxide Nmr spectrum caused by Eu(dpm)$_3$ and Pr(dpm)$_3$[271]

Shift reagent	H2	H3	H4	H5	H6	H7	H8
Eu(dpm)$_3$	+17.6	+3.9	+4.6	+3.1	+2.3	+2.4	+14.7
Pr(dpm)$_3$	−17.2	−4.3	−4.0	—	—	—	−18.8

[a] $\Delta\delta$ in p.p.m. for equimolar reagent/substrate; + represents a downfield shift.

The shifts for the quinoline *N*-oxide hydrogen atoms have also been reported with added Ni(AcAc)$_2$ and Co(AcAc)$_2$.[272] It has been suggested that the transmitted effect of a 3-methyl group is greater at position 4 by transmission through a bond with more double bond character (see p. 416); this suggestion appears to be substantiated by the greater downfield shift of H4 relative to H2 in 3-nitroquinoline. As mentioned before, from the ultraviolet absorption there is some evidence that in a 3- or 5-substituted 4-nitroquinoline the nitro group is twisted out of plane; this is said[273] to result in an upfield shift of one of the downfield protons. The ratio $\delta_{^1H}/\delta_{^1H}$ for position 2 was reported as 1.00.[273] A number of deuteriation studies have used the ^{1}H-nmr spectrum to confirm substitution sites,[274] and for rate studies in deuterium exchange on active methyl groups.[275-277] Intramolecular hydrogen bonding in 4-substituted quinaldinic acids[278] and intermolecular hydrogen bonding in salts of methylquinoline *N*-oxides[279-281] and of 4-methoxy- and 4-chloroquinoline *N*-oxide[282] have been studied by ^{1}H-nmr spectroscopy. For spectra run in toluene[280] and in acetone[839] concentration-dependent shifts were observed for H2 and H8. The composition of complexes formed by lepidine *N*-oxide, chloroacetic acid and water were studied by ^{1}H-nmr and molecular weight determinations.[840] The interaction of 4-nitroquinoline *N*-oxide with deoxyribonucleosides has also been examined by ^{1}H-nmr spectroscopy.[283]

The ^{13}C-nmr shifts and the $^1J(^{13}C, ^1H)$ coupling constants of quinoline *N*-oxide have been reported (solvent $CDCl_3$) and are given in Table 6.[857] The shifts were compared

TABLE 6. ^{13}C-Nmr Chemical Shifts (p.p.m.) and ^1J (^{13}C, ^{1}H) Coupling Constants (Hz) of Quinoline *N*-Oxide

	Carbon atom								
Parameter	2	3	4	5	6	7	8	9	10
Shift from TMS (p.p.m.)	135.2	121.1	125.3	128.1	128.6	130.0	119.2	141.2	130.3
^1J (^{13}C, ^{1}H) (Hz)	185.6	167.9	168.5	164.2	163.0	161.7	167.6	—	—

with those of the carbon atoms in quinoline and there was some discussion of the abnormal shielding of C8 in the *N*-oxide; this effect was thought to be due to steric interaction between H8 and the solvent shell of the *N*-oxide oxygen.

The ^{13}C-nmr shifts of quinoline *N*-oxide and of the 2-, 4-, 6- and 8-methylquinoline *N*-oxides and of 2,6-dimethylquinoline *N*-oxides have been determined in another study,[860] compared with the appropriate quinolines, and substituent chemical shifts were listed. A downfield shift of the 8-methyl signal was an anomaly; no explanation could be offered.

The ^{14}N-nmr shift of quinoline *N*-oxide was reported as $+94 (\pm 1)$ (acetone), $+95 \pm 1$ ($CHCl_3$) and $+105 \pm 1$ (methanol) p.p.m., with half-height widths of 47 ± 3, 160 ± 10 and 190 ± 10 Hz, respectively (shifts relative to internal nitromethane).[285] The shifts were discussed relative to those of other *N*-oxides.

Yavari and Roberts[853] have measured the ^{15}N chemical shifts of quinoline *N*-oxide and 8-hydroxyquinoline *N*-oxide in DMSO, trifluoroethanol and trifluoroacetic acid. The figures given (see Table 6A) are upfield from external nitric acid and downfield from tetramethylammonium chloride.

TABLE 6A. ^{15}N Chemical Shifts of *N*-Oxides in Different Solvents[853]

	Quinoline *N*-Oxide			8-Hydroxyquinoline *N*-oxide		
Shift	DMSO	CF_3CH_2OH	CF_3CO_2H[a]	DMSO	CF_3CH_2OH	CF_3CO_2H[a]
Shift (HNO_3) (p.p.m.)	95.3	106.6	144.1	104.8	109.9	138.1
Shift $(CH_3)_4\overset{+}{N}Cl^-$ (p.p.m.)	237.5	226.2	188.7	228.0	222.9	194.7

[a] Protonating solvent.

A comparative study[286] of ^{15}N-labelled quinoline and its ethiodide and *N*-oxide included indirect ^{15}N–^1H spin–spin coupling values, obtained by a comparison of the ^1H-nmr spectra with those of the corresponding ^{14}N compounds in a variety of solvents. The values obtained for $J_{^{15}N,H2}$ were 0 (aprotic solvents), +1 (CH_3CO_2D) and +1.2 Hz ($D_2O + CF_3CO_2D$); for $J_{^{15}N,H^3}$ the corresponding values were -5.0, -5.5 and -6.0 Hz. The change in *s* character of the ^{15}N atom bonding orbitals to carbon resulted in an increase in the $J_{^{15}N,H2}$ value and a decrease in the $J_{^{15}N,H3}$ value relative to the parent quinoline. The ^{15}N–^1H coupling constants of 4-$^{15}NO_2$-quinoline ^{14}N-oxide and of 4-$^{15}NO_2$-quinoline ^{15}N-oxide have also been reported.[287] The ^{19}F chemical shifts and the ^{11}B–^{19}F coupling constants have been recorded for a number of 4-substituted quinoline *N*-oxides.[288] There was very little change in chemical shift, but a regular increase in *J* value (coupling constants had negative signs) as the substituents became more electron withdrawing. Magnetic data for metal complexes containing quinoline *N*-oxides are mentioned in Table 27.

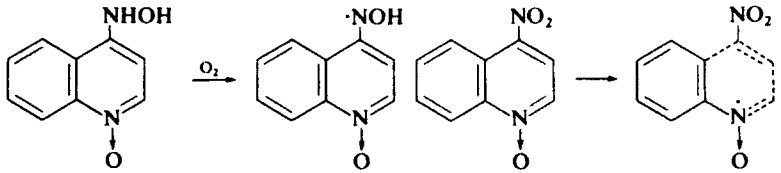
Electron spin resonance spectra have been recorded for a number of quinoline *N*-oxides, in particular for those with known carcinogenic activity. The radical anion of quinoline *N*-oxide has been prepared by electrochemical reduction and fully analysed.[289,290] In the more detailed examination[289] the use of six of the monomethylquinoline *N*-oxides allowed the complete assignment of hyperfine splitting constants, shown in Table 7.

The results were compared with calculated spin densities and good agreement was observed. Free radicals have been formed, and their esr spectra determined, from 4-hydroxyaminoquinoline *N*-oxide (**119**) (by oxidation)[291–293] and of 4-nitroquinoline *N*-oxide (**121**) (photoinduced)[294] and various substituted 4-nitroquinoline *N*-oxides.[295]

TABLE 7. Hyperfine Splitting Constants of the Quinoline *N*-Oxide Radical Anion and its Methyl Derivatives[289]

Substituent	a_N	a_{H2}	a_{H3}	a_{H4}	a_{H5}	a_{H6}	a_{H7}	a_{H8}	a_{CH_3}
None	6.00	4.04	0.85	7.82	3.66	0.41	2.38	2.71	—
2-CH_3	5.93	—	1.10	7.39	4.03	0.41	2.57	2.95	4.44
3-CH_3	6.45	3.75	—	7.86	3.18	1.13	2.08	2.92	0.28
4-CH_3	5.53	4.38	1.06	—	3.87	0.16	2.21	3.28	6.51
5-CH_3	6.32	4.32	0.65	7.24	—	0.65	2.53	2.53	2.53
6-CH_3	6.28	3.47	0.75	7.82	3.47	—	2.72	2.72	0.75
7-CH_3	6.02	4.51	1.20	7.16	3.60	0.20	—	2.56	2.25

The radical from 4-hydroxyaminoquinoline was shown to be (**120**) by an analysis of the $^{15}NO_2{}^{14}NO$, $^{14}NO_2{}^{15}NO$, $^{15}NO_2{}^{15}NO$, and various deuterium-labelled derivatives,[293] one H being lost in the oxidation.



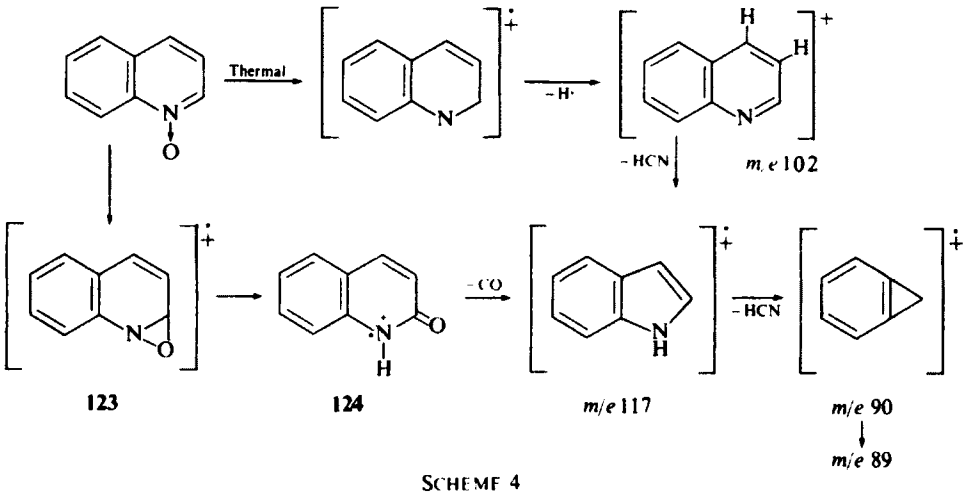
119 **120** **121** **122**

The irradiation of 4-nitroquinoline *N*-oxide in dioxan, benzene or hexane gave three different esr signals.[294] In a study of the change in esr spectra shown by isotopically labelled 4-nitroquinoline *N*-oxide (all possible ^{15}N labels, and three deuterated derivatives), the 'dioxan' radical had no spin on the nitro group nitrogen atom or on H2 or H3 so that a structure (**122**) can be drawn. The 'benzene' and 'hexane' radicals showed spin localization on the nitro group nitrogen atom, but none on the aromatic ring nitrogen, and no firm structures could be assigned. In a study of substituted 4-nitroquinoline *N*-oxides[295] it was shown that oxygen is necessary for the production of 'benzene' radicals; there was high localization of the radical on the nitro group, giving couplings of about 28 gauss. Okano *et al.* studied photoinduced radicals from 4-nitroquinoline *N*-oxide at 77 K and pH 7.0.[296] Photodynamic activity was shown by 4-nitroquinoline *N*-oxide.[843] It is reported[297] that DNA facilitates production of radicals from 4-nitroquinoline *N*-oxide, but hinders free radical formation from 4-hydroxyaminoquinoline *N*-oxide.

D. Mass Spectrometry

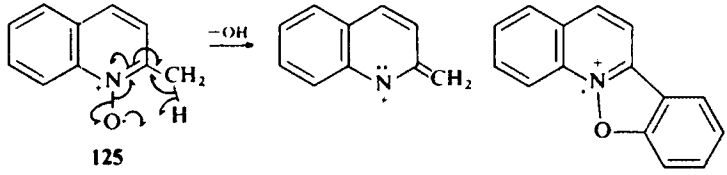
Bryce and Maxwell[298] first reported that *N*-oxides could be readily identified by a loss of 16 m.u. from the parent peak, thus distinguishing them from nitro compounds. However, Duffield and Buchardt, having noted only small M − 16 peaks in some of their mass spectra of quinoline *N*-oxides, were able to show[299] that the loss of oxygen was thermally induced. The observation of a strong M − 16 peak therefore can remain diagnostic, provided that a hot (180 °C) ion source is used. It seems agreed[300-302, 852] that the mass spectral breakdown of quinoline *N*-oxide follows the photochemical route, passing via

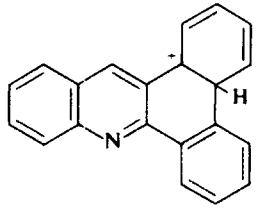
the oxaziridine (**123**) to carbostyril (**124**) as shown in Scheme 4. When there is oxygen loss to give M − 16, this ion then can lose a hydrogen atom to give M − 17, and subsequently HCN to give a peak at 102 or 101 m.u.

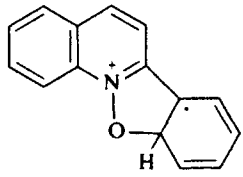


SCHEME 4

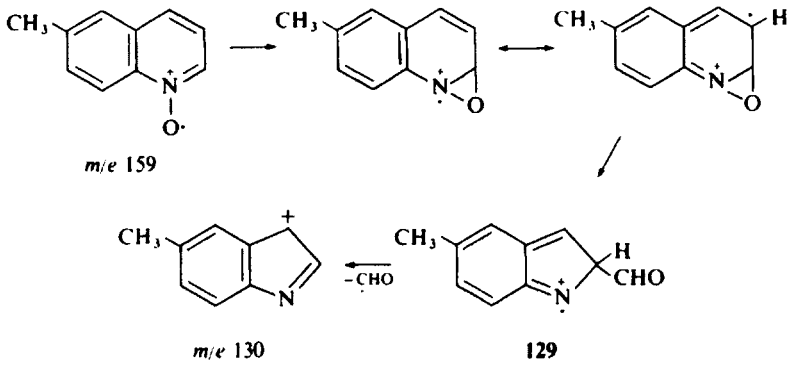
Both groups of workers[301,300] noted the considerable difference in mass spectral breakdown shown when the quinoline *N*-oxide carried a methyl group in position 2 or a phenyl group in position 2. In the former case a strong M − 17 peak was ascribed to an *ortho* effect with loss of OH as shown for 2-methylquinoline *N*-oxide (**125**). In the latter a strong M − 1 peak was ascribed to the formation of an oxygen-containing ring, as in formula (**126**). Studies on 2-phenyl- and 2,3-diphenylquinoline *N*-oxides and acenaphtho[1,2-*b*]quinoline *N*-oxide[303] confirmed the losses for 2-phenylquinoline *N*-oxide and the structure (**126**) for the M − 1 peak, but added a suggestion that the molecular ion could be represented by structure (**127**) from which M − 1, M − 17 and M − 28 losses could occur. The base peak in the spectrum of 2,3-diphenylquinoline *N*-oxide was M − 17, and the ion responsible for this was formulated as (**128**).




128

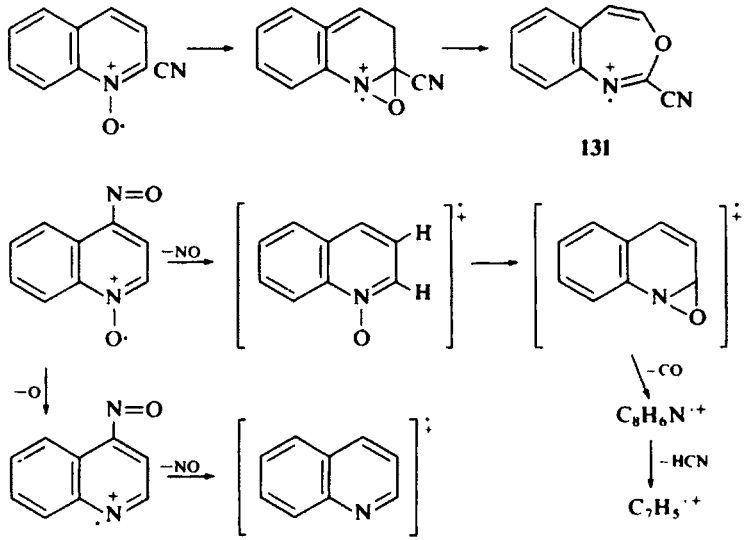

127

Buchardt *et al.*[300] also noted an abnormal breakdown from 4-methyl- or ö-methylquinoline *N*-oxides, with a direct loss of 29 m.u., and suggested a rearrangement to a 2H-indole aldehyde (**129**).



129

Other quinoline *N*-oxides for which detailed breakdown patterns have been suggested are 2-cyanoquinoline *N*-oxide (**130**),[304,301] where the oxazepine (**131**) was a suggested intermediate and the analogy with photochemical reaction is clear, and 4-nitroso- (**132**) and 4-nitroquinoline *N*-oxides.[305,306] In the last two cases (Scheme 5 shows the 4-nitroso derivative) loss of nitric oxide was an important step.

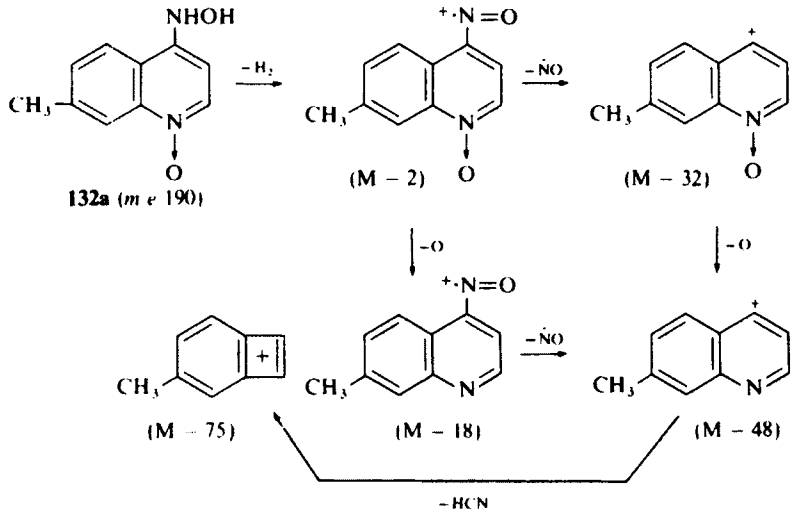


SCHEME 5

As an aid to diagnosis of metabolism and mechanism of carcinogenesis of 4-hydroxyaminoquinoline *N*-oxides, the mass spectra of the parent and of methyl derivatives were studied.[851] Major ions in the parent were at M−1, M−2, M−16,

M − 18, M − 47, M − 48, M − 60, M − 62, M − 75, M − 87, with a base peak at *m/e* 75. Methyl derivatives showed no M − 17 fragment in contrast to simple aromatic hydroxylamines. The suggested breakdown pattern is exemplified by that of 7-methyl-4-hydroxyaminoquinoline *N*-oxide (**132a**).

The fragmentation patterns of some 1,2-dimethyldecahydroquinoline *N*-oxides have been analysed.[307]



E. X-ray Diffraction

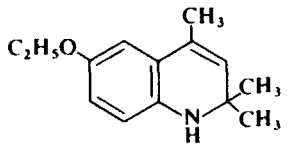
Few X-ray diffraction analyses of quinoline *N*-oxides have been reported. The 1 : 1 complex of quinoline *N*-oxide and mercury(II) chloride was examined by McPhail and Sim.[308] Other reports were on quinaldinic acid *N*-oxide,[309] the trichloroacetate of 2-methylquinoline *N*-oxide[310] and 8-hydroxyquinoline *N*-oxide.[311] From the last an N—O bond length of 1.333(2) Å and an intramolecular hydrogen bond length of 1.42 Å were obtained.[311] The crystal structure of 5-hydroxy-5,6,7,8-tetrahydroquinoline *N*-oxide showed the hydroxyl group to be axial, the cyclohexene to have a half chair conformation and the pyridine ring to have a small boat deformation.[312]

F. Dipole Moment, Dissociation Constants, Titration

The presence of the N—O bond in quinoline *N*-oxide should result in a considerable difference of dipole moment from that of quinoline (~2.25 D). The values reported are 4.24[313] and 4.07 ± 0.02 D,[314] both in benzene. From the latter figure was derived a figure of 19% double bond character in the N—O group. The charge distribution in the N—O group is reflected also in a dissociation constant (pK_a) for quinoline *N*-oxide of 0.70[343] (the pK_a for quinoline is 4.85). As expected, electron-donating substituents on the nitrogen-containing ring increase the pK_a value;[344] the effect of substituents has been thoroughly studied on pyridine *N*-oxides.[2] Quinoline *N*-oxides can be titrated using perchloric acid in acetic anhydride,[315-317] either potentiometrically[315,316] or with methyl violet and a pH meter.[317] The ionization constant of the cation of 8-hydroxyquinoline *N*-oxide (K_{a_1}) is 0.0486 ± 0.0004.[836]

G. *Separation and Identification*

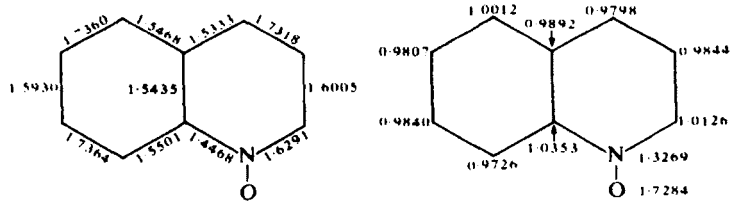
Quinoline *N*-oxides have been separated by paper chromatography[318-320] and quinolines have been analysed by peracetic acid oxidation followed by paper chromatography of the *N*-oxides thus obtained.[321] A variety of solvent systems were used and detection was by ultraviolet light (with or without an acridine spray), diazonium salts, iron(III) chloride, permanganate, molybdophosphoric acid, Ehrlich's reagent, Dragendorff's reagent and sodium pentacyanoamminoferrate. Separations by thin-layer chromatography, using silica gel[322,323] or alumina[322] with a variety of solvents, have also been reported. A colour test for quinoline *N*-oxide involved boiling the *N*-oxide with dimethylaniline and concentrated hydrochloric acid, subsequently adding ethanol to produce an intense blue colour.[324] Separation of *N*-oxides from the parent bases is easily achieved by medium-pressure liquid chromatography on silica gel;[325] details of the separation of the dihydroquinoline (**133**) from its *N*-oxide on neutral Bio-Sil A have been published.[326]



133 (ethoxyquin)

H. *Theoretical Chemistry*

A number of molecular orbital studies have been performed on quinoline *N*-oxide,[327-331] correlating the results with various physical properties. A set of bond orders and the calculated electron densities, using a Parisser–Parr–Pople calculation, are shown in Fig. 4.[331] HOMO and LUMO values were also calculated.



Bond order (in A) Electron density

Fig. 4. Bond order and electron densities in quinoline *N*-oxide[331]

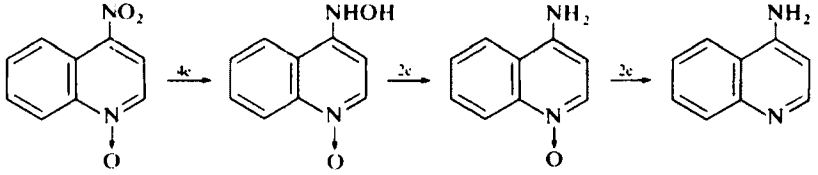
The measurement of the photoelectron spectrum[314] (21.22 eV) of quinoline *N*-oxide allowed assignment of many π energy levels and supported the conclusions previously drawn regarding the π nature of the ground ionic state in *N*-oxides. Simple MO calculations have been made also in attempts to assign electronic transitions from measured spectra,[211,215] particularly in the case of 4-nitroquinoline *N*-oxides and related compounds.[332,333] Attempts have been made to correlate frontier electron density[334] and super-delocalizability[334-336] with carcinogenic activity, and to calculate charge-transfer interaction between 4-nitroquinoline *N*-oxide and DNA.[337] Super-delocalizability was used as a measure of nucleophilic attack on the 4-nitro group. Spin

density calculations have been reported for the radicals from quinoline *N*-oxide anion and 4-hydroxyaminoquinoline *N*-oxide[294] and to determine the stable tautomeric form of 4-hydroxyaminoquinoline *N*-oxide.[338] Spin density calculations have also been reported for $Ni(AcAc)_2$(quinoline *N*-oxide)$_2$.[339] Molecular orbital theory has been used to calculate lowest unoccupied and highest occupied orbital electron densities at C2, C8a and O for discussion of photochemical reaction.[834]

2. Chemical Properties

A. Deoxygenation and Reduction

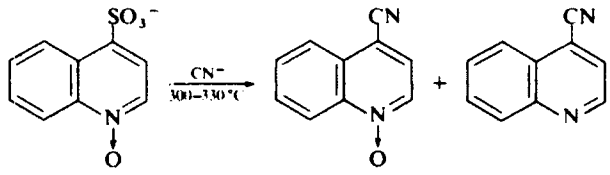
a. POLAROGRAPHY Quinoline *N*-oxide shows a two-electron first reduction wave with $E_{\frac{1}{2}}$ recorded as -1.30,[340] -1.809,[290] -1.54,[825], -1.840[212] and -1.164 V.[341] The half-wave potential for 0.1 N sulphuric acid was -0.802 V.[342] Polarographic measurements have also been recorded for quinaldine *N*-oxide,[342, 343, 825] 2-arylquinoline *N*-oxides,[344] quinaldinic acid *N*-oxide,[345] kynurenic acid *N*-oxide,[346, 833] lepidine *N*-oxide[825] and many 4-nitroquinoline *N*-oxides.[347, 332, 824] In the case of the 4-nitroquinoline *N*-oxides, which were compared with other nitroquinoline *N*-oxides, and the parent nitroquinolines,[332] a correlation was observed between the electron density at a given position and the size of the half-wave reduction potential, with 4-nitroquinoline *N*-oxide having the most positive value (most easily reduced). The reduction process is shown below.



b. DEOXYGENATION Included in this section are deoxygenations without concomitant substitution. Thus deoxygenation by phosphorus trihalides is included but the reaction with phosphoryl halides, which gives chlorinated quinolines, is not. Such deoxygenation-substitution reactions are dealt with in detail as substitutions (usually nucleophilic substitutions).

The simplest deoxygenation is thermal without an added reagent. Quinoline *N*-oxide has been reported to lose oxygen in the heated inlet of a mass spectrometer or on simple distillation.[348] Biffin *et al.* reported that quinoline *N*-oxide and quinaldine *N*-oxide were thermally deoxygenated in 27 and 19% yields, respectively, after 20 h in nitrobenzene at 190 °C.[349] Pyrolytic deoxygenation must also occur when the sulphonate (**134**) is heated with a cyanide at 300–330 °C and 5 mmHg since the major product is the deoxygenated cyanide (**135**).[63] In this category may also be deoxygenation using 3-sulpholene at 100 °C.[859]

Electrolytic reduction at a mercury cathode using tetramethylammonium chloride in methanol as the electrolyte gave a yield of 78% of quinoline from quinoline *N*-oxide.[350]



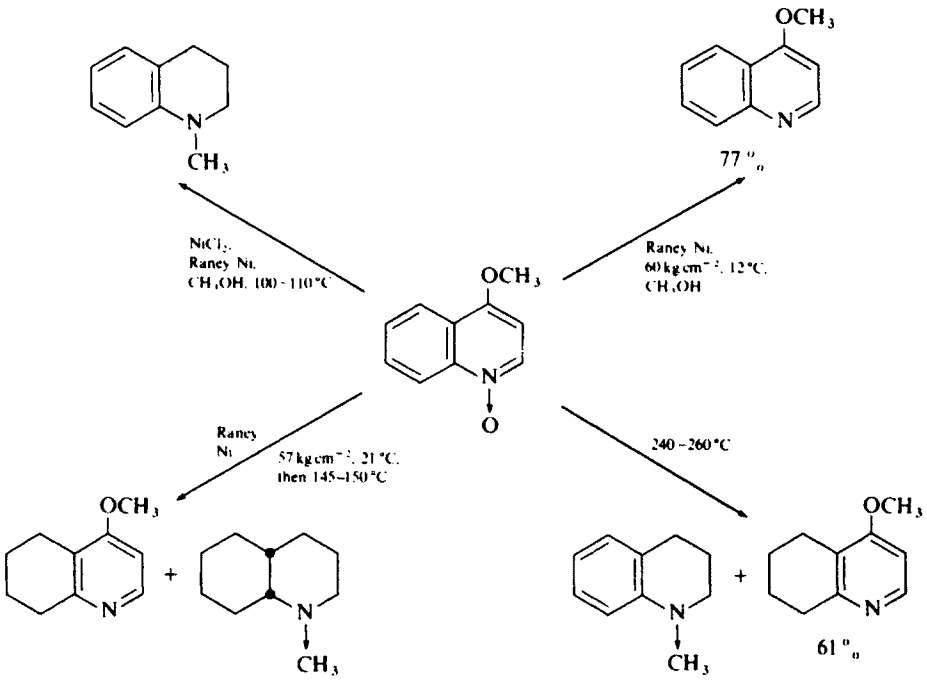
134 ~ 10% **135**; ~ 30%

Electrolytic reduction showed a two-electron process, as did polarography.[826] Electrolytic reduction of 4-nitroquinoline *N*-oxide on lead cathodes gave 1,2,3,4-tetrahydroquinoline, whereas copper or nickel cathodes gave 4-aminoquinoline.[351]

Photochemical deoxygenation has been reported to give high yields with high conversions using benzene solutions, Pyrex vessels, a high-pressure mercury lamp and boron trifluoride etherate.[352] The deoxygenation is thought to occur from a triplet *N*-oxide; 2-, 3- and 4-substituted quinoline *N*-oxides were used. A high yield of 2-cyanoquinoline has been obtained by photochemical deoxygenation in the presence of triphenylphosphine.[353] A much improved procedure used trimethyl phosphite, a high-pressure mercury lamp and a Pyrex filter, in methylene chloride as solvent;[858] the yields from 4-nitroquinoline *N*-oxide and 2-methyl-4-nitroquinoline *N*-oxide were 81% and 91%, respectively. Other photochemical deoxygenations have given poor yields,[354,355] although the addition of anthraquinone improved the yield of quinaldine from the *N*-oxide considerably.[355] Again the deoxygenation was assumed to come from triplet *N*-oxide via excited singlet *N*-oxide, singlet ketone and inter-system crossing to triplet ketone.[355] Support for the triplet route to deoxygenation comes from deoxygenation of 2-phenylquinoline *N*-oxides by γ-rays, where oxazepines are minor products.[356]

Catalytic hydrogenation has been frequently used to deoxygenate *N*-oxides, particularly when there are no other reducible groups on the quinoline nucleus or in side-chains. Representative deoxygenations are listed in Table 8. With palladium/charcoal few problems of over-reduction have been observed. Raney nickel has been used at ordinary temperature and pressure, and at raised temperatures and pressures.

A detailed study of the reduction of 4-methoxyquinoline *N*-oxide with changing temperatures and pressures is outlined in Scheme 6.[377] In the reduction of the thiolate



SCHEME 6[377]

TABLE 8. Deoxygenation of Quinoline *N*-Oxides without Concomitant Substitution

N-Oxide substituent(s)	Quinoline substituent(s)	Reagent	Yield(%)	References
None	None	Raney Ni, H_2	100	357, 358
		Ushibara Ni, H_2	80	359
		Electrochemical reduction	78	350
		Sulphur, liquid NH_3	43	360
		DMSO, H_2SO_4	80	349
		S_2Cl_2	75–85	361
		C_6H_5SCl	80–90	362
		PCl_3, $CHCl_3$	100	363, 371
		PBr_3, ethyl acetate	75	364
		$(C_6H_5)_3P$, 270–280 °C	89	365
		$(C_6H_5O)_3P$, ethyl acetate	71	366
2-Deuterio	2-Deuterio	PCl_3, $CHCl_3$, water-bath	84	367
2-Methyl	2-Methyl	Zinc + acetic acid	—	81
		DMSO, H_2SO_4	55	349
2-Styryl	2-Phenethyl	Pd/C, H_2	--	369
		Raney Ni, H_2	—	368,[a] 369
2-Phenyl	2-Phenyl	$FeSO_4$, KOH	65	27
4-Styryl	4-Styryl	PCl_3, $CHCl_3$	80	710
		Raney Ni, H_2	—	369
3-Chloro	3-Chloro	Raney Ni, H_2	—	370
4-Chloro	4-Chloro	Raney Ni, H_2	Quant.	357
		PCl_3, $CHCl_3$	30	371
8-Bromo	8-Bromo	PCl_3, $CHCl_3$	—	372
4-Chloro-2-methyl	4-Chloro-2-methyl	Zn, HCl	48	79
3,6-Dibromo	3,6-Dibromo	Raney Ni, H_2	—	373
8-Bromo-6-methyl	8-Bromo-6-methyl	PCl_3, water-bath	—	374
3-Nitro	3-Nitro	PCl_3, $CHCl_3$	90	134
	3-Amino	Pd/C, H_2	45	134
4-Nitro	4-Nitro	PBr_3, ethyl acetate, < 15 °C	76–100	375, 364, 376, 71
	4-Chloro	PCl_3, $CHCl_3$	81	371

[a] A number of other β-arylethylquinolines were also prepared.[368]

4-Nitro	4-Amino	Raney Ni, H_2; acid	79	377, 378, 357
3-Methyl-4-nitro	3-Methyl-4-amino	Pd/C, H_2	—	379
	3-Methyl-4-hydroxyamino	$NaBH_4$	95	379
4-Methyl-8-nitro	4-Methyl-8-nitro	PCl_3, $CHCl_3$, 15–20 °C	87	380
8-Methyl-4-nitro	8-Methyl-4-hydroxyamino	Pd/C, H_2	80	379
4,6-Dinitro	4,6-Diamino	Pd/C, H_2; acid	—	381
2-Bromo-4-nitro	4-Amino	Pd/C, H_2; acid	45	375
3-Bromo-4-nitro	4-Amino	Pd/C, H_2	—	138
3-Bromo-5-nitro	5-Amino	Pd/C, H_2	—	138
3-Bromo-8-nitro	8-Amino	Pd/C, H_2	—	138
8-Fluoro-4-nitro	8-Fluoro-4-hydroxyamino	Pd/C, H_2	84	379
5-Iodo-4-nitro	5-Iodo-4-nitro	PCl_3, $CHCl_3$	—	56
6-Bromo-5-nitro	6-Bromo-5-nitro	PCl_3, $CHCl_3$	96	371
2-Hydroxy	2-Hydroxy	Raney Ni, H_2	83	382
4-Hydroxy	4-Hydroxy	PCl_3, $CHCl_3$, 0 °C	70	383, 384[b]
		Raney Ni, H_2	85	377, 357, 371
4-Benzyloxy	4-Benzyloxy *or*	Raney Ni, H_2	81	357
	4-Hydroxy	Raney Ni, H_2	69	357
4-Methoxy	4-Methoxy	Raney Ni, H_2	93	357, 377
3-Hydroxy-2-methyl	3-Hydroxy-2-methyl	Pd/C,H_2	—	20
4-(Tetraacetyl-β-D-glucopyranothio)	4-(Tetraacetyl-β-D-glucopyranothio)	Raney Ni, H_2	—	385
4-Methoxy-6-methyl	4-Methoxy-6-methyl	Fe, acetic acid	78	112, 113
4-Thiocyanato	4-Thiocyanato	PCl_3, $CHCl_3$, 0 °C	70	383
4-Methoxy-2-(4-methoxy-1-oxido-2-quinolyl)	4-Methoxy-2-(4-methoxy-2-quinolyl)	PCl_3	—	98
5,7-Dibromo-8-hydroxy	5,7-Dibromo-8-hydroxy	PCl_3	—	374
3-Methoxy-4-nitro	4-Hydroxyamino-3-methoxy	$NaBH_4$	75	379
5-Nitro-8-hydroxy	5-Nitro-8-hydroxy	PCl_3	—	374
5,7-Dinitro-8-hydroxy	5,7-Dinitro-8-hydroxy	PCl_3	—	374
2-Phenyl-4-carboxylic acid	2-Phenyl-4-carboxylic acid	$FeSO_4$, KOH	—	95
2-Cyano-4-chloro	2-Cyano-4-chloro *and* 2-carboxamido-4-chloro	PCl_3, $CHCl_3$	—	386
6,7-Dimethoxy-3-ethoxycarbonyl	6,7-Dimethoxy-3-ethoxycarbonyl	PCl_3	—	189
3-Hydroxyamino	3-Amino	Pd/C, H_2	46	171

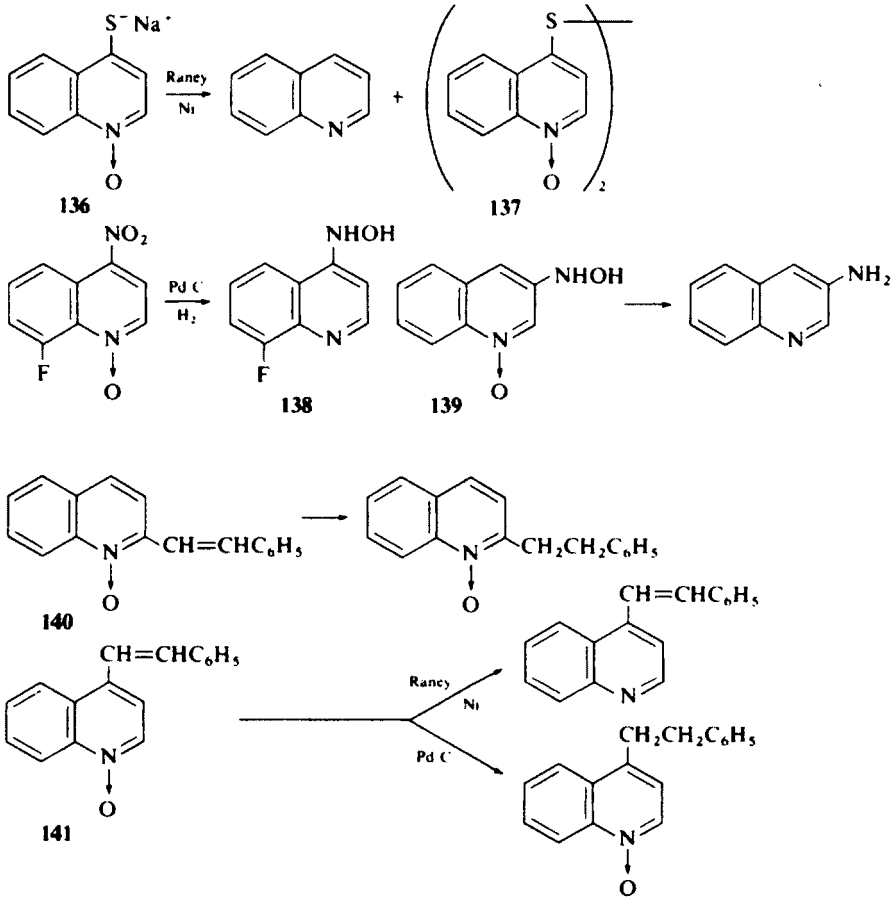
[b] At 62° C some 4-chloroquinoline is formed.

TABLE 8 (*cont.*)

N-Oxide substituent(s)	Quinoline substituent(s)	Reagent	Yield(%)	References
4-Amino	4-Amino	Pd/C, H_2	74	357
		PCl_3, $CHCl_3$	22[c]	384, 371
4-Acetamido	4-Acetamido	PCl_3, ethyl acetate	38[d]	384
3,4-Diamino	3,4-Diamino	Pd/C, H_2	—	387
2-Methyl-4-amino	2-Methyl-4-amino	Raney Ni, H_2	—	370
3-Methyl-4-hydroxyamino	3-Methyl-4-amino	Pd, H_2	—	379
2-Amino-3-carboxamido	2-Amino-3-carboxamido	Zn, CH_3CO_2H *or* Zn, ammonia	—	181

[c] 50–60% of *N*-oxide recovered.
[d] 36% of *N*-oxide recovered.

(**136**) with Raney nickel only half of the theoretical amount of hydrogen was absorbed, and the products were quinoline and the disulphide (**137**).[388] Nitro compounds are reduced to aminoquinolines, sometimes with retention and sometimes with loss of the *N*-oxide oxygen. In a few cases the hydroxyaminoquinoline has been obtained, as with compound (**138**),[379] although 3-hydroxyaminoquinoline *N*-oxide (**139**) gave 3-aminoquinoline.[171] An interesting difference in reduction pattern between palladium/charcoal

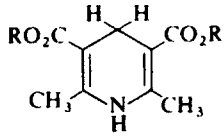


and Raney nickel was demonstrated with 2- and 4-styrylquinoline *N*-oxides (**140** and **141**).[369] Both catalysts, with one molar equivalent of hydrogen, gave the phenethylquinoline *N*-oxide from compound (**140**), but Raney nickel caused deoxygenation of compound (**141**). There is a report of the reduction of a series of 3-bromo-*x*-nitroquinoline *N*-oxides with palladium/charcoal, all of which gave the corresponding aminoquinoline, with the loss of the bromine atom.[138]

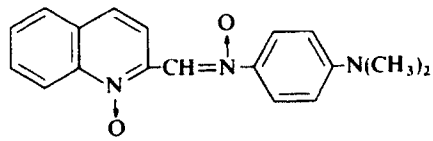
Hydrogen transfer can cause deoxygenation of quinoline *N*-oxide, although in many of the examples the *N*-oxide was studied as an oxidizing agent. Hydrogen donors used were dihydroanthracene,[389] cyclohexene,[390] 1,4-dihydronaphthalene,[390] tetralin,[390] the 1,4-dihydropyridine (**142**),[391,392] anabasine[393] and 2-phenylbenzothiazolidine or -benzimidazolidine.[394] Since the temperatures used were high, the stability of quinoline

N-oxide at 240 °C for 1.5 h was demonstrated, although quinoline *N*-oxide hydrochloride was unstable and deoxygenated at 200–215 °C.[391] The same group of workers reported 90–96% deoxygenation of quinoline *N*-oxide by boiling alcohols (methanol was least active, isopropanol most active) with potassium hydroxide added.[395,396]

A number of deoxygenation procedures use sulphur or compounds of sulphur. A number of *N*-oxides, including quinoline *N*-oxide, heated with sulphur in liquid ammonia at 100 °C gave yields between 35 and 60% of deoxygenated base (quinoline 37%).[360] Although sulphur dioxide has been used for preferential reduction of aliphatic amine *N*-oxides in the presence of quinoline *N*-oxides, the acetic anhydride adduct of quinoline *N*-oxide was reported to be deoxygenated[358] and sodium hydrosulphite reduced 2-phenylquinoline-4-carboxylic acid *N*-oxide.[28] Carbon disulphide in chloroform deoxygenated compound (**143**), producing carbon oxysulphide and sulphur,[397] and sulphur monochloride in boiling chloroform gave a 75–85% yield of quinoline from quinoline *N*-oxide.[361] Phenyl sulphur chloride gave an 80–90% yield of quinoline from

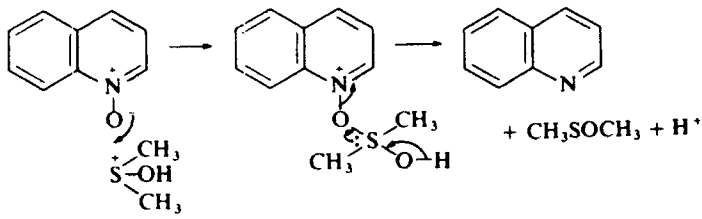


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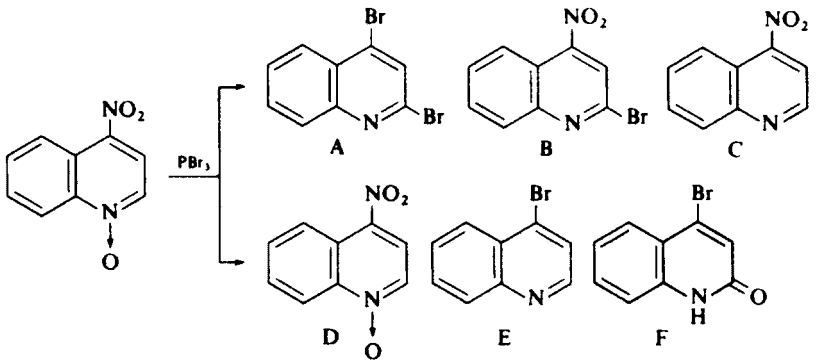
143

quinoline *N*-oxide, but a poor yield from 4-nitroquinoline *N*-oxide.[362] An interesting study of the use of dimethyl sulphoxide and sulphuric acid as a deoxygenating agent gave yields of 80 and 55% of quinoline and quinaldine from the respective *N*-oxides,[349,398] of which a proportion was due to thermal deoxygenation. The mechanism is shown in Scheme 7.



SCHEME 7

Phosphorus compounds have a high affinity for oxygen, and some of the most consistently successful deoxygenation procedures use trivalent phosphorus derivatives, notably the trichloride and the tribromide (note that pentavalent phosphorus compounds give substitution as well as deoxygenation—see p. 482. Hamana first reported the use of phosphorus trichloride[363] and tribromide[364,375] and studied the effect of solvent and of temperature. In summary, chloroform is the solvent of choice for the trichloride, whereas ethyl acetate has advantages for the tribromide, particularly at temperatures below 15 °C. The tribromide can cause nuclear bromination, and the full range of possible by-products is demonstrated by the reaction with 4-nitroquinoline *N*-oxide (**144**).[375]



Solvent	Temp. (°C)	A (%)	B (%)	C (%)	D (%)	E (%)	F (%)
$CHCl_3$	10	8.9	15.8	40.4	8.0	—	1
$CHCl_3$	61	18.5	9.8	28.4	—	15.5	1
$CH_3CO_2C_2H_5$	10	—	6.8	76.5	6.0	0.9	—
$CH_3CO_2C_2H_5$	78	17.2	3.0	6.6	—	47.3	—

If the initial product of deoxygenation is phosphoryl bromide, the by-products could result from attack by the phosphoryl bromide on the *N*-oxide. Other trivalent phosphorus compounds which have been used for deoxygenation of quinoline *N*-oxides are triphenylphosphine[365] and triphenyl phosphite.[399,366] Treatment of the quinoline *N*-oxide–boron trifluoride adduct with a mixture of potassium dihydrogen phosphate and phosphoric acid at 280–300 °C gave a small yield of quinoline, but this may have been due to thermal deoxygenation.[400] There is one report of partial conversion of a cyanide to a carboxamide[386] during deoxygenation by phosphorus trichloride.

The final group of deoxygenation reactions include a variety of reactions based on metals and salts. Zinc dust and acetic acid[181,1,81] or hydrochloric acid[79] has been used for a variety of quinoline *N*-oxides, including the mixed 2-(*n*-alkyl)-4-hydroxyquinoline *N*-oxides constituting the dihydrostreptomycin antagonist from *Pseudomonas pyocyanea*.[54] Iron and acetic acid,[112,401,113] iron(II) salts with potassium hydroxide[27,95] and tin(II) chloride with acetic acid[358] have also been used. Of the complex hydrides, tributyltin hydride[402] and sodium borohydride[403] have been reported to deoxygenate quinoline *N*-oxide. Sodium borohydride, with 4-chloro- or 4-nitroquinoline *N*-oxides, gave mixtures in which nucleophilic replacement of the nitro group or chlorine atom was observed, together with a small amount of reduction of the pyridine ring.[403] Deoxygenation occurred when quinaldine or lepidine *N*-oxide was condensed with benzylic alcohols and potassium hydroxide[404] to give arylvinyl quinoline (**145** and **146**); this may be another example of the alcohol deoxygenation quoted on p. 430.

Deoxygenation of quinoline *N*-oxide occurs during a synthesis of phenylglyoxylic acids, such as (**147**), from dibromoacetophenones.[405]

c. Reduction of Substituents on Quinoline *N*-oxides Virtually all the reductions performed on substituents, with retention of the *N*-oxide group, have been of nitro groups. A number of β-arylvinylquinoline *N*-oxides have been catalytically reduced to give the *β*-arylethylquinoline *N*-oxide; this is almost always possible, since reduction of the *N*-oxide is the slower process. Arylethylquinoline *N*-oxides thus prepared are listed in Table 9.

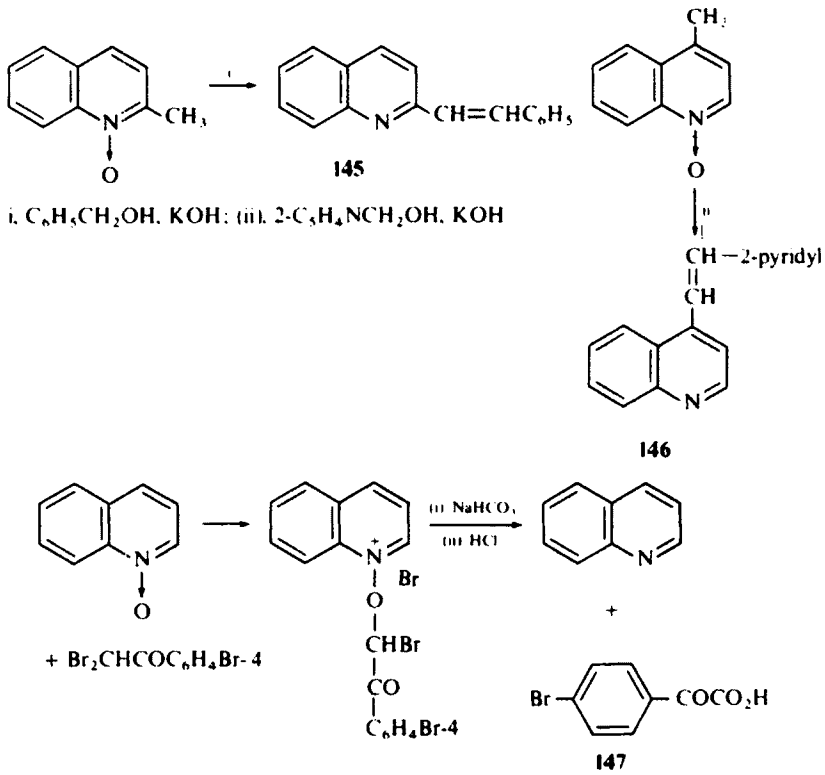
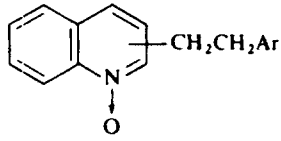


TABLE 9. β-Arylethylquinoline *N*-Oxides Prepared by Reduction



Position	Aryl	Reduction conditions	Yield (%)	M.p. (°C)	References
2	C_6H_5	Pd/C; Raney Ni; Pt	72, 88, 42	83–84	406, 369
2	2-Pyridyl	Raney Ni	47	76–68	368
2	2-Thienyl	Raney Ni	20	43–44	368
2	2-Tetrahydrofuryl	Raney Ni	24	57–59	368
4	C_6H_5	Raney Ni; Pd	—	161–162	369

Most of the reductive transformations of nitroarenes have been observed with nitroquinoline *N*-oxides. Most of the detailed study has been carried out on the 4-nitroquinoline *N*-oxides, because of their carcinogenic and mutagenic activity. Amines, hydroxyamines, nitroso and azoxy *N*-oxides prepared by reduction of nitro groups are grouped in Table 10.

TABLE 10. Reduction Products from Nitro- and Hydroxyaminoquinoline *N*-Oxides

Starting material substituent(s)	Product substituent(s)[a]	Reducing agent	Yield (%)	References	M.p. (°C) and derivatives
3-Hydroxyamino	Bisazo(1-oxido-quinoline)	$FeCl_3$, HCl	41	11	249–251 (dec.) m.p.
4-Nitro	4-Hydroxyamino	Hydrazine hydrate	49	51	198.5 m.p.;[407] hydrochloride 198;[407] sulphate 202 (dec.); picrate 162;[410] *NO*-diacetyl derivative 100[835]
		Phenylhydrazine	—	407	
		Ascorbic acid	87	408	
		Sodium borohydride	30	409	
		Pd/C; H_2	—	410	
4-Nitroso	4-Hydroxyamino	Phenylhydrazine	—	305	
	4-Amino	Pd/C, H_2	—	305	
4-Nitro	4-Amino	Pd/C; H_2; acid	—	411	272 m.p.;[411] hydrochloride 275 (dec.)[411]
	NN'-Di(1-oxido-4-quinolyinyl)hydrazine	Pd/C; H_2; neutral *or* zinc dust *or* ammonium sulphide	—	411	Hydrochloride 202
4-Azido	4-Amino	Pd; H_2	90	412	
		Hydrazine	53	412	
4-Hydroxyamino	4-Amino	2 N HBr, 240 °C	—	370	
	3-Bromo-4-amino	Conc. HBr, 200 °C	71	370	202–203 m.p.
	3-Chloro-4-amino	Conc. HCl, 200 °C	79	370	220 m.p.
3-Methyl-4-nitro	4-Amino-3-methyl	Phenylhydrazine	70	379	242–243 m.p.
3-(Dicarbethoxymethyl)-4-nitro	3-(Dicarbethoxymethyl)-4-amino	Pd/C; H_2	25	413	
4-Hydroxyamino-2-methyl	4-Amino-2-methyl	2 N HBr, 240 °C	49	370	240 m.p.
	4-Amino-3-chloro-2-methyl	HCl, 180 °C	79	370	222 m.p.
5-Methyl-4-nitro	4-Hydroxylamino-5-methyl	Phenylhydrazine	60	223	173–180 m.p.; hydrochloride 195–198
6-Methyl-4-nitro	4-Hydroxylamino-6-methyl	Phenylhydrazine	100	223	212–213 m.p.; hydrochloride 221–223
7-Methyl-4-nitro	4-Hydroxylamino-7-methyl	Phenylhydrazine	95	223	205 m.p.; hydrochloride 243–245
8-Methyl-4-nitro	4-Hydroxylamino-8-methyl	Phenylhydrazine	17	223, 379	146 m.p.; hydrochloride 189–190

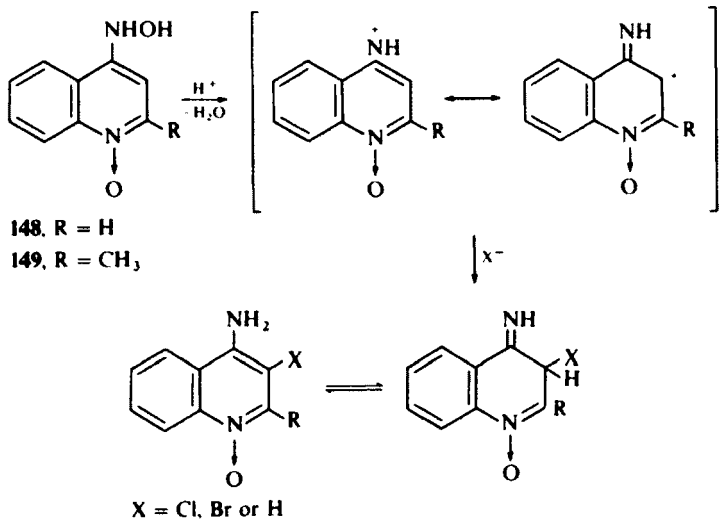
[a] All are *N*-oxides.

TABLE 10. Reduction Products from Nitro- and Hydroxyaminoquinoline *N*-Oxides

Starting material substituent(s)	Product substituent(s)[a]	Reducing agent	Yield (%)	References	M.p. (°C) and derivatives
6-*n*-Butyl-4-nitro	6-*n*-Butyl-4-hydroxyamino	Phenylhydrazine	92	414	216–217 m.p.; hydrochloride 169.5–170.5
6-*t*-Butyl-4-nitro	6-*t*-Butyl-4-hydroxyamino	Phenylhydrazine	93	414	Hydrochloride 181–181.5
6-*n*-Hexyl-4-nitro	6-*n*-Hexyl-4-hydroxyamino	Phenylhydrazine	—	414	Hydrochloride 179–180
6-Cyclohexyl-4-nitro	6-Cyclohexyl-4-hydroxyamino	Phenylhydrazine	100	414	Hydrochloride 187–188 (dec.)
3-Bromo-4-nitro	4-Hydroxyamino	Phenylhydrazine	27	379	
		Sodium borohydride	31	379	
	4-Aminoquinoline	Pd; H_2	42	379	
6-Chloro-4-nitro	6-Chloro-4-hydroxyamino	Phenylhydrazine	85	223	199–200 m.p.; hydrochloride 223
7-Chloro-4-nitro	7-Chloro-4-hydroxyamino	Phenylhydrazine	73	223	233 m.p.; hydrochloride 207
3,6-Dinitro	3,6-Diamino	Pd/C; H_2	—	387	265 (dec.) m.p.
4,6-Dinitro	4-Hydroxyamino-6-nitro	Phenylhydrazine	90	223	210 m.p.; hydrochloride 202–203
4,7-Dinitro	4-Hydroxyamino-7-nitro	Phenylhydrazine	85	223	207 m.p.; hydrochloride 197–198
3-Methoxy-4-nitro	4-Amino-3-methoxy	Pd/C; H_2	62	379	226–228 m.p.; hydrochloride 235 (dec.)
	4-Amino-3-hydroxy	Pd/C, H_2; then HBr	100	414	Hydrobromide 229.5 (dec.)
8-Hydroxy-5-nitroso	5-Amino-8-hydroxy	Sodium dithionate	—	151	180–182 (dec.) m.p.
4-Amino-3-nitro	3,4-Diamino	Pd/C; H_2	—	387	265 (dec.) m.p.

[a] All are *N*-oxides.

The most important reducing agents are hydrogen with a catalyst (the pH can be important in determining the degree of reduction) when the amine is generally produced, and hydrazine or phenylhydrazine, which offer a good route to the hydroxyamino compound. Other reagents which have been used are zinc dust or ammonium sulphide,[411] sodium borohydride (for nitro to hydroxyamino[409, 379]), sodium dithionate (nitro to amino[151]), and hydrochloric or hydrobromic acids at high temperature, which converted the 4-hydroxyaminoquinoline *N*-oxides (**148**) and (**149**) into the 4-amino derivatives with or without halogenation in position 3;[370] the proposed mechanism is shown.

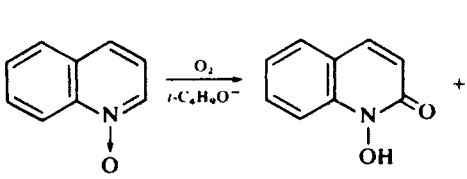


Many workers have studied the reduction of 4-nitroquinoline *N*-oxide, seeking analogies for biochemical reduction which might occur in animal tissue. Ascorbic acid reacts with 4-nitroquinoline *N*-oxide to give 4-hydroxyaminoquinoline *N*-oxide and 4-aminoquinoline *N*-oxide;[408] at pH 8.0 and 37° there is 87% conversion into 4-hydroxyaminoquinoline *N*-oxide. A later study of the effect of metals on the reduction showed that Cu^{II} and Mo^{VI} gave the hydroxyamino derivative; at a higher concentration of ascorbic acid Mo^{VI} reduced the hydroxyamine to the amine.[415] Glutathione and cysteine are oxidized by 4-hydroxyaminoquinoline *N*-oxide, but here the *N*-oxide is catalytic.[416] *In vivo* reduction of 4-nitroquinoline *N*-oxide to 4-hydroxyamino- and subsequently 4-aminoquinoline *N*-oxide, in rats[417, 418] or mice[419] was accompanied by the production of some 4-hydroxyquinoline *N*-oxide, particularly in areas adjacent to the injection site. Reducing activity in rat liver homogenate[420, 421] was reported to be due to a reductase using NADPH or NADH as donors. A variety of other nitro compounds failed to act as hydrogen acceptors; the product was 4-hydroxyaminoquinoline *N*-oxide. It was subsequently shown that a further photochemical reaction is possible,[423] giving first bisazo(1-oxido-4-quinoline) and then the corresponding azoxy derivative. From *E. coli, Candide utilis, Br. liquefaciens, Ps. aeruginosa* or *A. niger*, 4-nitroquinoline *N*-oxide, 4-hydroxyaminoquinoline *N*-oxide and 4-aminoquinoline *N*-oxide were shown to be formed with a small amount of 4-aminoquinoline.[424] For reduction using cell wall suspensions of *E. coli*, glucose was found to be essential in aerobic conditions but reduction still proceeded under anaerobic conditions.[246] Diaphorase was found to be an

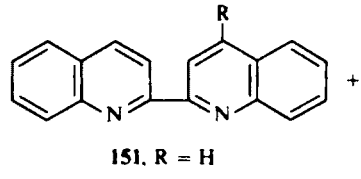
activating enzyme for the conversion of 4-nitro- to 4-hydroxyaminoquinoline *N*-oxide (or to some reactive intermediate).[425]

B. Oxidation and Dehydrogenation

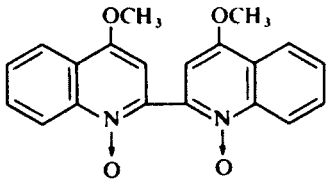
The quinoline nucleus can be ruptured by oxidizing agents; a number of examples have been given in Section II. 1 (p. 380). Briefly, it is possible to isolate *o*-nitrobenzoic acid from quinoline *N*-oxide, presumably via the *o*-nitrocinnamic acid,[23] while 2-phenylquinoline *N*-oxide has given *N*-benzoylanthranilic acid,[27,28] and 2-(*N*-methylamino)-quinoline *N*-oxide gave *o*-nitrocinnamonitrile.[30] Direct nuclear oxidation would appear to be involved in the reaction of quinoline *N*-oxides with lead tetraacetate, but these are dealt with among other reactions which give rise to carbostyril derivatives (p. 457).[61,32] There are a number of examples of oxidative coupling to give 2,2'-biquinolyl derivatives. Oxidation of quinoline *N*-oxide by oxygen at 70 °C in the presence of potassium *t*-butoxide gave 1-hydroxycarbostyril (**150**), 2,2'-biquinolyl (**151**) and the monoxide (**152**).[96] There was no reaction under nitrogen, and reaction was inhibited by hydroquinone, while irradiation increased the yield of hydroxycarbostyril to 52%; this yield was further increased (92%) using tetrahydrofuran, while the best yield of biquinolyl (**151**) was in *t*-butanol with *t*-butoxide. Other *N*-oxides were not oxidized under these conditions. The conventional procedure for the synthesis of biquinolyls, using palladium/charcoal has been used to prepare 4,4'-dimethoxybiquinolyl *NN'*-dioxide (**153**) but some deoxygenation occurred.[98] Very poor yields of the biquinolyls (**151**) and (**154**) have been reported by treatment of quinoline *N*-oxide with quinoline or 4-methylquinoline and 'platinated palladium/charcoal'.[426,821]



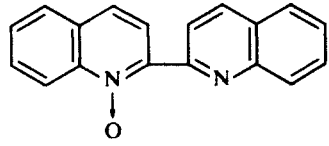
150



151, R = H
154, R = CH_3

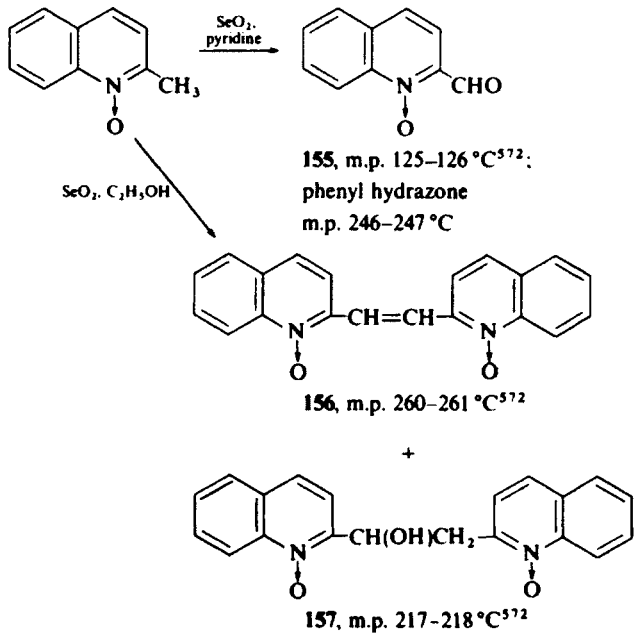


153



152

Alkyl side-chains on quinoline *N*-oxides can be oxidized to an aldehyde or ketone or to the carboxylic acid. Selenium dioxide has been used to oxidize 2-methylquinoline *N*-oxide to quinoline-2-aldehyde *N*-oxide (**155**);[386,427,104,428,399] the yields were variable, but in pyridine reached *ca.* 50%. Some aldehyde condensed with the starting material to give the di(1-oxido-2-quinolyl)ethene (**156**) and the alcohol (**157**). An interesting base-catalysed oxidation of 2-(hydroxymethyl)quinoline *N*-oxide (**158**) gave the phenylhydrazone (**159**) of the deoxygenated aldehyde.[429] Thallium triacetate or lead tetracetate has also been used to convert 2-methylquinoline *N*-oxide into the aldehyde (**155**), the monoacetate (**160**) and the deoxygenated aldehyde (**161**) and diacetate (**162**).[430,431] The reagents were less reactive and less selective with 4-methylquinoline *N*-oxide.[431] Two



possible reaction schemes were advanced for the reaction between thallium triacetate and the *N*-oxide;[430] one involved attack on the 1-acetoxy-2-methylquinolinium salt, the other on the thallium acetate adduct (**163**) (Scheme 8), leading to the monoacetate (**160**).

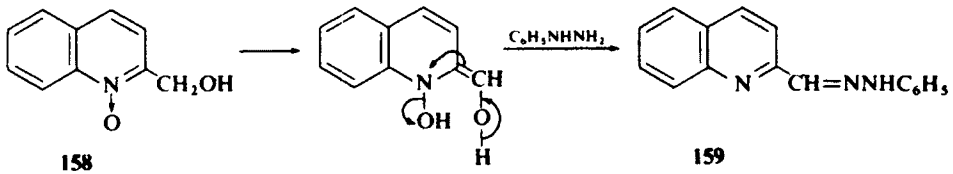
Some 4-quinolylacetonitriles have been converted, by oxidation with peracetic acid,[141,108,107,140,432] into the corresponding ketones; an example is provided by the compound (**164**).[432] The oxidation has been performed on the parent quinoline, giving in one reaction *N*-oxidation and ketone formation.[140,108]

Oxidation of quinoline *N*-oxides with unsaturated side-chains, such as styrylquinoline *N*-oxide (**165**),[433] or acrylonitriles[434] or the hydrazone (**166**),[104] or more vigorous oxidation of alkylquinoline *N*-oxides, gives carboxyquinoline *N*-oxides. Quinaldine *N*-oxide has been oxidized by alkaline hexacyanoferrate(III)[159] (other *N*-oxides, unsubstituted at position 2, gave carbostyrils), and lepidine *N*-oxide (**167**) by alkaline permanganate.[104]

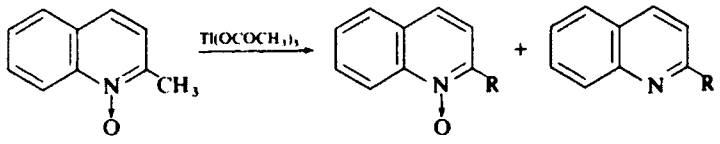
Compounds containing sulphur atoms attached directly to the quinoline ring can undergo a variety of oxidative transformations. Thioethers have been oxidized to sulphones or sulphoxides (see p. 382 for a cyclic example[42]). Oxidation of 4-quinolyl *p*-tolylthioether *N*-oxide (**168**) gave the sulphone (**169**),[67] while a range of thioethers of general formula (**170**) gave, with peracetic acid or with chlorine in methanol, the sulphonyl derivatives (**171**) in good yields.[435]

Quinoline-4-thiol *N*-oxide has been converted by oxidation into the sulphonic acid [isolated as sulphonamide (**172**); oxidized by chlorine[436]] and into the disulphide (**173**) (oxidant peracetic acid[437]). Quinoline-2-thiol *N*-oxide has been oxidized by iodine to the disulphide (**174**);[438] the polarography of the disulphide has been examined.[438]

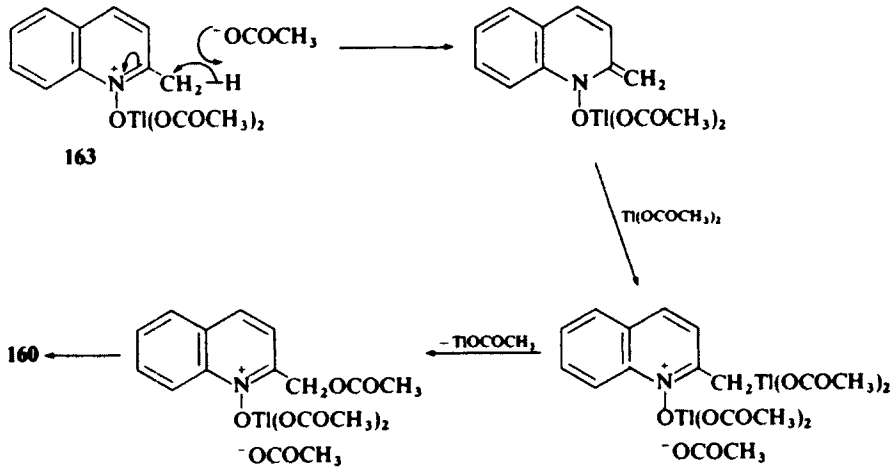
The other major group of substituents which are susceptible to oxidation are amines, hydroxylamines, nitroso compounds and azocompounds. Oxidation of tertiary amines has been mentioned earlier (p. 382); in general these aliphatic amine substituents are



158 159

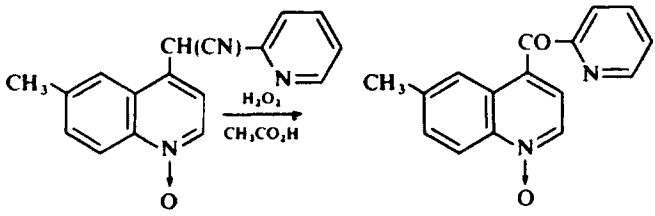


155, R = CHO 161, R = CHO
160, R = CH_2OCOCH_3 162, R = $CH(OCOCH_3)_2$

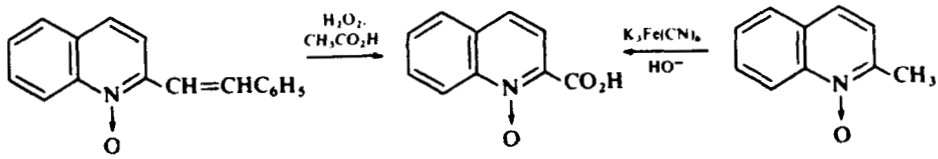


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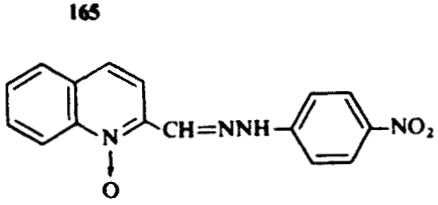
SCHEME 8



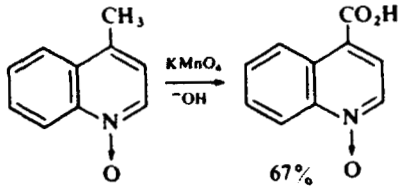
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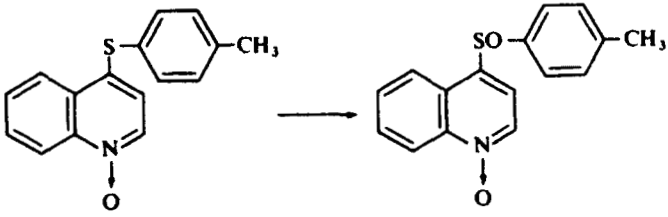
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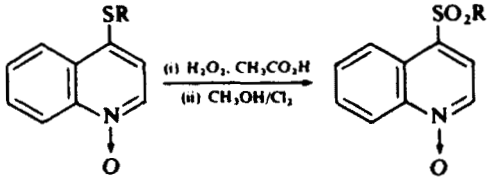
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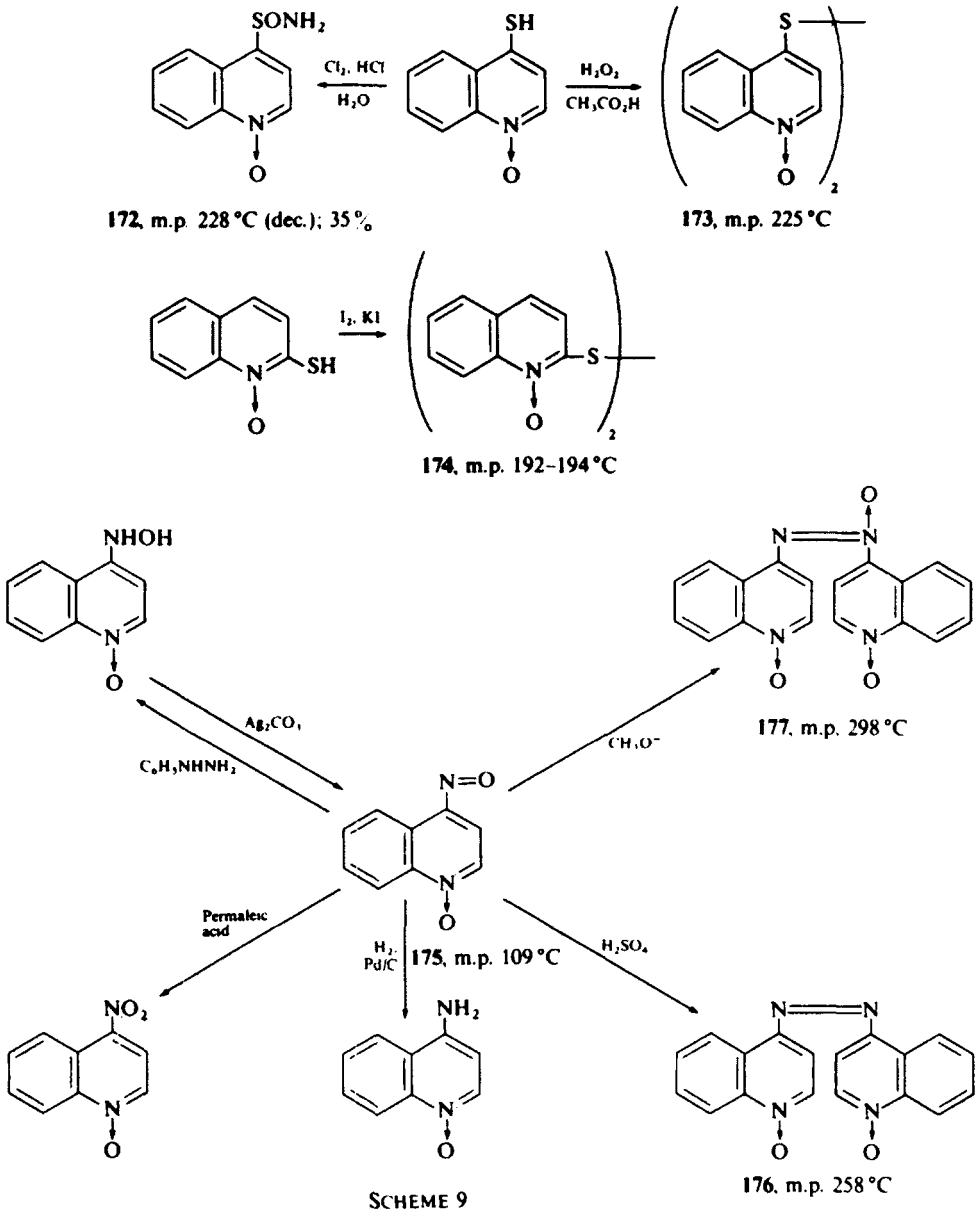
168 169, m.p. 149–150 °C



170 171

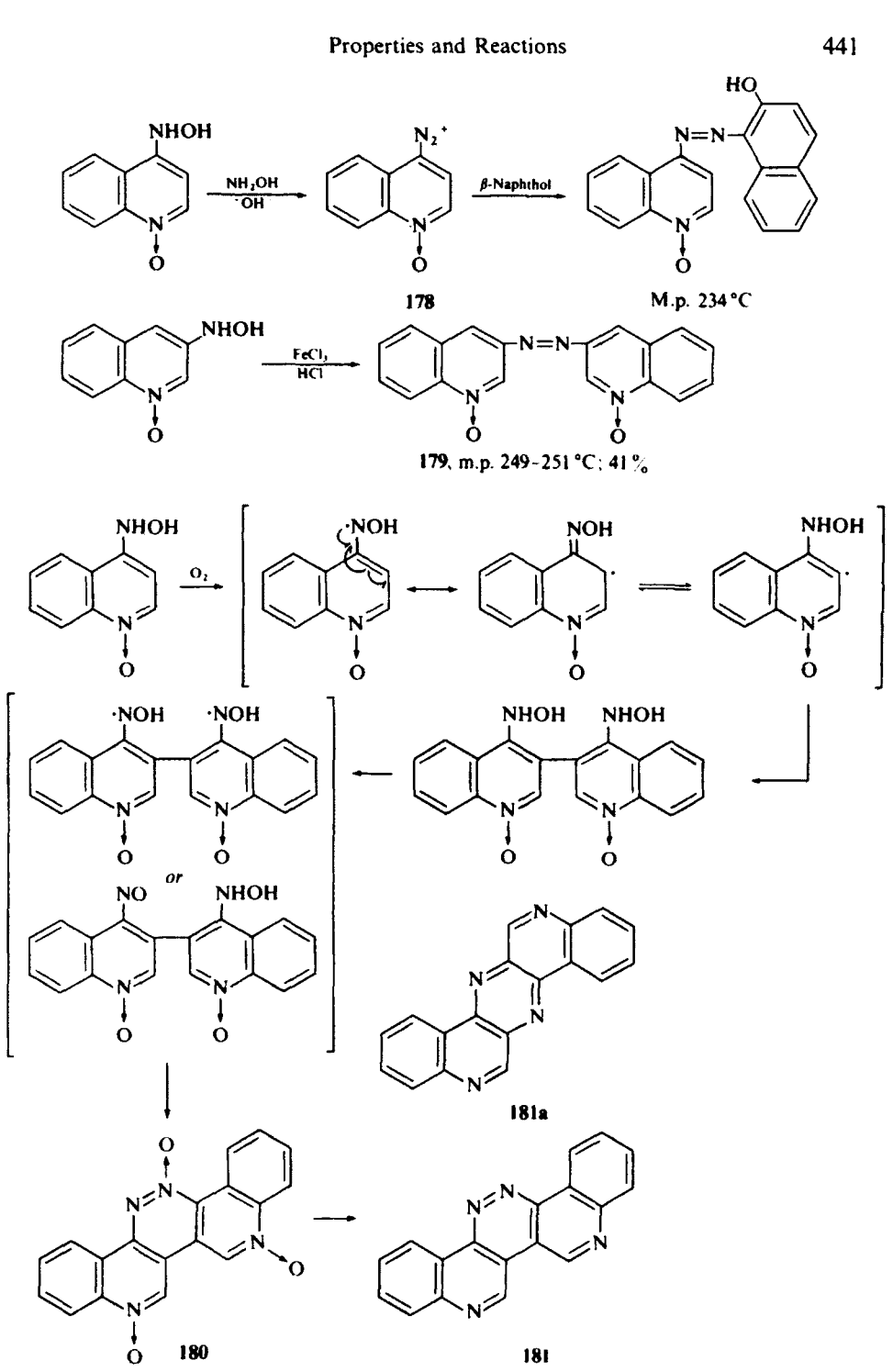
R in (170)	CH_3	C_2H_5	$(CH_3)_2CH$	$HOCH_2CH_2$	$C_6H_5CH_2$	C_6H_5	$NO_2C_6H_4$
Method (i) (%)	88	58	55	38	80	85	90
Method (ii) (%)	90	65	—	—	89	—	94
M.p. (°C) of (171)	210–212	128–130	174–176	177–178	215–216	143–144	195–196

more readily oxidized than the heterocyclic nitrogen. Particular interest has been shown in the oxidation of 4-hydroxyaminoquinoline *N*-oxide, in the search for 4-nitrosoquinoline *N*-oxide. A transient green colour, observed when 4-hydroxyaminoquinoline *N*-oxide was dissolved in alkaline aqueous ethanol, was advanced[439] as evidence for the intermediacy of the 4-nitroso compound (**175**) in the formation of the isolated products, the azo compound (**176**) and the azoxy compound (**177**). In subsequent work[235] 4-nitroquinoline *N*-oxide was isolated; in the presence of hydroxy-



SCHEME 9

lamine the diazo compound (**178**) was shown to be present, by trapping it with β-naphthol. Further evidence for the presence of the nitroso compound when the 4-hydroxyaminoquinoline *N*-oxide was oxidized by horseradish peroxidase[440] was followed by its isolation by Abramovitch and Smith[305] from oxidation using silver carbonate on Celite. Its preparation and reactions are summarized in Scheme 9. Oxidation of 3-hydroxyaminoquinoline *N*-oxide [with iron(III) chloride] also gave the corresponding bisquinolyl azo compound (**179**).[11] A large amount of free radical was


NHOH
NH2OH
·OH
N2+
β-Naphthol
HO
N=N
178
M.p. 234 °C
FeCl3
HCl
179, m.p. 249-251 °C; 41 %
O2
·NOH
NOH
or
NO
181a
180
181

SCHEME 10

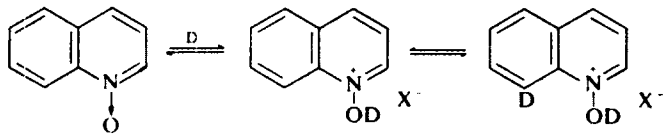
observed during the oxidation of 4-hydroxyaminoquinoline *N*-oxide.[292] A catalytic effect on vitamin C oxidation by 4-nitroquinoline *N*-oxide has been reported.[1398]

Small amounts of polycyclic compounds (**180**) and (**181**) were also found after treatment of 4-hydroxyaminoquinoline *N*-oxide with oxygen in an alkaline medium.[441] A radical mechanism was suggested,[292] as shown in Scheme 10. The polycycles (**181**) and (**181a**) were obtained after heating 4-hydroxyaminoquinoline *N*-oxide to 200–240 °C in water,[844] possibly via a diradical.

C. Electrophilic Substitution

Quinoline *N*-oxides react with alkyl halides[845] or oxonium salts[846] to give *N*-alkoxyquinolinium salts. Acylation is mentioned in later sections.

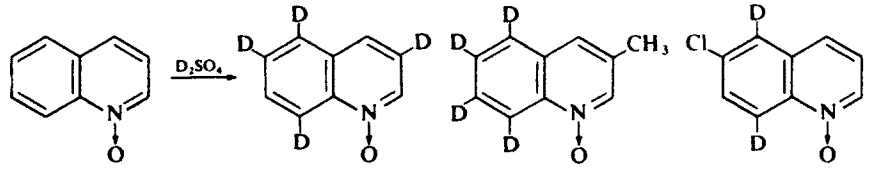
It is well known that the heterocyclic *N*-oxides are more readily substituted on the heterocyclic ring by electrophiles, notably at position 4, than are the parent heterocycles. The electrophilic substitution by deuterions has been studied by Kawazoe and Ohnishi[274] using D_2SO_4–D_2O mixtures, acid concentrations ranging from 45 to 96.5% and temperatures ranging from 150 to 250 °C. The order of substitution was position 8, followed by 5 and 6 (at 150 °C), with some substitution at 7 (at 200 °C), completed at 250 °C when some 3-substitution occurred. The surprising observation was made that there was little difference between the substitution of quinoline and of the *N*-oxide under acidic conditions; this contrasts with the electrophilic nitration, where 4-substitution can occur in high yield, since no substitution by deuterosulphuric acid occurred at positions 2 or 4, even at 250 °C. On the other hand, the *N*-oxide underwent deuterium exchange at position 2 under neutral or weakly basic conditions. The sites of exchange were observed by nmr spectroscopy, and the findings were confirmed by Katritzky and coworkers,[442,848] who measured rate profiles for the 8- and for the 5- and 6-protons. Both groups agree that the acid-catalysed exchange must take place through the conjugate acid (**182**).



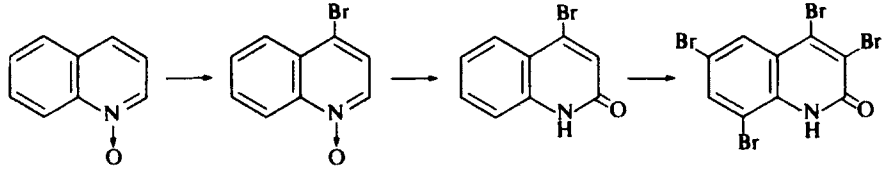
182

Uehara and Kawazoe[443] have prepared tritiated *N*-oxides, having first studied the deuteriation. Using concentrated deuterosulphuric acid at 260 °C they obtained 3,5,6,8-tetradeuterioquinoline *N*-oxide (**183**); 3-methylquinoline *N*-oxide gave first the 5,8-dideuterio derivative then 5,6,7,8-tetradeuterio compound (**184**). No substitution was observed at position 2 or 4, or in the methyl group. From 6-chloroquinoline *N*-oxide they obtained 5,8-dideuterio-6-chloroquinoline *N*-oxide (**185**), but the exchange was slower. Tritiation of quinoline *N*-oxide gave 3,5,6,(7),8-tritiated *N*-oxide. Exchange by tritium gas exposure was found unsatisfactory for 4-nitroquinoline *N*-oxide, but exchange was achieved by treatment of the *N*-oxide, adsorbed on neutral alumina, with tritium. The tritiated quinoline *N*-oxide was nitrated to give 4-nitroquinoline *N*-oxide bearing tritium labelling.

Ochiai and Okamoto first examined the bromination of quinoline *N*-oxide, obtaining a perbromide which, when heated with bromine water at 100 °C gave 2–3% of 4-bromoquinoline *N*-oxide (**186**) and 3,4,6,8-tetrabromocarbostyril (**187**), which was also obtained from 3-, 4- and 6-bromoquinoline *N*-oxides.[444] A similar reaction with 5-bromoquinoline *N*-oxide gave an isomeric tetrabromocarbostyril, the initial formation of a 4-bromoquinoline *N*-oxide being hindered by the 5-substituent.



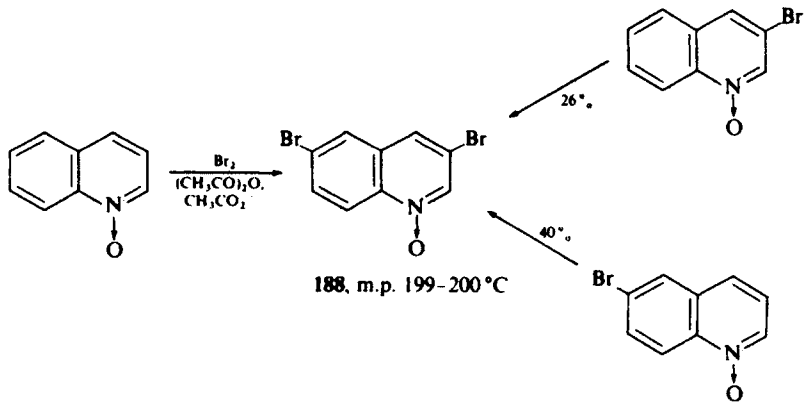
183 184 185



186 187

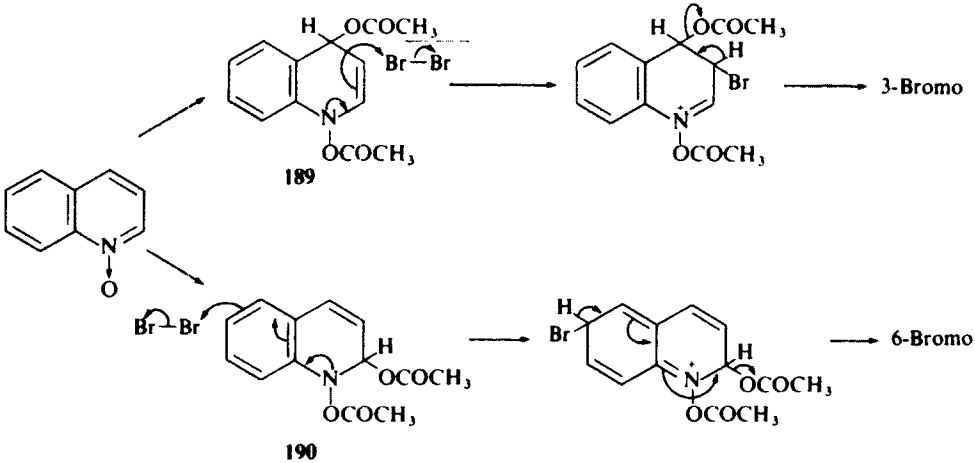
In contrast, bromination in acetic anhydride in the presence of sodium acetate gave 3,6-dibromoquinoline *N*-oxide (**188**) in 60% yield.[373,445] The dibromide (**188**) was obtained by a similar bromination from 3-bromoquinoline *N*-oxide or from 6-bromoquinoline *N*-oxide. It was suggested that addition of acetic anhydride to give the dihydroquinoline (**189** or **190**) is followed by bromination at position 3 or 6 as shown on p. 444.

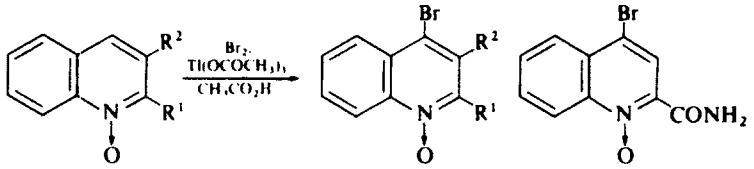
Bromination of quinoline *N*-oxide by bromine and thallium triacetate in acetic acid at 50 °C gave 4-bromoquinoline *N*-oxide (65.8%).[861] Quinaldine *N*-oxide and 3-bromoquinoline *N*-oxide gave 4-bromo derivatives (**191a** and **191b**); 2-cyanoquinoline *N*-oxide gave a mixture of 4-bromo-2-cyano- (**191c**) and the 4-bromo-2-carbamoylquinoline *N*-oxide (**191d**).



188, m.p. 199–200 °C

Iodine in 20% oleum reacted with quinoline *N*-oxide at room temperature to give 5-iodoquinoline and at 100 °C to give a diiodoquinoline *N*-oxide.[869] With iodine chloride in acetic acid quinoline *N*-oxide gave 3-iodocarbostyril (**191**);[446] whether the iodination precedes the formation of carbostyril is not clear. A number of substituted quinoline *N*-oxides have been halogenated. Bromination of 1-hydroxycarbostyril (**192**) gave the 6-bromo derivative (**193**);[445] 4-hydroxyquinoline *N*-oxide (**194**) gave 3-bromo-4-hydroxyquinoline *N*-oxide (**195**).[447] Bromination of 4-aminoquinoline *N*-oxide gave the 3-bromo derivative (**196**); similar treatment of 4-methoxyquinoline *N*-oxide gave a bromine-containing compound which gave only 4-hydroxyquinoline *N*-oxide after treatment with hydrobromic acid.[448] Oxine *N*-oxide (**197**) has been chlorinated (with





$R^1 = R^2 = H$; 65.8% **191d**, 11%

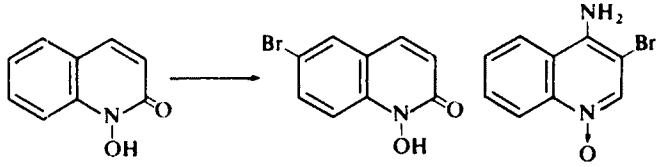
191a, $R^1 = CH_3$, $R^2 = H$; 63%

191b, $R^1 = H$, $R^2 = Br$; 95%

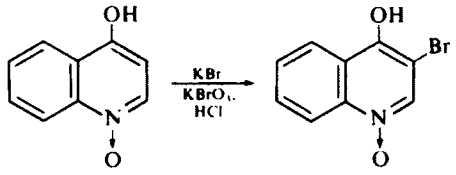
191c, $R^1 = CN$, $R^2 = H$; 22%

sulphuryl chloride) to give a mixture of 5-chloro and 5,7-dichloro derivatives (**198** and **199**),[374] brominated to give 5,7-dibromo-8-hydroxyquinoline *N*-oxide (**200**)[374] and iodinated to give a compound formulated as 5-iodo-8-hydroxyquinoline *N*-oxide (**201**).[151]

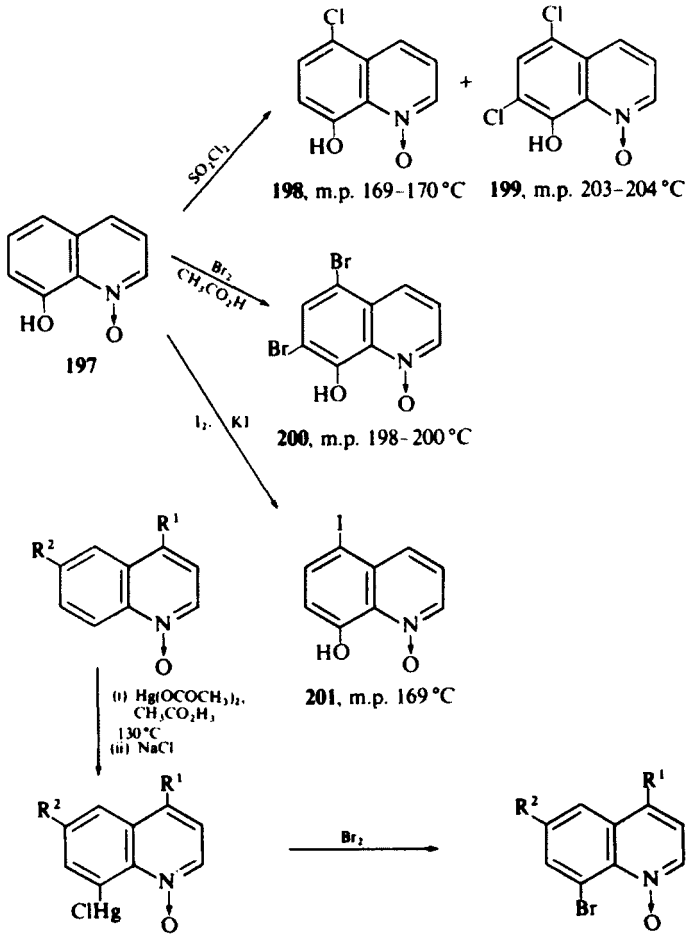
Early studies of the mercuration of quinoline *N*-oxide[372] and those of 6-methyl- and 4-bromoquinoline,[449] showed that the 8-mercurichlorides (**202–204**) were formed, all



192 **193**, m.p. 161 °C **196**, m.p. 202–204 °C

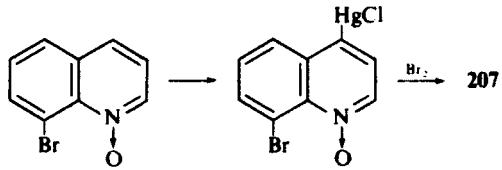


194 **195**, m.p. 212–214 °C



202, $R^1 = R^2 = H$, m.p. 235–236 °C; 72%
203, $R^1 = H$, $R^2 = CH_3$, m.p. 252 °C (dec.); 100%
204, $R^1 = Br$, $R^2 = H$, m.p. 130–132 °C (dec.); 35%
205, $R^1 = R^2 = H$, m.p. 102–104 °C
206, $R^1 = H$, $R^2 = CH_3$, m.p. 178 °C
207, $R^1 = Br$, $R^2 = H$, m.p. 89 °C

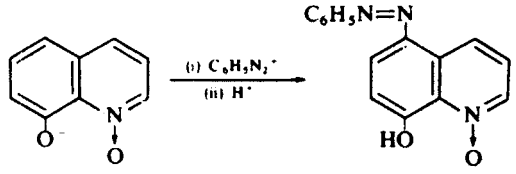
being converted by treatment with bromine into the corresponding 8-bromoquinoline *N*-oxides (**205–207**). Mercuration of 8-bromoquinoline *N*-oxide (**205**) gave the 4-mercurichloride (**208**). A later, more detailed, study[401] of the mercuration of quinoline *N*-oxide was performed at various temperatures (20–130 °C) and with mercury(II) acetate, perchlorate or sulphate. The product analysis was performed by gas chromatography of



208, m.p. 226 °C; 17%

the mixed quinoline bromides obtained after bromination and subsequent deoxygenation. In summary, total yields were high only when mercury(II) acetate was used at 130 °C; at this temperature 81% of the product was substituted at position 8, with minor amounts of 3-, 5-, 6- and 7-substitution. At lower temperatures the results were similar, as they were also with the perchlorate, with the exception that 3-substitution was not observed. The only strikingly different results were obtained with mercury(II) sulphate; all of the isomeric bromoquinolines were observed, but the major products were due to substitution at positions 3 and 8 in almost equal proportions. The predominance of substitution at position 8 has been explained in terms of coordination of the reagent with the oxygen atom, which arranges the mercury atom at a bond-forming distance from the carbon atom at position 8.[401]

It has been reported that quinaldine and lepidine *N*-oxides do not undergo azo coupling;[450] not unexpectedly, 8-hydroxyquinoline *N*-oxide does couple in an alkaline medium, giving the 5-phenylazo derivative (**209**).[451]



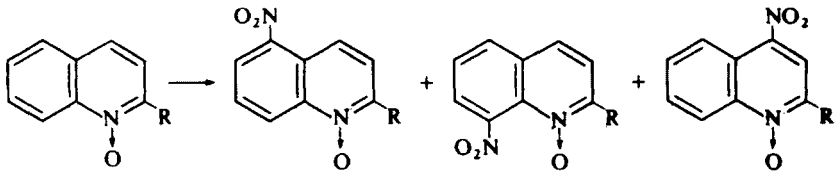
209, m.p. 183–184 °C; 78%

The most studied electrophilic substitution reaction of quinoline *N*-oxides has been nitration. Ochiai and co-workers early reported the temperature dependence of nitration when sulphuric acid and nitric acid (or metal nitrates) were used. At room temperature or below a mixture of 5- (**210**) and 8-nitroquinoline *N*-oxides (**211**) was formed, but at 70 °C or at higher temperatures the nitration gave good yields of 4-nitroquinoline *N*-oxide (**212**).[452,453] A rate study[454] supported the suggestion that nitration in the 5- and 8-positions involved the cation, while nitration at position 4 involved the free base. In the latter case a higher energy of activation was presumably involved, hence the predominance of the 4-nitro compound in the product at higher temperatures. Prolonged treatment with sulphuric acid and potassium nitrate gave 4,8-dinitroquinoline *N*-oxide (**213**).[452,455]

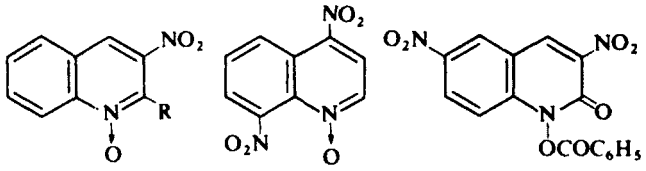
An observation by Ochiai and Satake[135] that nitration of quinaldine *N*-oxide gave better yields of the 4-nitro derivative (**214**) when the sulphuric acid concentration used was 80% rather than the previously used 96–100% was confirmed by Hamana and Nagayoshi[456] for a number of 6-substituted quinoline derivatives, and the conditions of choice for preparing 4-nitroquinoline *N*-oxides appear to be a temperature of 70–80 °C and a concentration of sulphuric acid of around 80–85%. At temperatures above 120 °C deoxygenation was observed.[452]

When other nitrating reagents are used, quinoline *N*-oxide gives 3-nitroquinoline *N*-oxide (**215**). Such reagents are benzoyl nitrate[134] or, in a modification, silver nitrate on the pre-formed benzoyl derivative (**216**). When nitration of 4-halogenoquinoline *N*-oxides was attempted, using benzoyl chloride and silver nitrate, the 3-halogeno-4-hydroxyquinolinium betaines (**219a** and **219b**) were obtained.[808] In the same paper it was reported that the same reagent, with 2-ethoxyquinoline *N*-oxide, gave *N*-benzoyloxycarbostyril.

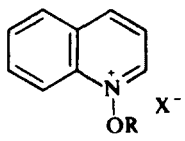
In general, nitrations where an *O*-acyl derivative can be formed have given 3-nitroquinoline *N*-oxide, as with tosyl chloride and sodium nitrite in dimethylformamide[457] (in this case nitrosation with subsequent oxidation was suggested). The production of 3-nitroquinoline *N*-oxides is often accompanied by the products of further



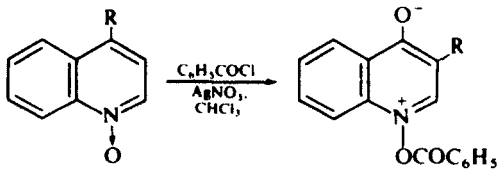
210, R = H **211**, R = H **212**, R = H
214, R = CH_3



215, R = H **213** **217**



216, R = COC_6H_5
218, R = CH_3
219, R = BF_3 (no X^-)



219a, R = Cl, m.p. 194–196 °C; 50 %
219b, R = Br, m.p. 199–202 °C; 20 %

reaction; thus, with excess of benzoyl nitrate appreciable quantities of 1-benzoyloxy-3,6-dinitrocarbostyril (**217**) were obtained.[458] Nitration of 1-methoxyquinolinium salt[459,460] (**218**) or of the boron trifluoride complex (**219**)[459,460] with metal nitrates also gave 3-nitroquinoline *N*-oxide, but from the boron trifluoride adduct (**219**), with benzoyl nitrate, only the 4-nitro derivative (**212**) was formed.[459–461] The mechanism of the reaction which produces 3-nitro derivatives has been commonly accepted as proceeding through a 1,4-dihydroquinoline intermediate,[462] as shown in Scheme 11, but Taylor[463] has disputed this suggestion, proposing an adduct with attack at position 4 by the nitro group, which subsequently rearranges to the 3-position (p. 453).

The full range of nitroquinoline *N*-oxides obtained by direct nitration is given in Table 11, and some comments on the course of nitration of substituted quinoline *N*-oxides follow.

The presence of alkyl groups makes little difference to the patterns of substitution already described, with the obvious exception that 4-methylquinoline *N*-oxides cannot undergo 4-substitution; there is a report that attempts to nitrate 2,4-dimethylquinoline

TABLE 11. Nitroquinoline *N*-Oxides Prepared by Direct Nitration of Quinoline *N*-Oxides

Starting material substituent(s)	Product substituent(s)	Reagent	Yield (%)	References	M.p. (°C) and derivatives
None	3-Nitro	$C_6H_5COONO_2$, $CHCl_3$, cold	44	134	
None[a]	3-Nitro	KNO_3, DMSO, 140 °C	47	460, 459	192–193[129]
None	3-Nitro	$NaNO_2$, DMF, *p*-$CH_3C_6H_4SO_2Cl$	60–80[c]	457	
None[b]	3-Nitro- (A) *and* 1-benzoyloxy-3,6-dinitrocarbostyril (B)	$AgNO_3$, $CHCl_3$, −15 to −20 °C	33[d]	464	M.p. of (B) 253–255 (dec.)
None	(A), 3,6-dinitro- (C), and 6-nitro (D)	CH_3COCl, $AgNO_3$, 15 to −20 °C	(A) 32 (C) 10 (D) trace	464	M.p. of (C) 237–238 M.p. of (D) 220–222
None	4-Nitro	HNO_3, H_2SO_4, 70 °C	80	67, 65, 70, 465, 68, 69, 466, 467, 72	154[67]
None	5-Nitro	$C_6H_5COONO_2$, BF_3	50	461	160–161
None	5-Nitro (E) *and* 8-nitro (F)	KNO_3, H_2SO_4, 0–20 °C	11–23 (E) 13–29 (F)	452, 453	M.p. of (E) 160–161[452] M.p. of (F), 180–182
None	4,8-Dinitro	KNO_3, H_2SO_4, 70 °C	55	455	220
2-(1-Oxido-2-quinolyl) (biquinolyl di-*N*-oxide)	4,4′-Dinitro	HNO_3 (*d* 1.42), 80–90 °C	21	98	290
2-Methyl	2-Methyl-3-nitro	$C_6H_5COONO_2$, $CHCl_3$	20–25	685	196–197.5
2-Methyl	2-Methyl-4-nitro	H_2SO_4, HNO_3, 70 °C	70	77, 468, 79, 71, 135	163[77]
2-Methyl	2-Methyl-5-nitro (G) *and* 2-methyl-8-nitro (H)	H_2SO_4, KNO_3, 0–20 °C	—	135	M.p. of (G) M.p. of (H) 225–227 (dec.)
2-Ethyl	2-Ethyl-4-nitro	H_2SO_4, KNO_3, 50 °C	70	84, 85	146–148[84]
2-*n*-Propyl	4-Nitro-2-*n*-propyl	H_2SO_4, KNO_3, 50 °C	—	84	158–160
2-Phenyl	4-Nitro-2-phenyl[e]	H_2SO_4 (70–75%), HNO_3	53	92, 94	132–132.5
2-Phenyl	2-(*m*-Nitrophenyl)[e]	H_2SO_4 (80–90%), HNO_3	78	94	198
2-Chloromethyl	2-Chloromethyl-4-nitro[f]	H_2SO_4, KNO_3, 50 °C	55	469	163
2-Hydroxymethyl	2-Hydroxymethyl-4-nitro	H_2SO_4, KNO_3, 55 °C	35	40	120 (dec.)

2-(2-Carboxyl-1-ethyl)	2-(2-Carboxy-1-ethyl)-4-nitro	H_2SO_4, KNO_3	54	40	155
2-Piperidinomethyl	4-Nitro-2-piperidinomethyl	H_2SO_4, KNO_3, 60–75 °C	75	40	100–102; hydrochloride, 133–133.5; picrate 176.8
3-Methyl	3-Methyl-4-nitro	H_2SO_4, KNO_3	77	223	179–180
4-Methyl	4-Methyl-8-nitro	H_2SO_4, KNO_3, water-bath	65	468, 380	220[380]
5-Methyl	5-Methyl-4-nitro	H_2SO_4, KNO_3	15	223	174–175
6-Methyl	6-Methyl-3-nitro	$C_6H_5COONO_2$, $CHCl_3$	—	470	227–228
6-Methyl	6-Methyl-3-nitro	KNO_3, DMSO[g]	24	460	229–231
6-Methyl	6-Methyl-4-nitro	H_2SO_4 (80%), KNO_3, 70–80 °C	80	456, 112, 471	183[456]
		or H_2SO_4 (85%), HNO_3, 20–25 °C	50	468, 460, 466, 472	
6-Methyl	6-Methyl-5-nitro	H_2SO_4 (85%), KNO_3, 20–25 °C	68	456	184–185
6-*n*-Butyl	6-(*n*-Butyl)-4-nitro	H_2SO_4, KNO_3, 90 °C	20	414	102
6-*t*-Butyl	6-(*t*-Butyl)-4-nitro	H_2SO_4, KNO_3, 90 °C	56	414	128–129
6-*n*-Hexyl	6-(*n*-Hexyl)-4-nitro	H_2SO_4, KNO_3, 90 °C	6	414	102
6-Cyclohexyl	6-Cyclohexyl-4-nitro	H_2SO_4, KNO_3, 90 °C	8	414	161–162
7-Methyl	7-Methyl-3-nitro	KNO_3, DMSO[h]	24	460	214–217
8-Methyl	8-Methyl-4-nitro	H_2SO_4, KNO_3	24	223, 379	153–154[223]
2,6-Dimethyl	2,6-Dimethyl-4-nitro	KNO_3, H_2SO_4 (80%) 75 °C	72	117	178–179
2,7-Dimethyl	2,7-Dimethyl-4-nitro	KNO_3, H_2SO_4 (80%) 75 °C	55	117	179–180

[a] Using the *O*-methyl methosulphate.
[b] By repeated treatment; low yield in single run.
[c] Using the 1-benzyloxyquinolinium chloride.
[d] Some quinoline *N*-oxide was recovered.
[e] Plus a small amount of 2-(*m*-nitrophenyl)-4-nitroquinoline *N*-oxide, m.p. 212 °C.
[f] Plus a small amount of 2-(chloromethyl)-*x*-nitroquinoline *N*-oxide, m.p. 139 °C.
[g] On the *O*-methyl methosulphate.
[h] On the *O*-methyl methosulphate.

TABLE 11 (*Cont.*)

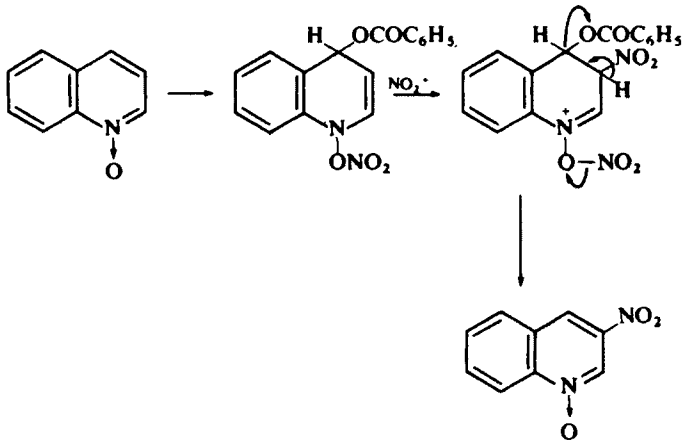
Starting material substituent(s)	Product substituent(s)	Reagent	Yield (%)	References	M.p. (°C) and derivatives
2-Chloro	2-Chloro-4-nitro	H_2SO_4, KNO_3, 70 °C	85	473	154–156
2-Bromo	2-Bromo-4-nitro	H_2SO_4, KNO_3, 70 °C	—	473	183
3-Fluoro	3-Fluoro-4-nitro	H_2SO_4 (79%), KNO_3, 90 °C	96	124	164–165
3-Chloro	3-Chloro-4-nitro	H_2SO_4, KNO_3	42	223	159–160
3-Bromo	3-Bromo-4-nitro	H_2SO_4, KNO_3, 100 °C	50	138	156
3-Bromo	3-Bromo-5-nitro *and* 3-bromo-8-nitro	H_2SO_4, KNO_3, 0–20 °C	70 and 12	138	149–150 (5-nitro); 234 (8-nitro)
3-Bromo	3-Bromo-6-nitro	$C_6H_5COONO_2$, $CHCl_3$	—	470	260–262
5-Chloro	5-Chloro-4-nitro	H_2SO_4, KNO_3	—	223	145–146
5-Iodo	5-Iodo-4-nitro	H_2SO_4, KNO_3	43	56	234–237
6-Chloro	6-Chloro-4-nitro	H_2SO_4 (85%), KNO_3, 110 °C	62	456, 471	193
6-Chloro	6-Chloro-5-nitro	H_2SO_4 (conc.), KNO_3, room temperature	73	456, 474, 471	213
6-Bromo	6-Bromo-4-nitro	H_2SO_4 (85%), KNO_3, 70–80 °C	68	456, 471	200–202
6-Bromo	6-Bromo-5-nitro	H_2SO_4 (95%), KNO_3, room temperature	66	456, 474, 471	215
7-Chloro	7-Chloro-4-nitro	H_2SO_4, KNO_3	90	475	
8-Fluoro	8-Fluoro-4-nitro	H_2SO_4, KNO_3, 90 °C	28	379	160
8-Chloro	8-Chloro-5-nitro	KNO_3, H_2SO_4	—	474	245–250
6,7-Dichloro	6,7-Dichloro-4-nitro	H_2SO_4, KNO_3	20	223	191
4-Nitro	4,5-Dinitro	KNO_3, fuming H_2SO_4, 10–20 °C	60	452	260–262 (dec.)
4-Nitro	4,6,8-Trinitro	HNO_3, P_2O_5, water-bath	60	130	189–191
5-Nitro	4,5-Dinitro	KNO_3, fuming H_2SO_4, 10–20 °C	25	452	260–262 (dec.)
6-Nitro	4,6-Dinitro	KNO_3, fuming H_2SO_4, water-bath	30	130, 471	218
2-Methyl-6-nitro	4,6-Dinitro-2-methyl	$NaNO_3$, H_2SO_4, 18–25 °C	46	135	194–195

8-Nitro	4,8-Dinitro	KNO_3, fuming H_2SO_4, water-bath	—	130	223 (dec.)
8-Nitro	4,6,8-Trinitro	HNO_3, P_2O_5, water-bath	30	130	189–191
2-Methyl-8-nitro	4,8-Dinitro-2-methyl	$NaNO_3$, H_2SO_4 (96%), 18–25 °C	69	135	219–220
2-Hydroxy	2-Hydroxy-6-nitro	HNO_3 (fuming), CH_3CO_2H, room temperature	—	168	203–205
2-Hydroxy	6,8-Dinitro-2-hydroxy	HNO_3 (*d* 1.5) room temperature	—	476	207
3-Methoxy	3-Methoxy-4-nitro	KNO_3, H_2SO_4	66	223	196
4-Hydroxy	4-Hydroxy-3-nitro	HNO_3, $(CH_3CO)_2O$, 65 °C	—	477	211
4-Methoxy	4-Methoxy-6-nitro- *and* 4-methoxy-7-nitro	HNO_3, H_2SO_4, 5–6 °C	— —	478, 479	200–202 (6-nitro); 179–180 (7-nitro)
5-Methoxy	5-Methoxy-3-nitro	C_6H_5COCl, $AgNO_3$, $CHCl_3$, room temperature	29	127	188–191
5-Tosyloxy	3-Nitro-5-tosyloxy	C_6H_5COCl, $AgNO_3$, $CHCl_3$, room temperature	40	127	197–199 (dec.)
6-Methoxy	6-Methoxy-4-nitro	KNO_3, H_2SO_4 (70%), 70–80 °C	5.6[i]	456, 471	204–205
6-Methoxy	6-Methoxy-5-nitro	KNO_3, H_2SO_4 (75%), 20–25 °C	90	456, 471, 479	182–184
7-Methoxy	7-Methoxy-3-nitro	C_6H_5COCl, $AgNO_3$, $CHCl_3$, room temperature	60	127	198–200 (dec.)
7-Tosyloxy	3-Nitro-7-tosyloxy	C_6H_5COCl, $AgNO_3$, $CHCl_3$, room temperature	50	127	213–216 (dec.)
8-Hydroxy	8-Hydroxy-5-nitro	HNO_3 (fuming), 20 °C	90	151, 374	191–193
8-Hydroxy	5,7-Dinitro-8-hydroxy	HNO_3 (fuming), CH_3CO_2H, 70–80 °C	80	374	213–214
5-Methoxy-3-nitro	3,6-Dinitro-5-methoxy *and* 3,8-dinitro-5-methoxy	C_6H_5COCl, $AgNO_3$, room temperature	—	127	183–184 (3,6-); 214–216 (dec.) (3,8-)

[i] With 40% of 6-methoxy-5-nitro derivative.

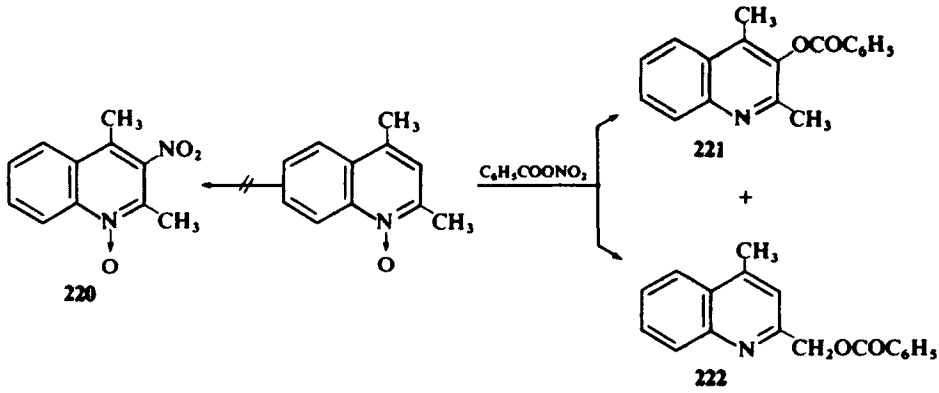
TABLE 11 (*cont.*)

Starting material substituent(s)	Product substituent(s)	Reagent	Yield (%)	References	M.p. (°C) and derivatives
7-Methoxy-3-nitro	3,6-Dinitro-7-methoxy	C_6H_5COCl, $AgNO_3$, room temperature	—	127	215–217 (dec.)
6-Carboxy	6-Carboxy-4-nitro	KNO_3, H_2SO_4, 100 °C	35	40	241
6-Sulphonamido	4-Nitro-6-sulphonic acid	HNO_3, H_2SO_4, 60–70 °C	32–36	40	230–235
4-Amino	4-Amino-3-nitro	HNO_3 (conc.), CH_3CO_2H	70–80	387	284; hydrochloride 232

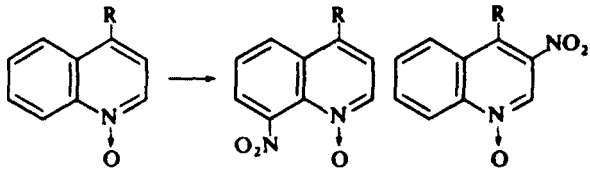


SCHEME 11

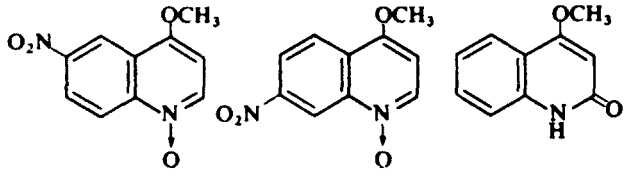
N-oxide with benzoyl nitrate at room temperature gave not the 3-nitro derivative (**220**) but the 3-benzoyloxyquinoline (**221**) and the 2-benzoyloxymethyl derivative (**222**).[461]



The presence of a substituent in the 4-position can also influence the substitution in the benzene ring by steric hindrance of attack at the *peri*-position; thus 4-methylquinoline *N*-oxide (**223**) and 4-methoxyquinoline *N*-oxide (**224**) have been reported to give only 8-nitro derivatives.[468, 479, 380] The latter case was shown to be more complex; nitration of compound (**224**) at 5–6 °C gave four compounds, which were identified as the 6-nitro derivative (**225**), the 7-nitro derivative (**226**) and 4-methoxycarbostyril (**227**).[478] Electron-donating groups can influence the position of substitution. The 3-nitro derivatives (**228** and **229**) were obtained from 4-hydroxyquinoline *N*-oxide,[477] and 4-aminoquinoline *N*-oxide,[387] respectively. Electron-withdrawing substituents on the benzene ring of quinoline *N*-oxide have little effect on the production of 4-nitro derivatives, as, for example, nitration has been achieved with 6-carboxyquinoline *N*-oxide,[40] a 6-sulphonamide[40] and 6- or 8-nitroquinoline *N*-oxide.[135] Nitration of 8-hydroxyquinoline *N*-oxide by fuming nitric acid in acetic acid gave the 5-nitro derivative (**230**) at temperatures below 20 °C and the 5,7-dinitro derivative (**231**) at 70–80 °C.[374] Nitration of 5-methoxyquinoline *N*-oxide with benzoyl chloride and silver nitrate gave

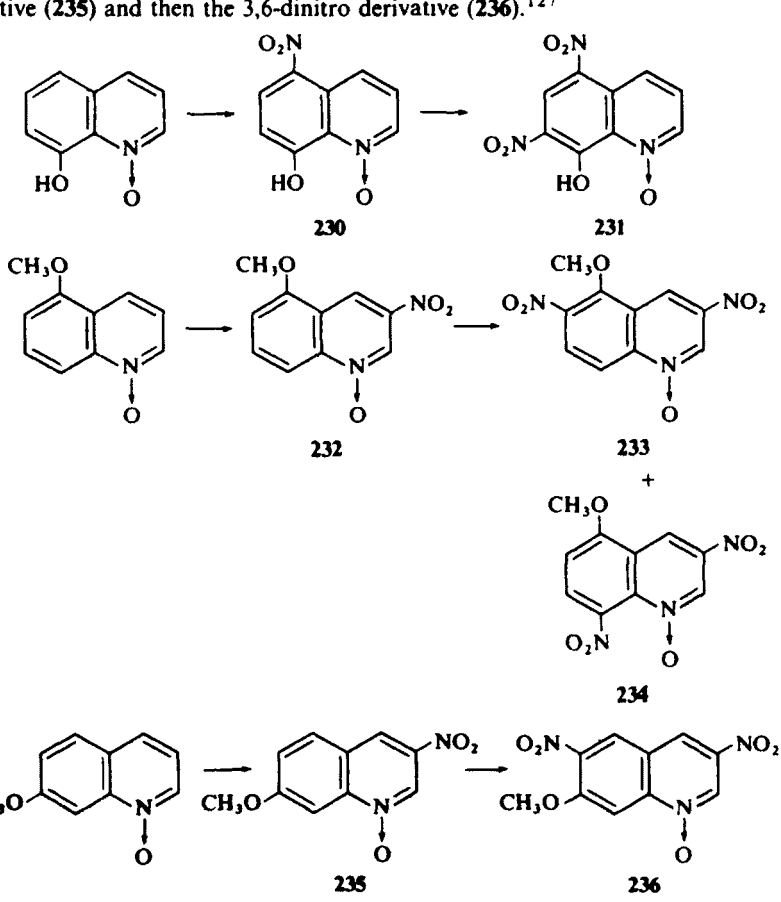


223, R = CH_3 **228**, R = OH
224, R = OCH_3 **229**, R = NH_2

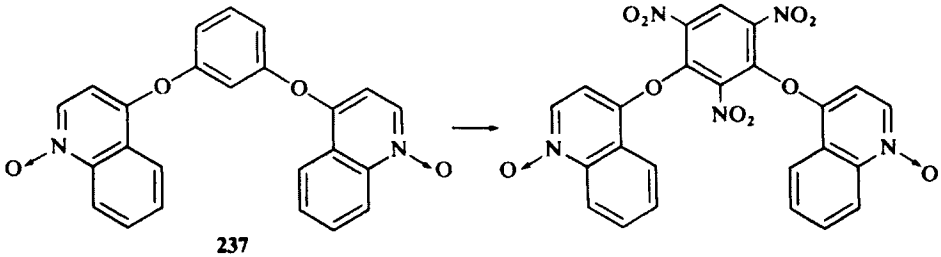


225 **226** **227**

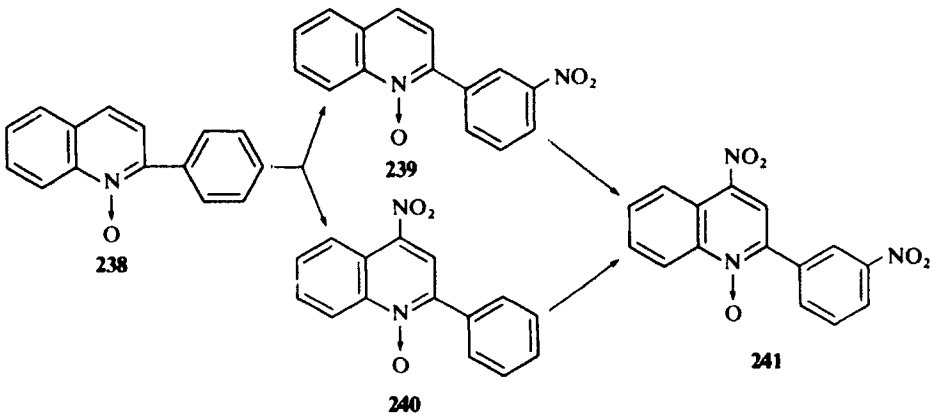
first the 3-nitro derivative (**232**) and then the 3,6-dinitro derivative (**233**) and the 3,8-dinitro derivative (**234**), while 7-methoxyquinoline *N*-oxide gave first the 3-nitro derivative (**235**) and then the 3,6-dinitro derivative (**236**).[127]



Nitration of aryl-substituted quinoline *N*-oxides can cause substitution on either the quinoline or the aryl ring. When the aryl group carries electron-donating substituents nitration generally occurs there first, as in the example of the bis(1-oxido-4-quinolyl) ether (**237**).[67] A thorough examination of the nitration of 2-phenylquinoline *N*-oxide (**238**) with sulphuric acid and potassium nitrate has shown the direction of nitration to be dependent on the acid concentration and largely independent of temperature.[94] Thus, concentrated sulphuric acid produced largely the *m*-nitrophenyl derivative (**239**), whereas 70–75% sulphuric acid gave the 4-nitro derivative (**240**); a small amount of dinitro compound (**241**) was also obtained.



237



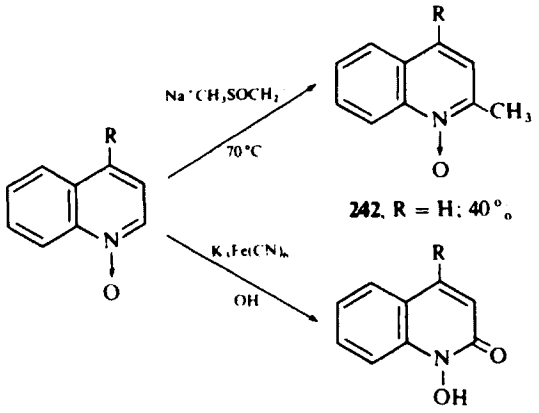
238 **239** **240** **241**

D. Nucleophilic Substitution

Analogy with quaternary quinolinium compounds would lead to the conclusion that the *N*-oxides would react with nucleophiles by substitution (or addition) at the 2- and 4-positions. Direct substitution of hydrogen is less usual than replacement of a better leaving group, such as halogen or nitro. This very large collection of reactions is subdivided into substitutions with retention of the *N*-oxide function, and substitutions (usually involving an alkyl or acyl derivative of the *N*-oxide) in which the oxygen atom is lost. Nucleophilic substitution of side-chain substituents are dealt with in Section III Ga (p. 547).

a. Substitutions in which the *N*-oxide Function is Retained (*i*) *Substitution at Position 2.* Base-catalysed deuterium exchange rates have been measured for quinoline *N*-oxide and compared with those of other systems.[480–482] Sodium methylsulphinylmethylide reacted with quinoline *N*-oxide to give quinaldine *N*-oxide (**242**),[483] in contrast to the reaction with quinoline, in which lepidine is formed. Since the position of

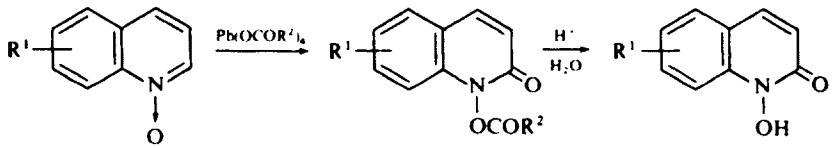
highest calculated electron density is not attacked, the suggestion was made that some coordination of the sodium ion with the *N*-oxide function is involved. There is another report[484] that naphthalene is formed from quinoline *N*-oxide and the methylsulphinylmethylide; in benzologues the nature of the base used was said to be important.[485]



242, R = H; 40%

243, R = H; 75%

244, R = CH_3; 20%



245a, R^1 = H, R^2 = C_6H_5 **245**, R^1 = H

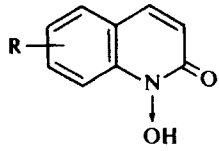
Nucleophilic attack by hydroxyl ions must be the first stage in the production of 1-hydroxycarbostyril (**243**) from quinoline *N*-oxide by alkaline hexacyanoferrate(III); the 4-methyl derivative (**244**) was also prepared.[159] Quinaldine *N*-oxide was not converted into 1-hydroxy-2-methyl-4-quinolone, but the methyl group was oxidized to give quinaldinic acid *N*-oxide.[159] Better yields of substituted 1-hydroxy-2-quinolones (**245**) were obtained by reaction between the appropriate *N*-oxide and lead tetraacetate.[486,32,460] Details of the reactions performed and of the products are given in Table 12. Ohta isolated *N*-benzoyloxycarbostyril (**245a**) from quinoline *N*-oxide and lead tetrabenzoate in benzene; the same compound was obtained by benzoylation of *N*-hydroxycarbostyril, and by oxidation of 2-benzoyloxyquinoline using permaleic acid.[61] It was suggested that the lead tetrabenzoate reaction might be homolytic.

Quinoline *N*-oxides react with Grignard reagents with loss of oxygen (p. 526), but it has been reported[488] that a number of 2-phenylquinoline *N*-oxides (**247**) have been obtained from the *N*-oxides and phenylmagnesium bromide, the deoxygenated material (**248**) being the minor product (Table 13). At lower temperature the dihydro derivative (**246**) was isolated.

The 3-pyridylmagnesium bromide (**249**) reacted with quinoline *N*-oxide to give a mixture of the 3-(2-quinolyl)pyridine (**250**) and the *N*-oxide (**251**).[489]

Tricyclohexylborane reacted with quinoline *N*-oxide to give a mixture of 2-cyclohexylquinoline, the *N*-oxide (**251a**) and quinoline.[822] The best yield (28%) of the substituted *N*-oxide was obtained in ethanolic solution. Treatment of quinoline *N*-oxides with

TABLE 12. 1-Hydroxy-2-quinolones (**245**) by Lead Tetraacetate Hydroxylation



Substituent(s) on compound (**245**)	Yield (%)	M.p. (°C)	References
None	73[a]	188–189	486, 460, 487
4-Methyl	81	224–226	486, 460, 487
6-Methyl	79	200–201	486, 460, 487
3,6-Dimethyl	46	172–174	32
3,7-Dimethyl	46	169–170	32
6,7-Dimethyl	49	228–230	32
3-Bromo	63	187–188	486, 460, 487
4-Chloro	66	200–202	486, 460, 487
3-Nitro	62	214–216	32
4-Nitro	30	205–206	32
5-Nitro	23	220–223	32
6-Nitro	47	285–286	32

[a] 23% Yield in acetic acid.

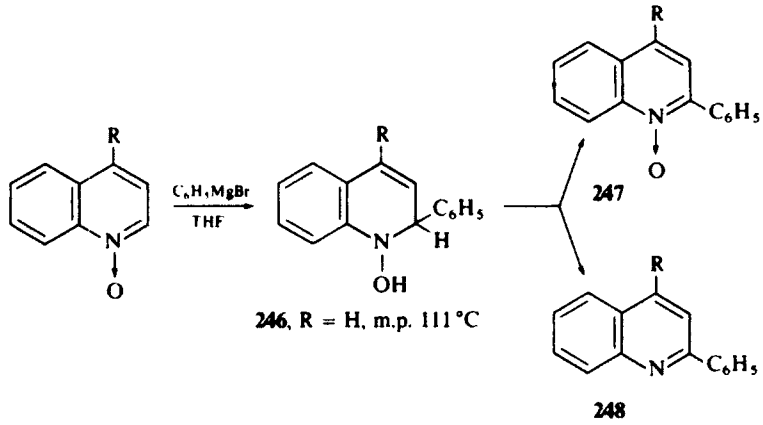
TABLE 13. 2-Phenylquinoline *N*-Oxides (**247**) and 2-Phenylquinolines (**248**) from *N*-Oxides[488]

R	Temperature (°C)	Yield of (**247**) (%)	Yield of (**248**) (%)	M.p. of (**247**) (°C)
H	Room	40[a]	20	144–145
	70	60	30	
CH_3	70	45	30	121
Cl	Room	63	—	122–123
CH_3O	50	64	13	119–121; hydrochloride 155–156
C_2H_5O	50	65	16	158

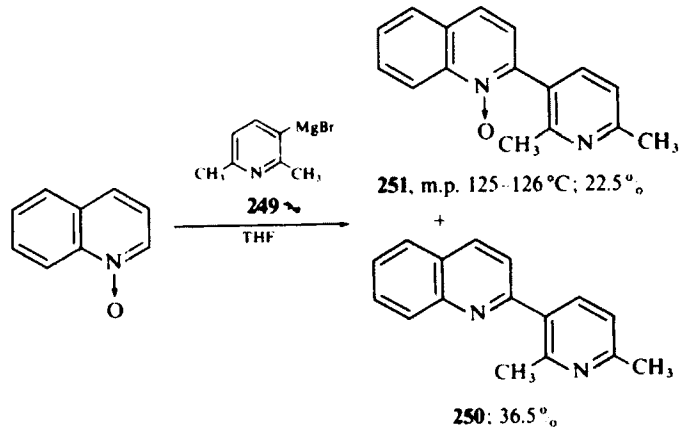
[a] 25% of compound **246** was isolated.

cyanide ion can give good yields of 2-cyanoquinolines with deoxygenation (p. 490). Oxidative cyanation, with a mixture of potassium cyanide and potassium hexacyanoferrate(III), has been used to provide good yields of 2-cyanoquinoline *N*-oxides (**252**).[168,490,101] Cyanoquinoline *N*-oxides thus prepared are listed in Table 14. No substitution was observed with 2-trifluoromethylquinoline *N*-oxide,[490] although a trace of the 4-cyano compound was obtained from 3-trifluoromethylquinoline *N*-oxide.

The reaction between 6-nitroquinoline *N*-oxide and potassium cyanide gave a number of products derived from attack by cyanide ion at position 2 with retention of oxygen.[168] Thus, the iminomethyl ether (**253**), the amide (**254**) and the carbostyril (**255**) were all obtained (the last compound only at higher temperatures), and further reaction gave the 5-cyano derivatives (**256** and **257**), in which the nitro group has been replaced by a methoxyl group.



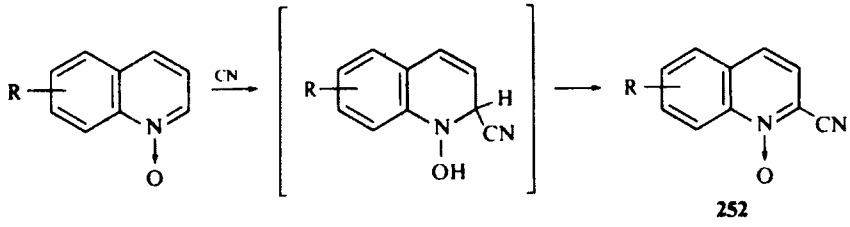
246, R = H, m.p. 111 °C



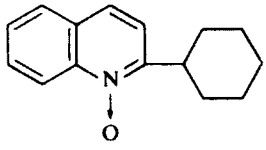
251, m.p. 125–126 °C; 22.5 %

+

250: 36.5 %



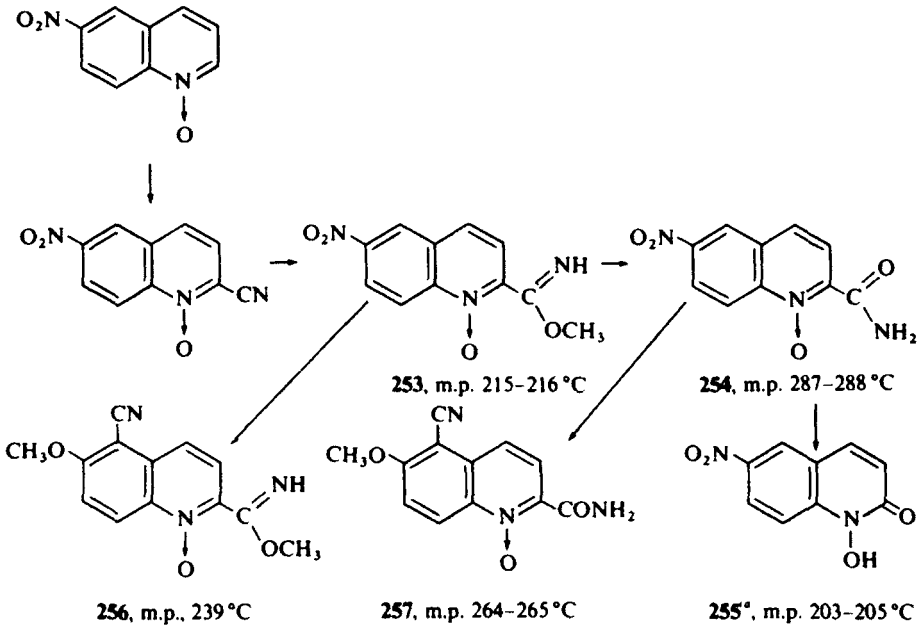
252



251a, m.p. 153 °C

TABLE 14. 2-Cyanoquinoline *N*-Oxides (**252**) Prepared by Oxidative Cyanation

R	H	3-CF_3	4-CF_3	4-CH_3O	6NO_2
Temperature (°C)	75	50	35	90	Room
Yield (%)	85	53	47	17	32
M.p. (°C)	171	212	169	163	257–258
References	490, 810	490	490	490	168



253, m.p. 215–216 °C

254, m.p. 287–288 °C

256, m.p., 239 °C

257, m.p. 264–265 °C

255[a], m.p. 203–205 °C

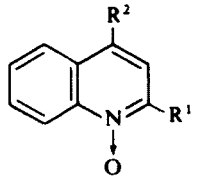
A number of straightforward nucleophilic replacement reactions of 2-halogenoquinoline *N*-oxides are recorded in Table 15. An earlier report of the formation of 2-azidoquinoline *N*-oxide with azide ion in hot methanol[11] was not confirmed,[491] although the later workers were successful with azide at room temperature.[491] There is a report of a phosphate adduct of quinoline *N*-oxide (not isolated) which can be used for oxidative phosphorylation.[492]

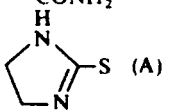
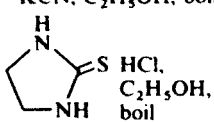
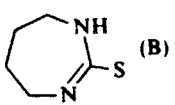
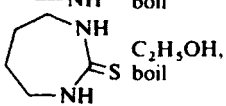
(*ii*) *Substitution at Position 3.* Direct nucleophilic substitution of hydrogen at position 3 requires further activation, as, for example, by a nitro group at position 4. In such cases, when carbon nucleophiles are used, the more usual direct replacement of the 4-nitro group gives way to substitution at position 3. Thus, sodium diethylmalonate has been reported to give the substituted malonate (**258**), with a small amount of 4-aminoquinoline *N*-oxide,[413] with the suggested mechanism shown on p. 471.

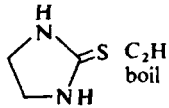
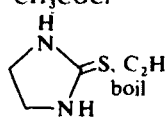
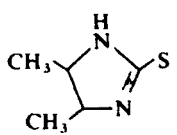
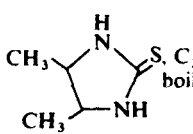
Nucleophilic attack at position 3 by a morpholine enamine was followed by cyclization to give the *N'*-hydroxypyrroloquinolone (**259**).[509] When the pyrrolidine enamine was used, or at higher temperatures with the morpholine enamine, the pyrroloquinolone (**260**) was obtained by the route shown on p. 471.

[a] Ref. 32 gives m.p. 285 °C.

TABLE 15. Compounds Obtained by Nucleophilic Substitution of 2- or of 4-Halogenoquinoline *N*-Oxides

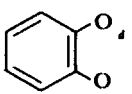
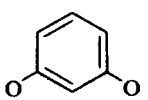
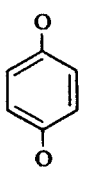


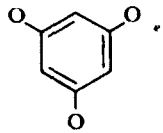
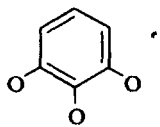
Starting material substituent(s)	Product R¹	Product R²	Product Other substituents	Reagent and temperature (°C)	Yield (%)	Refs.	M.p. (°C) and derivatives
2-Chloro	$C(CN)_2$	—	1-Benzoyl-oxy	$CH_2(CN)_2$, $(C_2H_5))_3N$, C_6H_5COCl	—	13	
2-Chloro	CH_3O	H	—	CH_3ONa, CH_3OH, boil	69	14	70–72
2-Chloro	HO	H	—	HCl (20%), boil	50	14	186–189
2-Chloro	C_2H_5O	H	—	C_2H_5ONa, C_2H_5OH, boil	58	14	75–77
2-Chloro	C_6H_5O	H	—	C_6H_5ONa	85	14	127–128
2-Chloro	C_2H_5S	H	—	C_2H_5S Na	78	14	70
2-Chloro	C_6H_5S	H	—	C_6H_5S Na	95	14	134–134.5
2-Chloro	N=N=N—	H	—	NaN_3, acetone, 25 °C	58	11, 491	103–104
2-Chloro	$(CH_3)_2N$	H	—	$(CH_3)_2NH$	92	14	82.5
2-Chloro	C_6H_5NH	H	—	$C_6H_5NH_2$	54	14	211–212
2-Chloro	$C_5H_{10}N$	H	—	Piperidine	84	14	171–172
2-Chloro	Morpholine	H	—	Morpholine	92	14	92
2-Chloro	$CONH_2$	H	—	KCN, C_2H_5OH, boil	43	14	218–220
2-Chloro	 (A)	H	—	 HCl, C_2H_5OH, boil	—	493, 494	Hydro-chloride
2-Bromo	 (B)	H	—	 C_2H_5OH, boil	—	493	

2-Bromo	HS	H	Various	NaSH, DMF *or* NaSH, Na_2S, HCl	—	495	Sodium or zinc salts
2,3-Dibromo	(A)	H	3-Br	 C_2H_5OH, boil	—	493, 494	
2-Chloro-4-methyl	HO	CH_3	—	20% HCl, boil	87	14	220–222
2-Chloro-4-methyl	CH_3O	CH_3	—	CH_3ONa, CH_3OH, boil	75	14	89–90
2-Chloro-4-methyl	C_2H_5O	CH_3	—	C_2H_5ONa, C_2H_5OH, boil	85	14	64
2-Chloro-4-methyl	C_6H_5O	CH_3	—	C_6H_5ONa	100	14	117–118
2-Chloro-4-methyl	C_2H_5S	CH_3	—	C_2H_5SNa	87	14	146–148
2-Chloro-4-methyl	C_6H_5S	CH_3	—	C_6H_5SNa	97	14	188–190
2-Chloro-4-methyl	$(CH_3)_2N$	CH_3	—	$(CH_3)_2NH$	94	14	97–98
2-Chloro-4-methyl	C_6H_5NH	CH_3	—	$C_6H_5NH_2$	99	14	214
2-Chloro-4-methyl	$C_5H_{10}N$	CH_3	—	Piperidine	86	14	155–156
2-Chloro-4-methyl	Morpholine	CH_3	—	Morpholine	85	14	88–89
2-Chloro-4-methyl	$CONH_2$	CH_3	—	KCN, CH_3OH, boil	65	14	245–247
2,4-Dichloro	O[a]	Cl	1-Benzyloxy	C_6H_5COCl, $AgNO_3$	—	473	
2-Chloro-4-nitro	O[b]	NO_2	—	$(CH_3CO)_2O$, CH_3CO_2Na	—	473	161–162
2-Chloro-4-nitro	O[c]	Cl	1-Acetoxy	CH_3COCl	—	473	101–103
2-Chloro-6-propoxy	(A)	—	6-C_3H_7O	 S, C_2H_5OH, boil	—	493, 494	Hydriodide
2-Bromo-7-methoxy		—	7-CH_3O	 S, C_2H_5OH, boil	—	493, 494	Hydrochloride

[a] 1-Benzoyloxy-4-chloro-carbostyril.
[b] 4-Nitrocarbostyril *N*-oxide.
[c] 1-Acetoxy-4-chlorocarbostyril.

TABLE 15 (*cont.*)

Starting material substituent(s)	Product R¹	Product R²	Product other substituents	Reagent and temperature (°C)	Yield (%)	Refs.	M.p. (°C) and derivatives
4-Chloro	H	$C_6H_5CH(CH_3)CN$	—	$C_6H_5CH(CH_3)CN$, $C_6H_5\overset{+}{N}(C_2H_5)_3Cl^-$, NaOH	72	863	217–218
4-Chloro	H	2-Pyridyl-CH(CN)	—	2-Pyridyl-CH_2CN, $NaNH_2$, boiling benzene	83	496	154–155 Hydrate 130–132
4-Chloro	H	2-Quinolyl-CHCN	—	2-Quinolyl-CH_2CN, $NaNH_2$, boiling benzene	—	496	139–140 Hydrate 85
4-Bromo	H	OH	—	KOH aq, As_2O_3	60	383	238–239
4-Chloro	H	C_6H_5O	—	C_6H_5ONa	36	497, 67	106–107 (hydrate)
4-Chloro	H	$NH_2CH_2CH_2O$	—	$NH_2CH_2CH_2ONa$	80	498, 67	Hydrochloride 213–214
Chloro	H	4-CH_3-2,6-$(NO_2)_2C_6H_2O$	—	4-CH_3-2,6-$(NO_2)_2C_6H_2OH$, base	100	67	Explodes
4-Chloro	H		—	1,2-$(HO)_2C_6H_4$, NaOH, H_2O, boil	20–25	67	229 ($2H_2O$)
4-Chloro	H		—	1,3-$(HO)_2C_6H_4$, NaOH, H_2O, boil	20	67	235 ($2H_2O$); trinitro 205; pentachloro 212
4-Chloro	H		—	1,4-$(HO)_2C_6H_4$, NaOH, H_2O, boil	20–25	67	230 ($2H_2O$)

4-Chloro	H		—	1,3,5-$(HO)_3C_6H_3$, NaOH, H_2O, boil	13	67	230 ($3H_2O$); tetranitro 183; pentachloro 69
4-Chloro	H		—	1,2,3-$(HO)_3C_6H_3$, NaOH, H_2O, boil	15	67	233 ($3H_2O$); tetranitro 183; hexachloro 220
4-Chloro	H	8-Quinolyloxy	—	8-Hydroxyquinoline	—	498, 67	328
4-Chloro	H	SH	—	$NaOCH_3$, H_2S	75	435, 383[f]	112–113
4-Chloro	H	SH[f]	—	Thiourea, then NaOH	—	437	140–141; sodium salt 140
4-Chloro	H	HO_2CCH_2S	—	Thioglycolic acid, NaOH, water-bath	Poor	499	200–201
4-Chloro	H	CH_3S	—	CH_3SNa, CH_3OH, boil	55	435	Oil; picrate 168–170[383]
4-Bromo	H	CH_3S	—	CH_3SNa, CH_3OH, boil	58	435	
4-Chloro	H	C_2H_5S	—	C_2H_5SNa, CH_3OH, boil	70	435, 499	101–105[499]
4-Bromo	H	C_2H_5S	—	C_2H_5SNa, CH_3OH, boil	63	435	
4-Chloro	H	$(CH_3)_2CHS$	—	$(CH_3)CHSNa$, CH_3OH, boil	35	435	52–53
4-Chloro	H	$HOCH_2CH_2S$	—	$HOCH_2CH_2SNa$, CH_3OH, boil	35	435	127–129
4-Chloro	H	R—S[g]	—	RSH,[g] KOH	55	385	80; deacetylated material 185

[d] Bis-derivative.
[e] Tris-derivative.
[f] With some 4,4'-diquinolyldisulphide di-*N*-oxide m.p. 225 °C[437] or 230–231 °C.[383]
[g] R = 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl; also made from 1-oxido-4-quinolylthiolate and the glucopyranose-1-bromide.[502]

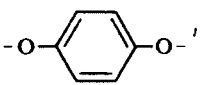
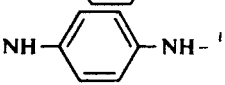
TABLE 15 (*cont.*)

Starting material substituent(s)	Product R¹	Product R¹	Other substituents	Reagent and temperature (°C)	Yield (%)	Refs.	M.p. (°C) and derivatives
4-Chloro	H	$C_6H_5CH_2S$	—	$C_6H_5CH_2SNa$, CH_3OH, boil	79	435	161–162
4-Chloro	H	C_6H_5S	—	C_6H_5SNa, CH_3OH, boil	82	435, 497	98–101[435]
4-Chloro	H	*p*-$CH_3C_6H_4S$	—	*p*-$CH_3C_6H_4SNa$	70	498, 67	
4-Chloro	H	*p*-$O_2NC_6H_4S$	—	*p*-$O_2NC_6H_4SNa$, CH_3OH, boil	89	435	121–123
4-Chloro	H	2-Br-5-$CH_3C_6H_3S$	—	2-Br-5-$CH_3C_6H_3SH$, NaOH	—	500	165; sulphone 181
4-Chloro	H	3-Br-4-$CH_3C_6H_3S$	—	3-Br-4-$CH_3C_6H_3SH$, NaOH	—	500	153; sulphone 181
4-Chloro	H	3-Cl-4-$CH_3C_6H_3S$	—	3-Cl-4-$CH_3C_6H_3SH$, NaOH	—	500	165; sulphone 159
4-Bromo	H	NCS	—	KSCN, CH_3OH, boil	80	383	135–136; thiol 140–141
4-Bromo	H	NCSe	—	KSeCN, acetone, boil	90	383	147–148
4-Chloro	H	NHOH	—	NH_2OH, CH_3OH	—	410	210 (dec.); hydrochloride 192 (dec.); picrate 162 (dec.)
4-Chloro	H	$NHNH_2$	—	Hydrazine hydrate, room temperature	71	51, 67	168 (explodes);[51] hydrochloride 235.5;[51] picrate 177
4-Chloro	H	N=N=N—	—	NaN_3, C_2H_5OH, 115	45	51	141–142 (explodes); picrolonate 168; hydrochloride 141–143[435]

4-Chloro[k]	H	$C_5H_{10}N$	—	Piperidine, C_2H_5OH	—	503	69; hydrobromide 112–113
4-Chloro	H	$(CH_3)_2N(CH_2)_3$-N⟨piperazine⟩N—	—	$(CH_3)_2N(CH_2)_3$-N⟨piperazine⟩NH, $NaHCO_3$, $CH_3OCH_2CH_2OH$	—	504, 505	Trimaleate 118–120
4-Chloro-2-methyl	CH_3	CH_3O	—	CH_3OH, KOH, boil	80	874	135–136
4-Chloro-2-methyl	CH_3	$CH_2{=}CHCH_2O$	—	$CH_2{=}CHCH_2OH$, KOH, boil	~80	874	140.5–142.5
4-Chloro-2-methyl	CH_3	$(CH_3)_2C{=}CHCH_2O$	—	$(CH_3)_2C{=}CHCH_2OH$, KOH, boil	~80	874	98–98.5
4-Chloro-2-methyl	CH_3	$CH{\equiv}CCH_2O$	—	$CH{\equiv}CCH_2OH$, KOH, boil	~80	874	198–199
4-Chloro-2-methyl	CH_3	8-Quinolyloxy	—	8-Hydroxyquinoline, base	—	128	262–263 ($1.5H_2O$)
4-Chloro-2-methyl	CH_3	8-(5,7-Dichloro-quinolyloxy)		5,7-Dichloro-8-hydroxyquinoline, base	—	128	248–249 ($1.5H_2O$)
4-Chloro-2-methyl	CH_3	o-HOC_6H_4O[l]	—	1,2-$(HO)_2C_6H_4$, base	25	128	116 (hydrate)
4-Chloro-2-methyl	CH_3	m-HOC_6H_4O[j]	—	1,3-$(HO)_2C_6H_4$, base	53	128	157
4-Chloro-2-methyl	CH_3	p-HOC_6H_4O[k]	—	1,4-$(HO)_2C_6H_4$, base	55	128	196
4-Chloro-2-methyl	CH_3	p-$CH_3C_6H_5NH$	—	p-$CH_3C_6H_4NH_2$, HCl, boil	50	77	Hydrochloride 226
4-Chloro-2-methyl	CH_3	o-HOC_6H_4NH	—	o-$HOC_6H_4NH_2$, HCl, boil	45	77	Hydrochloride 98

[k] Or 4-bromo or 4-iodo.
[l] With 12% di(1-oxidoquinaldin-4-yl) ether, m.p. 232 °C (dihydrate).
[j] With 12% di(1-oxidoquinaldin-4-yl)ether, m.p. 238 °C (dihydrate).
[k] With 13.6% di(1-oxidoquinaldin-4-yl) ether, m.p. 233 °C (dihydrate).

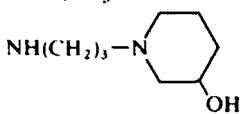
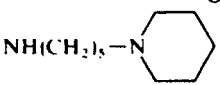
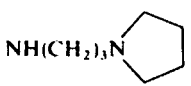
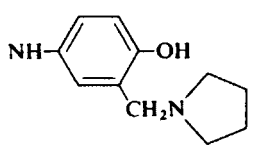
TABLE 15 (*cont.*)

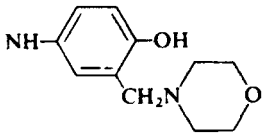
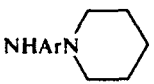
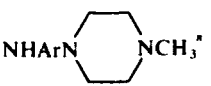
Starting material substituent(s)	Product R^1	Product R^2	Other substituents	Reagent and temperature (°C)	Yield (%)	Refs.	M.p. (°C) and derivatives
4-Chloro-2-styryl	$C_6H_5CH{=}CH$	CH_3O	—	CH_3ONa, CH_3OH, heat	80	433, 506	145
4-Chloro-2-styryl	$C_6H_5CH{=}CH$	C_2H_5O	—	C_2H_5ONa, C_2H_5OH, heat	60	433, 506	137
4-Chloro-2-styryl	$C_6H_5CH{=}CH$	n-C_3H_7O	—	n-C_3H_7ONa, C_3H_7OH, heat	42	433, 506	151
4-Chloro-2-styryl	$C_6H_5CH{=}CH$		—	$1,4\text{-}(HO)_2C_6H_4$, KOH, H_2O, boil	22	433, 506	184
4-Chloro-2-styryl	$C_6H_5CH{=}CH$		—	$1,4\text{-}(NH_2)_2C_6H_4$, dioxan, HCl, heat	42	433, 506	197
4-Chloro-6-methyl	H	OH	6-CH_3	KOH, H_2O	22	112, 113	
4-Chloro-6-methyl	H	OCH_3	6-CH_3	CH_3ONa, CH_3OH, boil	83	112, 113	163.5–164; trihydrate 70.5; picrate 176
4-Chloro-6-methyl	H	C_2H_5O	6-CH_3	C_2H_5ONa, C_2H_5OH	74	112, 113	167.5–168; trihydrate 73; picrate 186.5
4-Chloro-6-methyl	H	n-C_3H_7O	6-CH_3	n-C_3H_7ONa, C_3H_7OH	32	112, 113	201; dihydrate 76; picrate 140–141
4-Chloro-6-methyl	H	i-C_3H_7O	6-CH_3	i-C_3H_7ONa, i-C_3H_7OH	53	112, 113	207–207.5; dihydrate 94; picrate 213–213.2
4-Chloro-6-methyl	H	C_6H_5O	6-CH_3	C_6H_5OH, base	61	112, 113	127–127.5; hydrate 102; picrate 170–171

4-Chloro-6-methyl	H	2-$CH_3C_6H_4O$	6-CH_3	2-$CH_3C_6H_4OH$, base	49	112, 113	138–139; hydrate 96–97
4-Chloro-6-methyl	H	3-$CH_3C_6H_4O$	6-CH_3	3-$CH_3C_6H_4OH$, base	61	112, 113	121–121.5; hydrate 80–81; picrate 154.5–155
4-Chloro-6-methyl	H	*n*-C_4H_9NH	6-CH_3	*n*-$C_4H_9NH_2$, CuCl, KI, C_2H_5OH, heat	42	112, 113	206–207.5
4-Chloro-6-methyl	H	NH_2NH	6-CH_3	NH_2NH_2 (98%), C_2H_5OH	52	112, 113	Dihydrate 171; hydrochloride 218; acetone hydrazone 204–205 (dihydrate); ethyl acetoacetate derivative 137.5–139
4-Chloro-6-methyl	H	4-$O_2NC_6H_4NHNH$	6-CH_3	4-$O_2NC_6H_4NHNH_2$, C_2H_5OH	51	112, 113	129–130
4-Chloro-3-nitro	H	NCS	3-NO_2	KSCN, C_2H_5OH, boil	55	383	169–170 (dec.)
4-Chloro-3-bromo	H	NCS	3-Br	KSCN, C_2H_5OH, boil	85	383	159–160
4-Chloro-2-methyl	CH_3	*m*-NHC_6H_4NH[m]	—	*m*-Phenylenediamine	—	128	275
4-Chloro-2-methyl	CH_3	*p*-NHC_6H_4NH[m]	—	*p*-Phenylenediamine	60	128	Dihydrochloride 280 (dec.)
4-Chloro-2-phenyl	C_6H_5	CH_3O	—	CH_3ONa, CH_3OH	80	488	119–121
4-Chloro-2-phenyl	C_6H_5	C_2H_5O	—	C_2H_5ONa, C_2H_5OH	—	488	158
4,7-Dichloro	—	$(C_2H_5)_2NCH_2$-$CH(OH)CH_2NH$	7-Cl	$(C_2H_5)_2NCH_2$-$CH(OH)CH_2NH_2$, HCl, C_2H_5OH	30	507, 57	Dihydrochloride 218–221;[507] 1,5-naphthalene disulphonate 298–308[507]

[l] Bis-derivative.
[m] Bis(4-quinolyl).

TABLE 15 (*cont.*)

Starting material substituent(s)	Product R^1	Product R^2	Other substituents	Reagent and temperature (°C)	Yield (%)	Refs.	M.p. (°C) and derivatives
4,7-Dichloro	—	$(C_2H_5)_2N(CH_2)_3CH(CH_3)NH$	7-Cl	4-$(C_2H_5)_2N(CH_2)_3CH(CH_3)NH_2$, 180	67	508	Picrate 207; meconate 180
4,7-Dichloro	—		7-Cl	1-(3-Aminopropyl)-3-piperidinol, HCl	25	507, 57	199–209[50]
4,7-Dichloro	—		7-Cl	*N*-(5-Aminopentyl) piperidine, HCl	31	507, 57	174–176 ($\frac{1}{2}H_2O$)
4,7-Dichloro	—	$NH(CH_2)_3N(C_2H_5)_2$	7-Cl	*NN*-Diethylpropane-1,3-diamine, HCl	60	507, 57	150–152
4,7-Dichloro	—	$NHCH_2CH_2N(C_2H_5)CH_2CH_2OH$	7-Cl	2-(2-Aminoethyl)-ethylaminoethanol, HCl	2	507, 57	148–150
4,7-Dichloro	—		7-Cl	3-(1-Pyrrolidinyl)-propylamine, HCl	46	507, 57	185–187
4,7-Dichloro	—	$NH(CH_2)_3NHC_3H_7$-*i*	7-Cl	*N*-(Isopropyl)-propane-1,3-diamine, HCl	57	507, 57	176–179
4,7-Dichloro	—	$NH(CH_2)_2N(C_2H_5)_2$	7-Cl	*NN*-Diethylethylene-diamine, HCl	33	507, 57	185–187
4,7-Dichloro	—	$NH(CH_2)_3NHC_8H_{17}$	7-Cl	*N*-Octyl-1,3-propane-diamine, HCl	51	507, 57	107–108
4,7-Dichloro	—		7-Cl	4-Hydroxy-3-pyrrolidinomethyl-aniline, HCl, aq. EtOH, 100	18	57, 58	238

4,7-Dichloro	—		7-Cl	4-Hydroxy-3-(*N*-morpholino)-methylaniline, phenol, 100	20	57, 58	235–236
4,7-Dichloro	—	$NHArN(C_2H_5)_2$	7-Cl	4-Hydroxy-3-(diethylamino-methyl)aniline, phenol, 100	33	57, 58	226
4,7-Dichloro	—	$NHArN(C_2H_5)CH_2CH_2OH$	7-Cl	4-Hydroxy-3-(*N*-ethyl-*N*-hydroxy-ethylaminomethyl)-aniline, phenol, 100	26	57, 58	224–225
4,7-Dichloro	—		7-Cl	4-Hydroxy-3-(*N*-piperidinomethyl)-aniline, HCl, aq. EtOH	17	57, 58	251
4,7-Dichloro	—		7-Cl	4-Hydroxy-3-(*N'*-methyl-*N*-piperazinylmethyl)-aniline, HCl, aq. EtOH	27	57, 58	244–245
4,7-Dichloro	—	$NHArN(CH_3)C_{10}H_{21}$"	7-Cl	4-Hydroxy-3-(*N*-methyl-*N*-decyl-aminomethyl)-aniline, aq. EtOH, HCl	34	57, 58	215–216

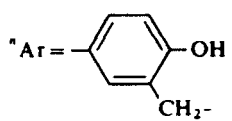
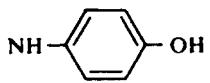
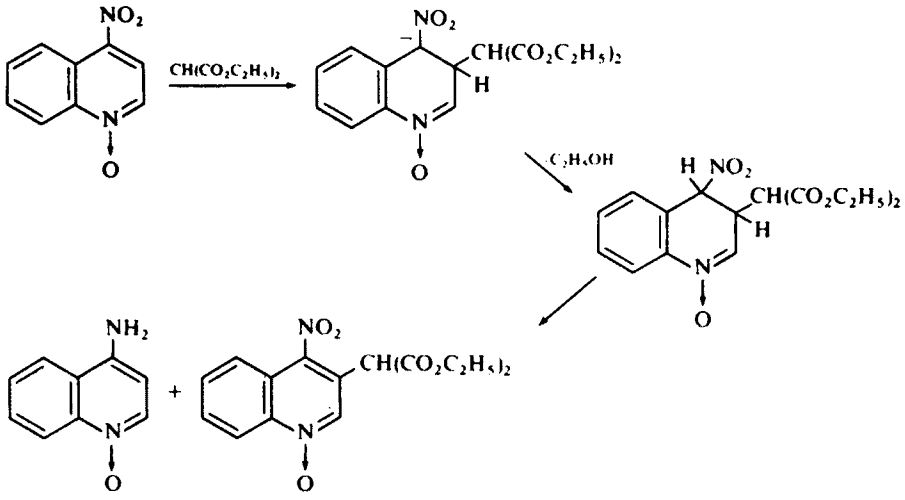


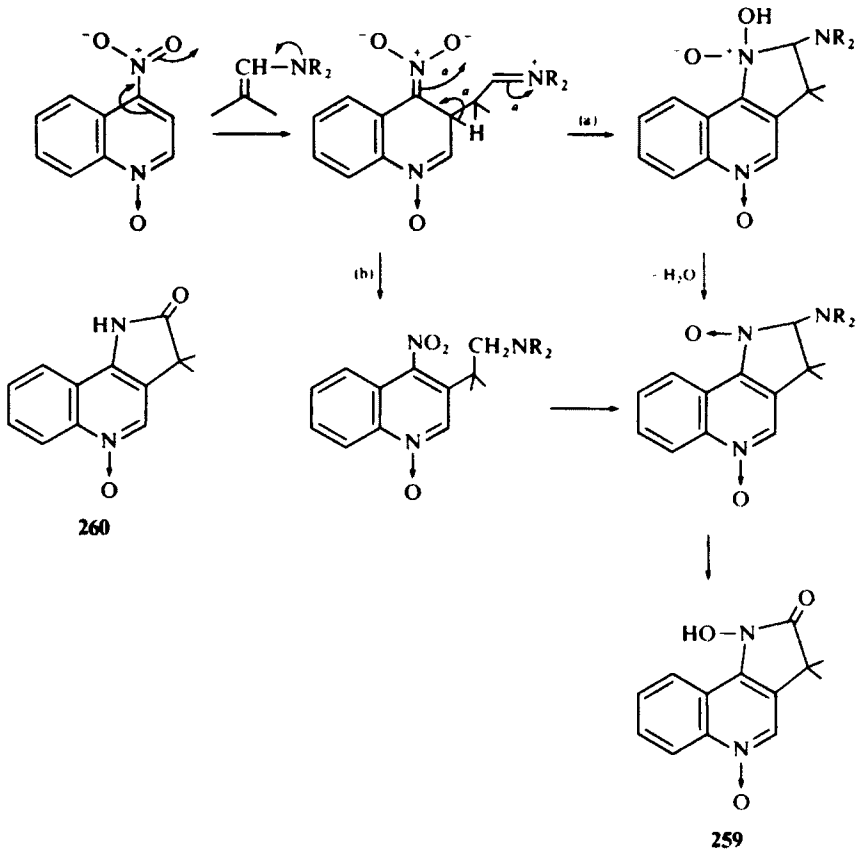
TABLE 15 (*cont.*)

Starting material substituent(s)	Product			Reagent and temperature (°C)	Yield (%)	Refs.	M.p. (°C) and derivatives
	R^1	R^2	Other substituents				
4,7-Dichloro	—		7-Cl	*p*-Aminophenol, HCl, H_2O, EtOH, 100	49	57, 58	285 (dec.)
2-Methyl-4,7-dichloro	CH_3	$2\text{-}HOC_6H_4O$	7-Cl[a]	1,2-$(HO)_2C_6H_4$, base	—	128	210 (H_2O)
2-Methyl-4,7-dichloro	CH_3	$3\text{-}HOC_6H_4O$	7-Cl	1,3-$(HO)_2C_6H_4$, base	52	128	216 (H_2O)
2-Methyl-4,7-dichloro	CH_3	$4\text{-}HOC_6H_4O$	7-Cl[b]	1,4-$(HO)_2C_6H_4$, base	67	128	212 (H_2O)
4-Chloro-8-nitro	—	$4\text{-}ClC_6H_4NH$	$8\text{-}NO_2$	*p*-Chloroaniline, C_2H_5OH, boil	70	455	196

[a] Plus some bis-derivative, m.p. 247–248 °C.
[b] Plus 14% of bis-derivative, m.p. 250–251 °C.



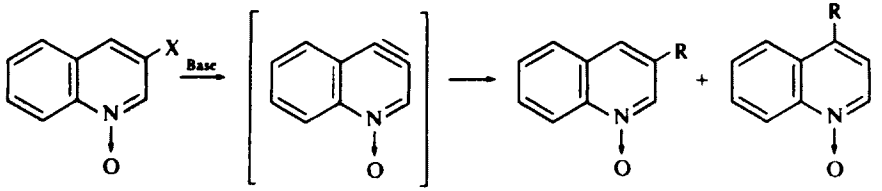
258, m.p. 101–102 °C; 35 %
C-methyl derivative, m.p. 94–95 °C



260

259

The reaction between 3-bromoquinoline *N*-oxide (**261**) and ammoniacal copper(II) sulphate at 165 °C was reported to give 3-aminoquinoline *N*-oxide (**262**) in 32% yield.[126] With piperidine at 115 °C[510] and with potassium amide in liquid ammonia[511] evidence for the intermediate 3,4-quinolyne *N*-oxide (**263**) was obtained. With piperidine a mixture of 3- and 4-piperidinoquinoline *N*-oxide (**264** and **265**) was obtained.[126] In contrast, 4-chloroquinoline *N*-oxide gave only 4-piperidinoquinoline *N*-oxide (**265**) by the normal addition–elimination mechanism. Treatment of 4-nitroquinaldine *N*-oxide with acetyl chloride was reported[79] to give 3-chloro-4-nitroquinaldine *N*-oxide (**266**),

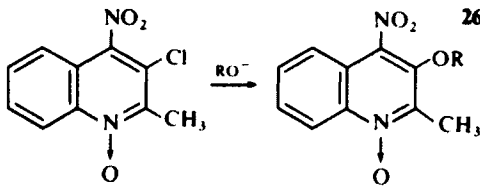


261, X = Br
272, X = F

263

264, R = $C_5H_{10}N$, 20%; m.p. 142 °C[25] (picrate 165–166 °C[625]; 182 °C[25])

265, R = $C_5H_{10}N$, 22% (picrate, m.p. 132–133 °C)

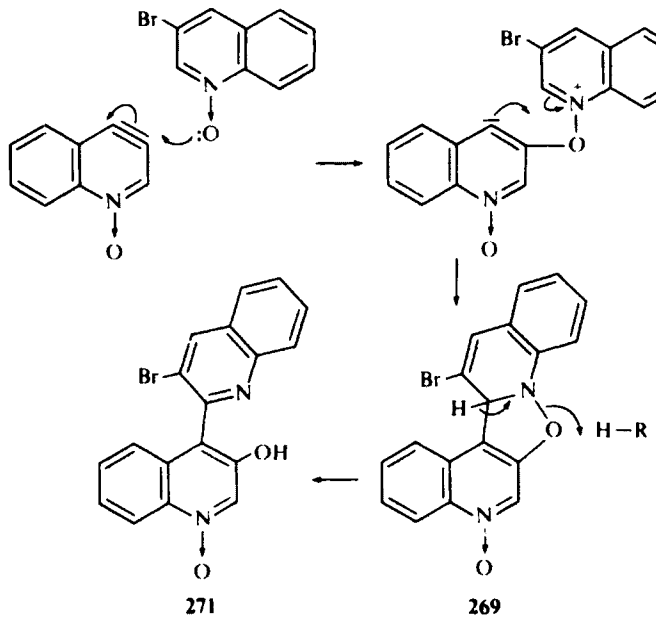


262, R = NH_2

270, R = NH_2

266

267, R = C_6H_5
268, R = 4—$CH_3C_6H_4$

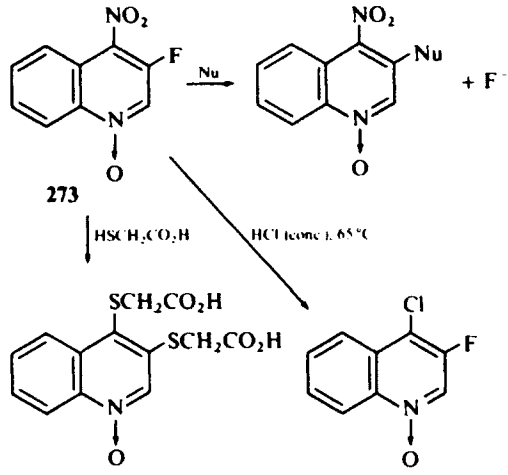


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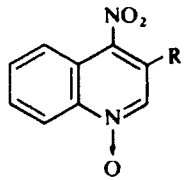
which with phenols in a basic medium gave 3-phenoxy derivatives (**267** and **268**). With a metal amide, 3-amino- and 4-aminoquinoline *N*-oxides (**262** and **270**) were obtained, as well as compound (**271**), whose formation was suggested to be via the pentacyclic intermediate (**269**), by *N*-oxide attack on the quinolyne.[511]

Other nucleophilic substitutions at position 3 have involved displacement of fluoride, as in the preparation of 3-piperidinoquinoline *N*-oxide (**264**) from 3-fluoroquinoline *N*-oxide (**272**);[25] no suggestion of a quinolyne intermediate was made for this reaction. When activated by an adjacent nitro group, as in compound (**273**), the 3-fluoro substituent has been replaced by a wide variety of nucleophiles, as shown in Table 16.[124] In one case (thioglycolic acid) both substituents were replaced to give compound (**274**); with concentrated hydrochloric acid only the nitro group was replaced, giving 3-fluoro-4-chloroquinoline *N*-oxide (**275**).



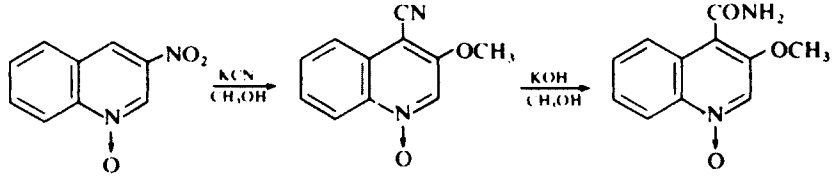
274, m.p. 208 °C (dec.); 50 % **275**, m.p., 168–169 °C

TABLE 16. Products of Nucleophilic Replacement of 3-Fluoro-4-nitroquinoline *N*-Oxide[124]



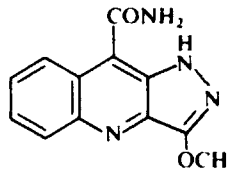
R	Reagent and temperature (°C)	Yield (%)	M.p. (°C)
NH_2	NH_3, aq.; 60	71	218
C_6H_5NH	$C_6H_5NH_2$, methanol; room	75	164–165.5
$C_5H_{10}N$	$C_5H_{10}NH$, methanol, room	43	167.5
$HOCH_2CH_2NH$	$HOCH_2CH_2NH_2$, methanol room	100	211 (dec.)
C_6H_5NHNH	$C_6H_5NHNH_2$, room	79	138 (dec.)
CO_2HCH_2NH	$CO_2HCH_2NH_2$, $NaHCO_3$, H_2O, room	76	200.5 (dec.)
CH_3O	CH_3O^-, CH_3OH	51	—

Reaction between 3-nitroquinoline *N*-oxide (**276**) and potassium cyanide in boiling methanol gave the 4-cyano-3-methoxy derivative (**277**), presumably by attack by cyanide at position 4 followed by displacement of the now activated nitro group.[168,804] The tricyclic compound (**278**) was also obtained; here substitution by cyanide at position 4 was thought to be followed by cyclization and deoxygenative cyanation at position 2.



276 **277**, m.p. 236–237 °C; 38% M.p. 243–244 °C; 83%

+



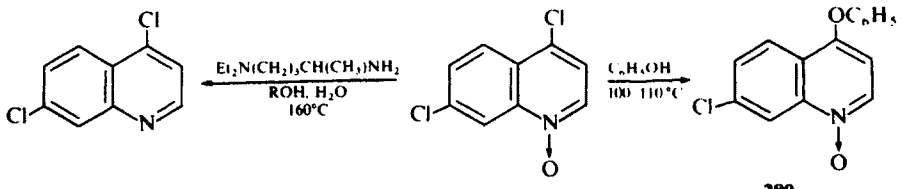
278; 20%

(*iii*) *Substitution at Position 4.* Virtually all of the substitutions by nucleophiles of 4-substituted quinoline *N*-oxides have as the leaving group halide or nitrite. The various compounds obtained by replacement of halogens are grouped in Table 15 (p. 460) with the similar replacements of the 2-halogenoquinoline *N*-oxides. Very little comment is required since most nucleophiles react normally. Rates of replacement of 4-halogenoquinoline *N*-oxide with piperidine in ethanol were shown to be ten times faster than those for the corresponding halogenoquinolines and faster than those of 4-halogeno-1-nitronaphthalenes.[503] Of the three examined, bromine was the most reactive, followed by iodine and chlorine; $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values were obtained. Among amine replacements the only reported anomaly was in the lack of reactivity shown by *NN*-diethylpentane-1,4-diamine. With 4,7-dichloroquinoline *N*-oxide (**279**) the diamine caused deoxygenation in aqueous alcohols at 160 °C, and formation of 7-chloro-4-phenoxyquinoline *N*-oxide (**280**) when phenol was used as the solvent.[57] Hydrazine and 4-nitrophenylhydrazine gave with 4-chloroquinoline *N*-oxides the substituted hydrazines (**281**–**283**);[67,51,112,113] the reaction with hydrazines is finely balanced and an excess of reagent can cause deoxygenation. Phenylhydrazine did not give the substituted hydrazine (**284**) with 4-chloro-6-methylquinoline *N*-oxide.[112,113]

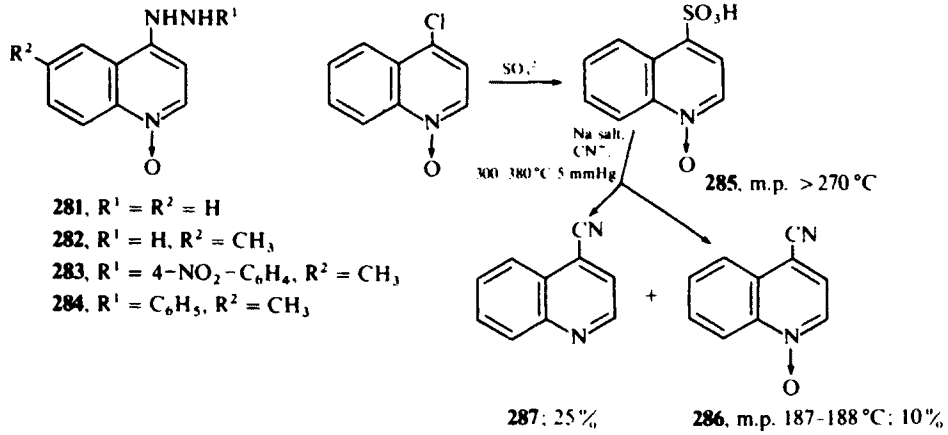
Boiling with sodium sulphite solution was reported to give, from 4-chloroquinoline *N*-oxide, the sulphonic acid (**285**); the sodium salt on fusion with a metal cyanide gave a mixture of 4-cyanoquinoline *N*-oxide (**286**) with the deoxygenated compound (**287**).[163]

Phase-transfer catalysis has been used to convert 4-chloroquinoline *N*-oxide into 4-aroylquinoline *N*-oxides (**287a**–**287f**).[863] The reagents were derivatives of benzaldehyde cyanohydrins, and the intermediates were hydrolysed directly by dilute hydrochloric acid.

Sodium sulphide reacts with 4-halogenoquinoline *N*-oxides to give the mercaptan (**288**) and, usually, some disulphide (**289**);[383] an interesting related reaction gave the tricyclic compound (**290**) by cyclization of the side-chain on to the first-formed thiolate.[42]



279 280



281, $R^1 = R^2 = H$
282, $R^1 = H$, $R^2 = CH_3$
283, $R^1 = 4\text{-}NO_2\text{-}C_6H_4$, $R^2 = CH_3$
284, $R^1 = C_6H_5$, $R^2 = CH_3$

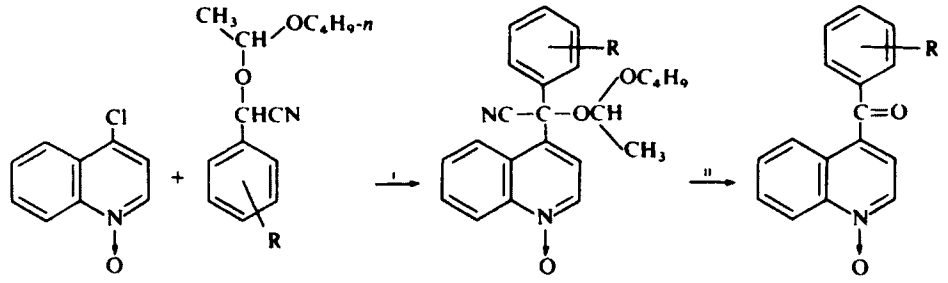
285, m.p. > 270 °C

287: 25%

286, m.p. 187–188 °C; 10%

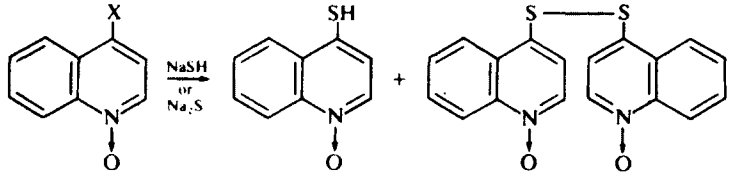
Because of the ready availability of 4-nitroquinoline *N*-oxides by direct nitration (p. 448) and the ready nucleophilic substitution of the nitro group by nucleophiles, a large number of such reactions are known, and are summarized in Table 17.

The kinetics of nucleophilic replacement of nitro groups in various 4-nitroquinoline *N*-oxides have been studied in an attempt to correlate the rate constants with carcinogenicity. Attempts have also been made to correlate frontier electron density and superdelocalizability for nucleophilic attack on a nitro group in the 4-position with fungicidal activity[335] and carcinogenic activity.[334]

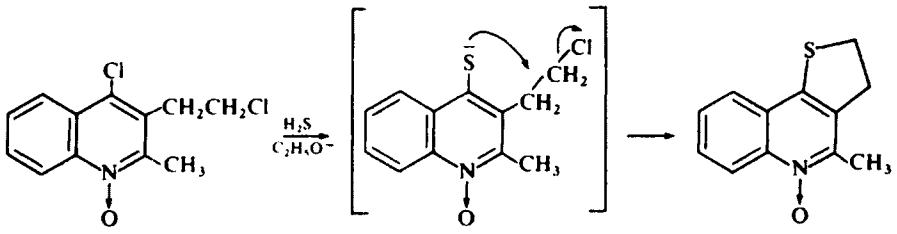


i, $C_6H_5\dot{N}(C_2H_5)_3Cl^-$, NaOH (50%), benzene, 50 °C
ii, 10% HCl

287a, R = H; 72%
287b, R = *p*-Cl; 60%
287c, R = *p*-CN; 44%
287d, R = *p*-CH_3; 38%
287e, R = *p*-OCH_3; 48%
287f, R = *o*-Cl; 40%

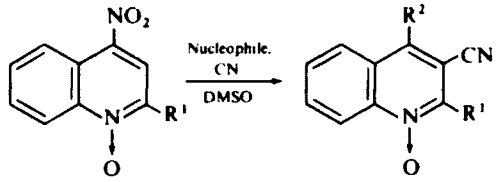


288 **289**



290

There are a number of reactions in which replacement of the nitro group in 4-nitroquinoline *N*-oxide by a nucleophile in the presence of potassium cyanide has given 3-cyano-4-substituted quinolines.[519] The reactions were carried out in dimethyl sulphoxide. Nucleophiles used to replace the nitro groups were ethyl cyanoacetate, malonitrile, piperidine or cyanide, and a number of 2-substituted quinoline *N*-oxides were also found to react. The products and yields are summarized in formula (**291**).



291

R^1	R^2	Yield (%)
H	$CH(CN)CO_2C_2H_5$	27
Piperidinyl	$CH(CN)_2$	57
Piperidinyl	$CH(CN)CO_2C_2H_5$	62
Pyrrolidinyl	$CH(CN)_2$	32
Pyrrolidinyl	$CH(CN)CO_2C_2H_5$	35
Morpholinyl	$CH(CN)_2$	31
Morpholinyl	$CH(CN)CO_2C_2H_5$	36
Dimethylamino	$CH(CN)_2$	41.5
Dimethylamino	$CH(CN)CO_2C_2H_5$	53
CH_3	$CH(CN)_2$	30
CH_3	$CH(CN)CO_2C_2H_5$	21
Piperidinyl	CN	44
Piperidinyl	Piperidinyl	51

TABLE 17. Nucleophilic Replacements of 4-Nitroquinoline *N*-Oxides

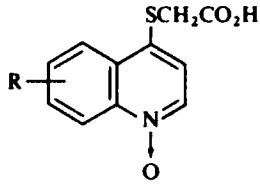
Substituent(s) in product	Reagent and temperature (°C)	Yield (%)	References	M.p. (°C) and derivatives
None	Sodium borohydride	Poor	403	
4-Chloro	Acetyl chloride, 0, room or 45	83	67, 503, 512	133
	Hydrochloric acid	95	145	
4-Bromo	Hydrobromic acid (30%)	60	503, 145	126.5–127[145]
4-Chloro-2-methyl	HCl, C_2H_5OH, 95	73	77, 79	139.5; hydrochloride 178
4-Methoxy-2-methyl	CH_3ONa, CH_3OH, room	49	874	135–136
4-Bromo-2-methyl	HBr (conc.), water-bath	55	79	Hydrobromide 180
2-Carboxyethyl-4-chloro	Acetyl chloride	70	40	188
4-Chloro-2-styryl	HCl, C_2H_5OH, boil	—	433	—
4-Chloro-2-(*p*-methoxystyryl)	HCl, C_2H_5OH, boil	69	433, 506	Hydrochloride 200
4-Chloro-3-methyl	HCl (conc.), 70	—	223	215–217
4-Chloro-5-methyl	HCl (conc.), 70	—	223	149–150
4-Chloro-6-methyl	HCl (conc.)	91	112, 113	141; hydrochloride 182–183
4-Bromo-6-methyl	HBr (48%)	67	112, 113	145–146
4-Chloro-8-methyl	HCl (conc.), 70	—	223	140–141
3,4-Dichloro	HCl (conc.), 70	—	223	162
3-Bromo-4-chloro	HCl (conc.)	50	67	152–153
4-Chloro-3-fluoro	HCl (conc.), 65	—	124	168–169
4,5-Dichloro	HCl (conc.), 70	—	223	164–165
4,6-Dichloro	HCl (conc.)	75	67	183–185
4,7-Dichloro	HCl (conc.)	83	508	
6-Bromo-4-chloro	HCl (conc.)	75	67	186–188
4-Chloro-6-nitro	HCl (conc.)	50	67	193
4-Chloro-6-methoxy	HCl (conc.), water-bath	85	456	172–175
4-Chloro-6-carboxy	HCl (conc.)	55	40	266–268
4-Chloro-8-nitro	HCl (15%), 80	60	455	236
4-Chloro-2-methyl-8-nitro	HCl (20%), 70–78	63	135	164–166
4-Chloro-6-methyl-5-nitro	HCl (conc.)	75	67	149–150
4,6,7-Trichloro	HCl (conc.) 70	—	223	200
6-Bromo-4-chloro-5-nitro	HCL (conc.)	50	67	195–197
4-Hydroxy	H_2SO_4 (40%), 130–140	71	67	238 (dec.)
4-Methoxy	CH_3ONa, CH_3OH, boil	85	65	54–55
4-*n*-Butoxy	$C_4H_9O^-$	—	817	51 (hydrate)

TABLE 17 (*cont.*)

Substituent(s) in product	Reagent and temperature (°C)	Yield (%)	References	M.p. (°C) and derivatives
4-(β-Diethylamino)ethoxy	$(C_2H_5)_2NCH_2CH_2O^-$	—	817	
4-Phenoxy	C_6H_5ONa	—	497	106–107
4-Phenylthio	C_6H_5SH, NaOH	—	497	87–90
4-Carboxymethylthio	HO_2CCH_2SH, C_2H_5OH, 35	78	20, 513, 803	205–207 (dec.)
4-Cysteinyl	Cysteine, aq. C_2H_5OH, room	60	803, 514	135.2–136[803]
4-Homocysteinyl	$HO_2CCH(NH_2)CH_2CH_2SH$, H_2O, room	—	515, 516	121–121.5
4-(D,L-Methioninyl)	$HO_2CCH(NH_2)CH_2CH_2SCH_3$, 50% aq. C_2H_5OH, 37	—	515	210 (dec.)
4-(β-Aminoethylthio)[a]	$HSCH_2CH_2NH_2$	—	514	207–209 (dec.); hydrochloride 189; *N*-acetyl 114; *N*-acetylpicrate 190
4-Morphinyloxy	Sodium morphine, C_2H_5OH, boil	—	517	80; hydrochloride 225 (dec.)
2-Methyl-4-hydroxy	H_2SO_4 (40%), 130–140	—	67	246–248
3-Bromo-4-hydroxy	H_2SO_4 (40%), 130–140	—	67	212–214
6-Chloro-4-hydroxy	H_2SO_4 (40%), 130–140	30	67	258–260
4-Hydroxy-8-nitro	H_2SO_4 (40%), 130–140	35	67	231–233
6-Bromo-4-hydroxy-5-nitro	H_2SO_4 (40%), 130–140	30	67	258–260
3,4-Di(carboxymethylthio)[b]	$HSCH_2CO_2H$, H_2O, room	50	124	208 (dec.)
4-Carboxymethylthio-2-methyl	$HSCH_2CO_2H$, C_2H_5OH, 35	85	513	209–210 (dec.)
4-Carboxymethylthio-7-chloro	$HSCH_2CO_2H$, C_2H_5OH, 35	71	513	205–208 (dec.)
4-Carboxymethylthio-6-nitro	$HSCH_2CO_2H$, C_2H_5OH, 35	67	513	195–198 (dec.)
4-Carboxymethylthio-8-nitro	$HSCH_2CO_2H$, C_2H_5OH, 35	75	513	185–818
6-Carboxy-4-ethoxy	C_2H_5OK, C_2H_5OH, boil	—	40	225
4-Piperidino	$C_5H_{10}NH$, C_2H_5OH, boil	—	503	69; hydrobromide 112–113 (hydrate); hydrochloride 178
4,4'-Hydrazino[c]	NH_2NH_2, C_2H_5OH, Cu, 100	90	518	Dihydrochloride 211
4,4'-Hydrazino-2,2'-dimethyl[c]	NH_2NH_2, C_2H_5OH, Cu, 100	—	518	Dihydrochloride 222

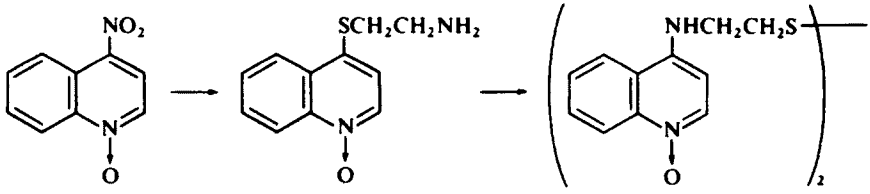
[a] With some bis(1-oxido-4-quinolylaminoethyl)disulphide, m.p. 146 °C (dec.); hydrochloride m.p. 185–186 °C (dec.).
[b] From 3-fluoro-4-nitroquinoline *N*-oxide.
[c] Bis(1-oxido-4-quinolyl) derivative.

Replacement by thioglycolic acid to give 4-quinolyl sulphides such as compounds (**292–296**) was shown to follow bimolecular reaction kinetics and, as with the 4-halogenoquinolines, the accelerating power of the *N*-oxide function was considerable.[513] A later study[520] of nucleophilic replacement by ethoxide ions of a large number of 4-nitroquinoline *N*-oxides correlated well with the work using thioglycolic acid[513] and with a study of polarographic half-wave reduction potentials,[332] but no definite correlation with carcinogenic activity could be shown. In all of the above cases changes in ultraviolet absorption were used to measure rates. The reaction between 4-nitroquinoline *N*-oxide and glutathione was accelerated by rat liver supernatant.[521]



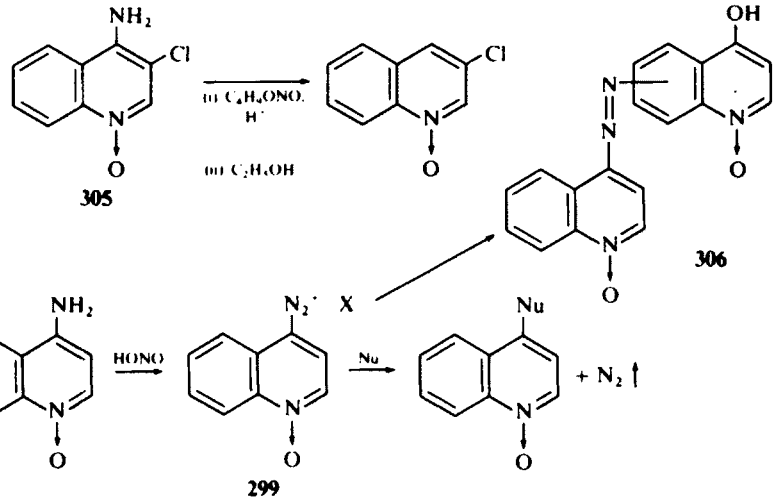
292, R = H, m.p. 205–207 °C; 78 %
293, R = 2-CH_3, m.p. 209–210 °C; 85 %
294, R = 7-Cl, m.p. 205–208 °C; 71 %
295, R = 8-NO_2, m.p. 185–188 °C; 75 %
296, R = 6-NO_2, m.p. 195–198 °C; 67 %

Reaction between 4-nitroquinoline *N*-oxide and β-amino(thioethanol) was reported to give the normal nucleophilic replacement product (**297**) under mild conditions, but to rearrange on heating in aqueous solution, producing the disulphide (**298**).[514] A similar reaction was observed with the *S*-cysteinyl derivative.

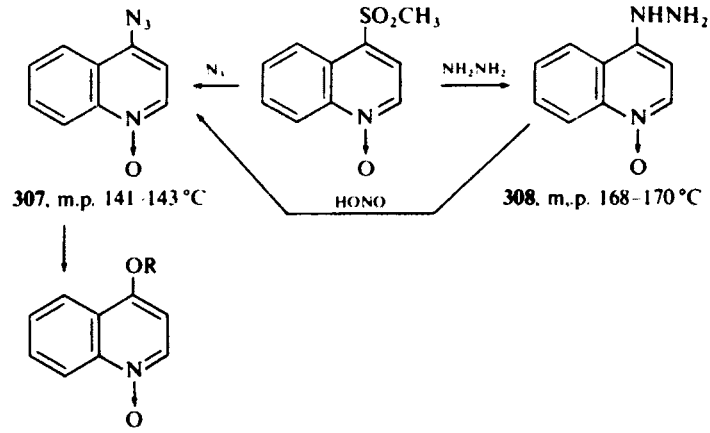


297 **298**

A few other leaving groups have been used to produce 4-substituted quinoline *N*-oxides. The diazonium salt (**299**) gave 4-iodoquinoline *N*-oxide (**300**) on treatment with triiodide ion,[522,503] and the chloride (**301**), bromide (**302**), cyanide (**303**) and thiocyanate (**304**) under standard conditions.[522] Deamination of 3-chloro-4-aminoquinoline *N*-oxide (**305**) was achieved by diazotization and subsequent treatment with ethanol.[370] When heated, the diazonium salt (**299**) gave the coupled product (**306**); the position of coupling was not determined.[522] Displacement of the methylsulphonyl group has been used to obtain 4-azidoquinoline *N*-oxide (**307**),[435] which has also been obtained by the action of nitrous acid on 4-hydrazinoquinoline *N*-oxide;[317] the 4-methylsulphonyl group[435] or the *p*-methylphenylsulphonyl group[67] was also displaced by hydrazine to give the substituted hydrazine (**308**). A number of 4-alkoxyquinoline *N*-oxides (**309–311**) and 4-hydroxyquinoline (4-quinolone) *N*-oxide (**312**) were obtained by treatment of 4-azidoquinoline *N*-oxide with alkoxides, or with sodium hydroxide.[412]



Ref.	Compound	Nu	Reagent	M.p. (°C)
356, 448	(**300**)	I	KI_3	166[356]
356	(**301**)	Cl	CuCl	133–134
356	(**302**)	Br	CuBr	136
356	(**303**)	CN	CuCN	188–190
356	(**304**)	SCN	CuSCN	155–157



307, m.p. 141–143 °C

308, m.p. 168–170 °C

312, R = H, m.p. 231 °C; 100 %

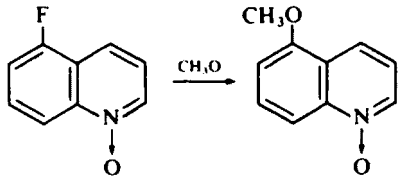
309, R = CH_3, m.p. (picrate) 158.9 °C; 100 %

310, R = C_2H_5, m.p. 39–42 °C, picrate 164–165 °C; 75 %

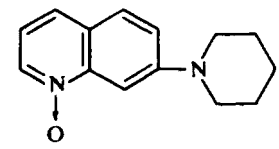
311, R = $C_6H_5CH_2$, m.p. 132–134 °C; 74 %

(*iv*) *Substitution at Position 5, 6, 7 or 8.* The most interesting study of nucleophilic substitution on the benzene ring of quinoline *N*-oxides has been made with the fluorides.[25] The 5-fluoro derivative (**313**) reacted with methoxide to give the 5-methoxy derivative (**314**), but not with piperidine; fluorine in the 7-position could be replaced by

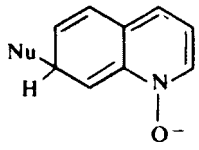
piperidine, giving compound (**315**), but 6- and 8-fluoro substituents could not be replaced. The explanations were based on the relative stabilities of the intermediate anions (**316** and **317**), the latter being said to be the more stable.



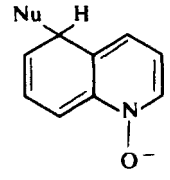
313 **314**, m.p. 94 °C



315, m.p. 142 °C; picrate m.p. 157 °C

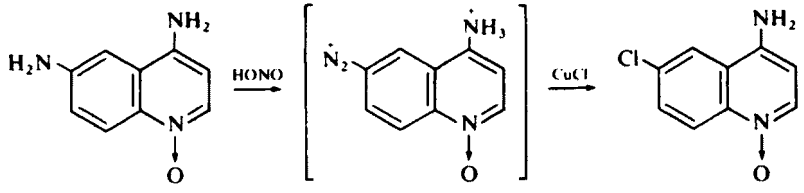


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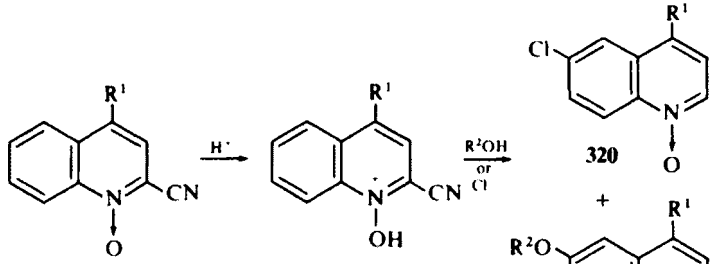
316

An example of selective diazotization is available.[381] When 4,6-diaminoquinoline *N*-oxide (**318**) was treated with nitrous acid, and the diazonium salt solution with copper(I) chloride, 6-chloro-4-aminoquinoline *N*-oxide (**319**) was obtained.



318 **319**

Photochemical substitution by alkoxy groups, specifically in the 6 position, has been reported when the *N*-oxide was irradiated (high-pressure mercury lamp) in a mixture of strong acid and alcohol.[523] If hydrogen chloride was used the 6-chloro or 6-alkoxy derivatives (**320**) or (**321**) were obtained; if sulphuric acid was used the 6-alkoxy derivative (**321**) was the main product, with some 6-hydroxy derivative.



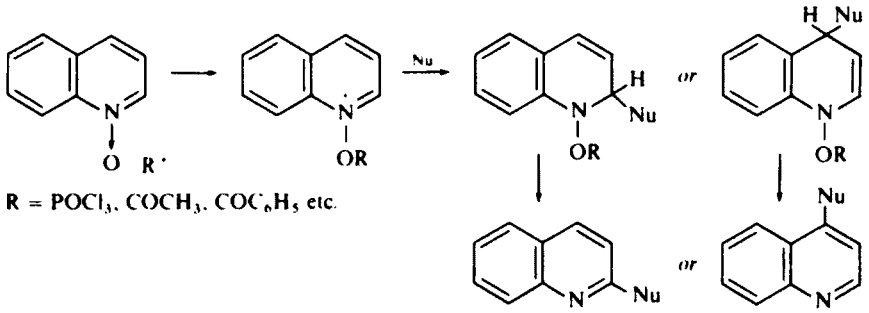
320

321

R^1 = H, CH_3; R^2 = CH_3, C_2H_5, $(CH_3)_2CH$, $(CH_3)_3C$

(*v*) *Reaction with Ethynyl Anions.* There is a patent report[524] of the reaction between quinoline *N*-oxide and sodium acetylide in dimethyl sulphoxide to give an ethynylquinoline *N*-oxide; the position of substitution is not specified.

b. SUBSTITUTIONS WITH DEOXYGENATION A very large number of reactions have been reported where oxygen is lost while a nucleophilic substitution reaction occurs. Almost all of these involve attack by an electrophile R (usually a derivative of an acid) on the oxygen atom to form a quinolinium species; the enhanced electron deficiency at position 2 or 4 leads to rapid addition of a nucleophile, and the elimination of a molecule of ROH completes the sequence (Scheme 12).



SCHEME 12

The reactions will be grouped according to the electrophilic reagent, these groups being sub-divided according to the nucleophiles used.

(*i*) *Reactions with Phosphorus Halides.* Phosphorus halides (particularly the trihalides) can cause deoxygenation without simultaneous nucleophilic substitution (p. 430), but more commonly have been used to convert quinoline *N*-oxides into 2- or 4-halogeno- or 2,4-dihalogenoquinolines. Direct replacement of hydrogen or replacement of some other, better, leaving group can be achieved. Such deoxygenations with halogen substitution are grouped in Table 18; phosphoryl halides, sulphuryl chloride and thionyl chloride have been used.

Groups which could be noted as stable to halogenative deoxygenation are styryl,[110] methoxyl[479] and carboxyl[93] in position 4 (one of the more sensitive positions for substituent groups), and the secondary alcohol which is present in quinine alkaloids.[48,49,371,529,528] Groups transformed during the reaction were the hydroxylamino group in compound (**322**),[410] the azoxy group in compound (**323**)[50] and hydroxyl groups in the 2-hydroxy derivatives (**324**–**326**)[476] and the 4-hydroxy derivative (**327**).[477] A nitro group in position 4 is usually replaced.

No firm rules can be deduced for relative substitution rates of positions 2 and 4, although most of the examples where both positions were free, but only one substituent entered, show a preference for position 2. Bachman and Cooper found that with 6-substituted quinoline *N*-oxides, quinoline itself and the 6-nitro derivative gave more 4-chloro- than 2-chloro derivative.[805] In at least one case[530] this may reflect steric hindrance as well as reduced activity, the 5-nitroquinoline *N*-oxide (**328**) giving only the 2-chloro-5-nitro derivative (**329**). The double role of phosphorus tribromide and phosphorus trichloride—deoxygenation with or without substitution—has been mentioned (p. 430) and there have been several careful studies of the conditions necessary for either.[526,384,375,376] Treatment of 4-ethoxyquinoline *N*-oxide with phosphoryl chloride

TABLE 18. Halogenoquinolines Prepared by Deoxygenative Halogenation of *N*-Oxides

Substituent(s) in starting material	Substituent(s) in product	Reagent and temperature (°C)	Yield (%)	References
None	4-Chloro	PCl_5 or sulphuryl chloride[a]	73	1, 5, 6
None	2-Chloro- and 4-chloro	$POCl_3$, ice, then boil	Ratio of 1 : 1.7	805
		$POCl_3$, PCl_3, 50–60, then 70–80		59
2-Methyl	4-Chloro-2-methyl	Sulphuryl chloride		194
2-Trifluoromethyl	4-Chloro-2-trifluoromethyl	$POCl_3$	43	9
2-Phenyl	4-Chloro-2-phenyl	$POCl_3$, 130–140	65	27
2-(*o*-Methoxyphenyl)	4-Chloro-2-(*o*-methoxyphenyl)	$POCl_3$, water-bath, then boil	56	64
3-Methyl	2-Chloro-3-methyl	$POCl_3$, boil	78	525
	2-Bromo-3-methyl	$POBr_3$, boil	83	525
3-Trifluoromethyl	2-Chloro-3-trifluoromethyl	$POCl_3$	77	9
4-Trifluoromethyl	2-Chloro-4-trifluoromethyl	$POCl_3$	82	9
4-Styryl	2-Chloro-4-styryl	$POCl_3$, $CHCl_3$	65	110
4-(Quinuclidinylmethanol)	2-Chloro-4-Q[b]	$POCl_3$, $CHCl_3$	—	48, 49
4-(Dihydroquinuclidinylmethanol)	2-Chloro-4-QH_2[c]	$POCl_3$, HCl	—	48, 49
2-(*m*-Chlorophenyl)-6-methyl	4-Chloro-2-(*m*-chlorophenyl)-6-methyl	$POCl_3$	78	122
2-(*p*-Methoxyphenyl)-6-methyl	4-Chloro-2-(*p*-methoxyphenyl)-6-methyl	$POCl_3$, 90	75	31
2-(*p*-Methylphenyl)-6-methyl	4-Chloro-2-(*p*-methylphenyl)-6-methyl	$POCl_3$	47	122
2-(*p*-Chlorophenyl)-7-methyl	4-Chloro-2-(*p*-chlorophenyl-7-methyl	$POCl_3$	50	122
2-(*p*-Methoxyphenyl)-7-methyl	4-Chloro-2-(*p*-methoxyphenyl)-7-methyl	$POCl_3$, 90	76	31
2-(1-oxidoquinolin-2-yl)[d]	4-Chloro-2-(4-chloroquinolin-2-yl)	$POCl_3$	24	98
4-Phenyl	2-Chloro-4-phenyl	$POCl_3$	83	92
6-Chloro	2,6-Dichloro	$POCl_3$, ice, then boil	49	805
	4,6-Dichloro		35	

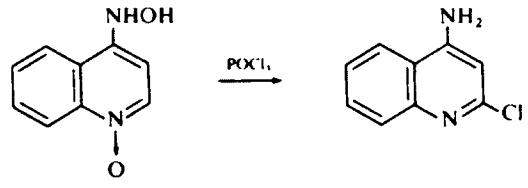
[a] Some 2-chloroquinoline was formed.[504]
[b] Q = quinuclidinylmethanol, i.e. cinchonine, cinchonidine.
[c] QH_2 = dihydroquinuclidinylmethanol, i.e. dihydrocinchonine, dihydrocinchonidine.
[d] 2,2-Biquinoline dioxide.

TABLE 18 (*cont.*)

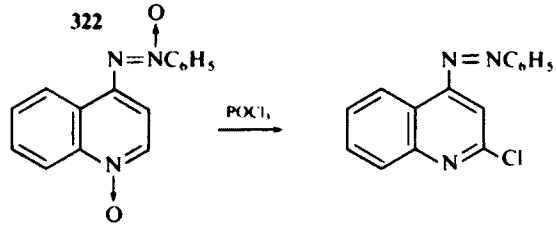
Substituent(s) in starting material	Substituent(s) in product	Reagent and temperature (°C)	Yield (%)	References
4-Nitro	4-Chloro	SO_2Cl_2	—	512
4-Nitro	2,4-Dichloro	$POCl_3$	83	67, 453
4-Nitro	4-Chloro[e]	PCl_3, $CHCl_3$, water-bath	81.5	526
4-Nitro	2,4-Dibromo	$POBr_3$, $CHCl_3$, 61	51	375
5-Nitro	2-Chloro-5-nitro (A), 4-Chloro-5-nitro (B), 3-Chloro-5-nitro (C)	$POCl_3$	35 (A), 10 (B), 20 (C)	33
5-Nitro	2-Chloro-5-nitro	SO_2Cl_2	—	453
6-Nitro	2-Chloro-6-nitro 4-Chloro-6-nitro	$POCl_3$, ice, then boil	16 56	805
8-Nitro	2-Chloro-8-nitro	SO_2Cl_2	—	453
2-Methyl-4-nitro	4,7-Dichloro-2-methyl	$POCl_3$, 100–110	75	527
6-Methyl-8-nitro	2,4-Dichloro-6-methyl	$POCl_3$	—	468
7-Methyl-8-nitro	2-Chloro-7-methyl-8-nitro	$POCl_3$	50	136
4-Methyl-8-nitro	2-Chloro-4-methyl-8-nitro	$POCl_3$	—	468
3-(Dicarbethoxymethyl)-4-nitro	4-Chloro-3-(dicarbethoxymethyl)	PCl_3	33	413
4-Nitro-2-phenyl	4-Chloro-2-phenyl	PCl_3, $CHCl_3$	—	92
4,6-Dinitro	2,4-Dichloro-6-nitro	$POCl_3$, water-bath	80	130
4,6,8-Trinitro	2,4-Dichloro-6,8-dinitro	$POCl_3$, water-bath	80	130
4-Nitro-2-(4-nitro-1-oxidoquinolin-2-yl)	4-Bromo-2-(4-bromoquinolin-2-yl)	PBr_3	12	98
4-Picolinoyl	2-Chloro-4-picolinoyl	$POCl_3$, $CHCl_3$, boil	95	107
4-Quinaldinoyl	2-Chloro-4-quinaldinoyl	$POCl_3$	~100	108
6-Methyl-4-picolinoyl	2-Chloro-6-methyl-4-picolinoyl	$POCl_3$, HCl, $CHCl_3$, boil	~100	432
2-Hydroxy	2,4-Dichloro	$POCl_3$, 150–155	—	476
6-Methoxy	2-Chloro-6-methoxy 4-Chloro-6-methoxy	$POCl_3$, ice, then boil	55 35	805
6-Methoxy-2-phenyl	4-Chloro-6-methoxy-2-phenyl	$POCl_3$, water-bath, then boil	88–91	64
6-Methoxy-2-(*m*-chlorophenyl)	4-Chloro-6-methoxy-2-(*m*-chlorophenyl)	$POCl_3$, water-bath, then boil	63	64

6-Methoxy-2-(*p*-chlorophenyl)	4-Chloro-6-methoxy-2-(*p*-chlorophenyl)	$POCl_3$, water-bath, then boil	73	64
6-Methoxy-2-phenyl	4-Chloro-6-methoxy-2-phenyl	$POCl_3$	88–91	64
6-Methoxy-4-R[f]	2-Chloro-6-methoxy-4-R[f]	$POCl_3$, $CHCl_3$, boil	80	528, 529
6-Methoxy-4-RH_2[f]	2-Chloro-6-methoxy-4-RH_2[f]	$POCl_3$, $CHCl_3$, boil	80	528, 529
2-Hydroxy-3-bromo	2-Chloro-3-bromo	$POCl_3$	—	476
2-Hydroxy-3-nitro	2-Chloro-3-nitro	$POCl_3$	—	476
4-Hydroxy-3-nitro	2,4-Dichloro-3-nitro	$POCl_3$, 70–80	—	477
4-Methoxy-7-nitro	2-Chloro-4-methoxy-7-nitro	$POCl_3$	—	478
4-Methoxy-8-nitro	2-Chloro-4-methoxy-8-nitro	$POCl_3$	—	479
5-Methoxy-6-nitro	2-Chloro-5-methoxy-6-nitro	$POCl_3$	56	530
3,6-Dinitro-2-hydroxy	2-Chloro-3,6-dinitro	$POCl_3$, 150–155	—	476
4-Carboxy	4-Carboxy-2-chloro[g]	$POCl_3$, or $SOCl_2$ or SO_2Cl_2	—	93, 104
3-Acetamido	3-Acetamido-2-hydroxy	$POCl_3$	—	171
4-Hydroxyamino	2-Chloro-4-amino	$POCl_3$	—	410
4-Phenylazoxy	2-Chloro-4-phenylazo	$POCl_3$	—	50

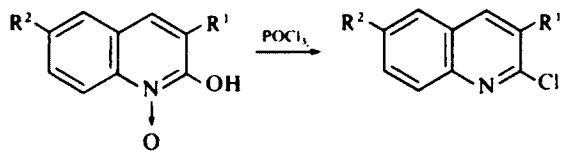
[e] Some 2,4-dichloroquinoline at other temperatures and with other solvents.
[f] R = quinuclidinemethanol, i.e. quinine-RH_2 = dihydroquinuclidinemethanol.
[g] Isolated as acid chloride.[104]



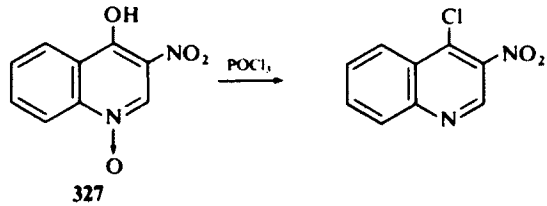
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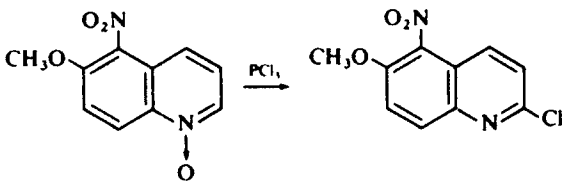
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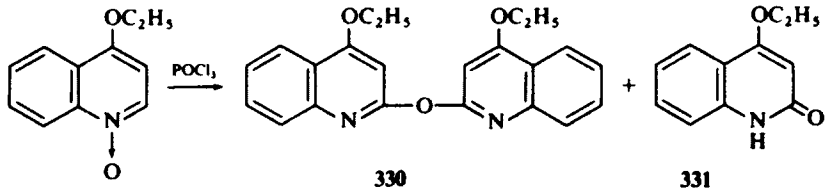
324, $R^1 = Br$, $R^2 = H$
325, $R^1 = NO_2$, $R^2 = H$
326, $R^1 = R^2 = NO_2$



327



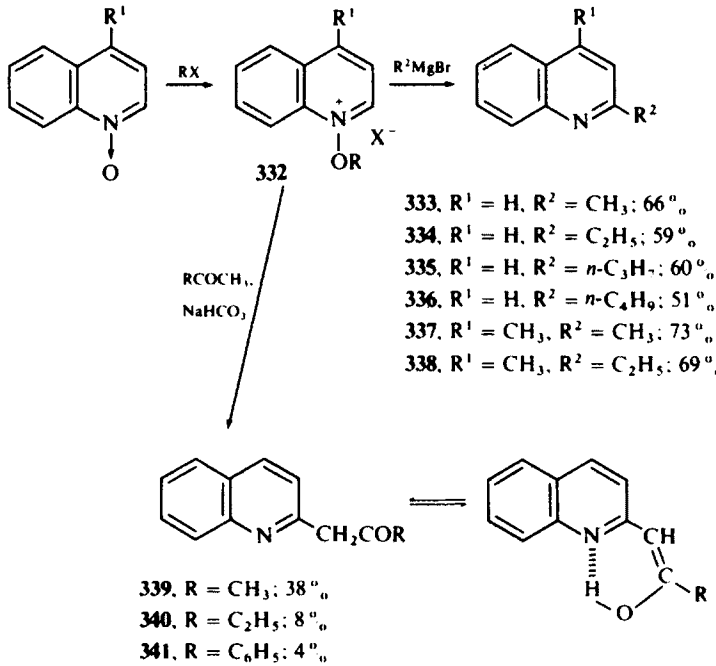
328 329



330 331

was reported to give the ether (**330**) and the carbostyril (**331**).[512] Carbostyrils have often been isolated as byproducts from halogenative deoxygenation.

(*ii*) *Reactions Involving Alkoxyquinolinium Intermediates.* The next few sections involve intermediates in which the oxygen atom of the *N*-oxide has been alkylated or acylated. The *N*-oxides are well known to react with alkyl halides or with dialkyl sulphates to give alkoxyquinolinium salts of general type (**332**). The quinolinium salts show increased activity in nucleophilic substitution reactions, the alkoxyl group leaving to form the quinoline. Grignard reagents thus produce satisfactory yields of 2-alkylquinolines (**333–338**).[531]



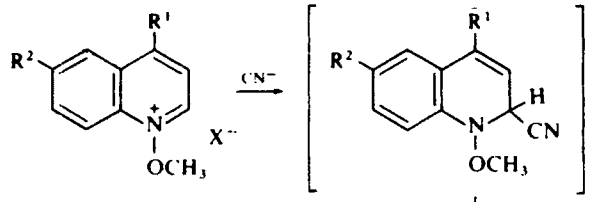
333, $R^1 = H$, $R^2 = CH_3$; 66%
334, $R^1 = H$, $R^2 = C_2H_5$; 59%
335, $R^1 = H$, $R^2 = n\text{-}C_3H_7$; 60%
336, $R^1 = H$, $R^2 = n\text{-}C_4H_9$; 51%
337, $R^1 = CH_3$, $R^2 = CH_3$; 73%
338, $R^1 = CH_3$, $R^2 = C_2H_5$; 69%

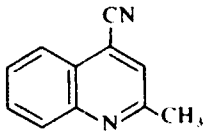
339, $R = CH_3$; 38%
340, $R = C_2H_5$; 8%
341, $R = C_6H_5$; 4%

A remarkably mild alkylation procedure uses methyl ketones and an aqueous–alcoholic solution of sodium bicarbonate, although the yield of quinaldinyl ketone (**339–341**) was only reasonable when acetone was used.[532] The most commonly reported nucleophilic deoxygenation of quaternary salts uses cyanide ions to produce 2-cyanoquinolines. The yields are often high, as shown by the examples (**342–345**); the general mechanism for nucleophilic deoxygenation is shown. Traces of 4-cyanoquinolines have been reported[533,534] but when only the 4-position was available yields of 4-cyano-2-methylquinoline (**346**) were very low.

The reaction between 1-methoxyquinolinium methosulphate and malononitrile in dimethyl sulphoxide gave a variety of products, dependent on temperature.[868] At 60–70 °C the 2- and the 4-dicyanomethylquinolines (**345a** and **345b**), and *N*-methoxy-2- and -4-(dicyanomethylidene)quinolines (**345c** and **345d**) were formed. At 100–110 °C, 2-aminoquinoline and a compound formulated as the ylide (**345e**) were obtained.

A systematic study of the reaction between varying quaternary quinolinium salts and butanethiol showed that 2-, 3- or 4-substituted quinolines could be obtained together with a substantial proportion of quinoline formed by simple deoxygenation.[537] In





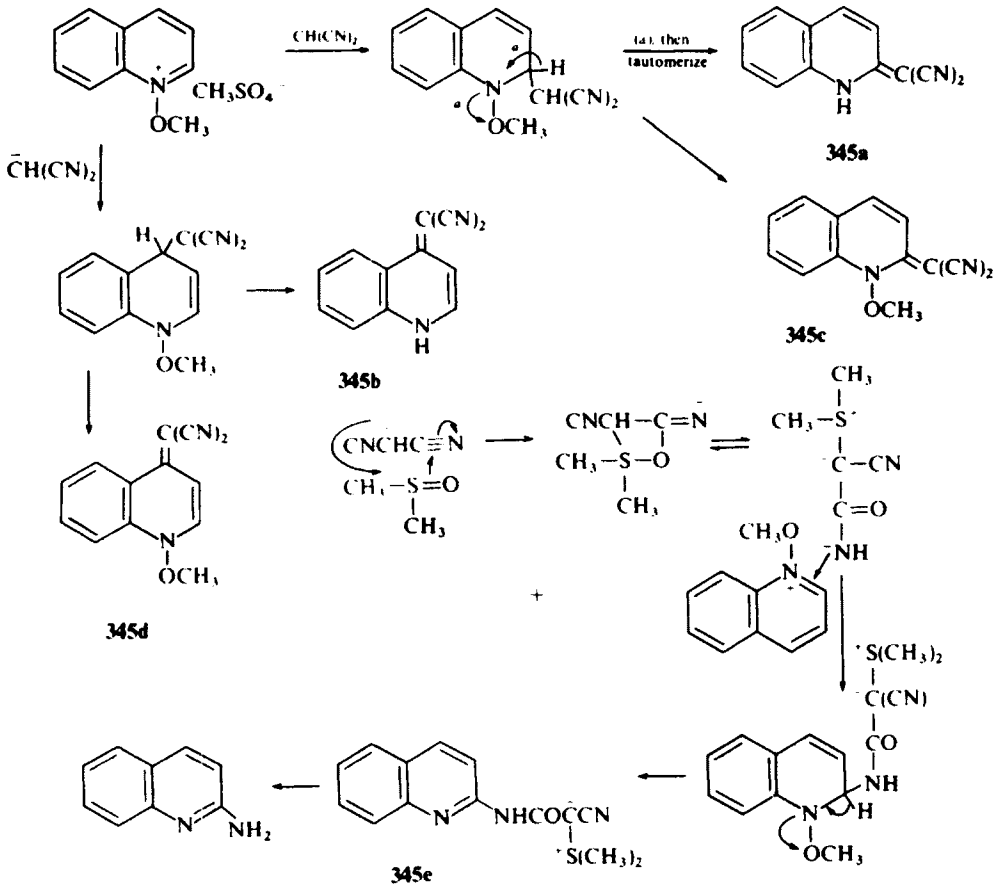
346; 7.2%

342, $R^1 = R^2 = H$; 93%[413,535,536]

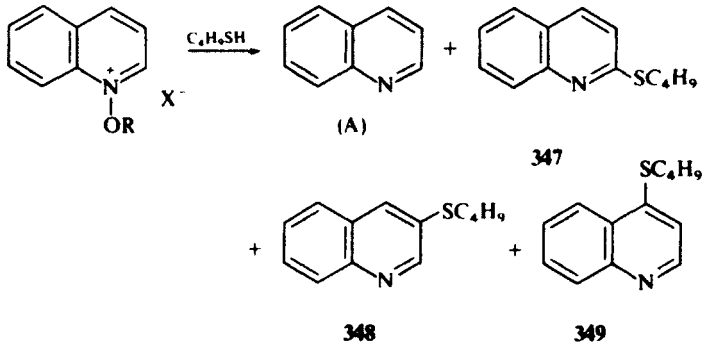
343, $R^1 = CH_3$, $R^2 = H$; 65%[413,535,536]

344, $R^1 = H$, $R^2 = CH_3O$; 67%[797]

345, R^1 = dihydroquinuclidinyl, $R^2 = CH_3O$[797]

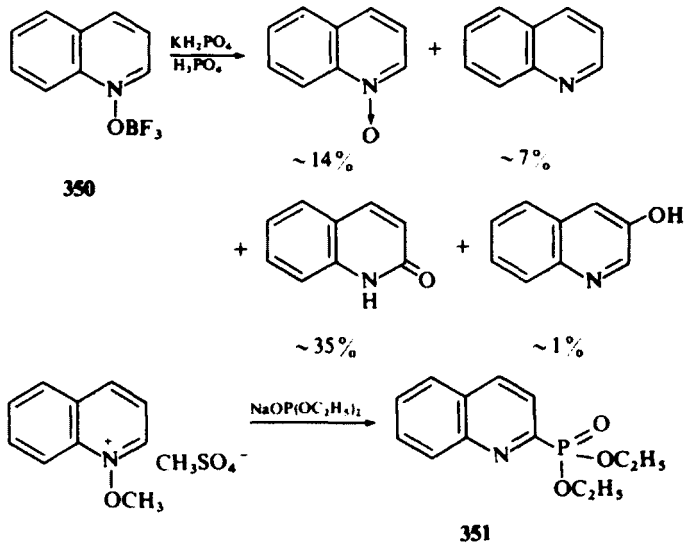


summary, ethoxyquinolinium salts and *p*-toluenesulphonyloxyquinolinium salts gave mainly 3-butylthioquinoline (**348**); acetoxy- and benzenesulphonyloxyquinolinium salts gave mainly 2-butylthioquinoline (**347**). A small amount of 4-butylthioquinoline (**349**) was usually isolated. Reaction conditions differed for the various salts used, and it is difficult to advance reasons for the changing substitution patterns.

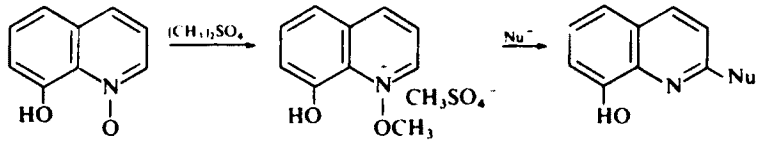


R	A (%)	Total sulphides (%)	(347) (%)	(348) (%)	(349) (%)
C_2H_5	36	21	15	76	8
p-$CH_3C_6H_4SO_2$	34	28	17	70	13
CH_3CO	28	23	90	10	—
$C_6H_5SO_2$	20	33	81	11	8

A related reaction using phosphoric acid with potassium dihydrogen phosphate at 280–300 °C on the boron trifluoride complex from quinoline *N*-oxide (**350**) gave largely carbostyril, with a trace of 3-hydroxyquinoline.[400] Sodium diethyl phosphite gave, with 1-methoxyquinolinium methosulphate, the phosphonate (**351**).[538-540,820]



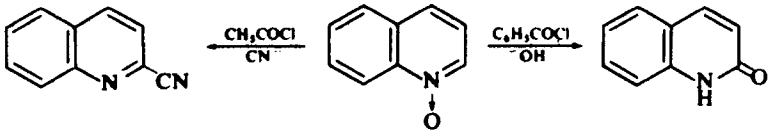
Methylation of 8-hydroxyquinoline *N*-oxide has been reported to give the 1-methoxyquinolinium salt (**352**), which reacted with nucleophiles to give 2-substituted-8-hydroxyquinolines.[541]



352

(*iii*) *Reactions Initiated by Acid Halides Other than Phosphorus and Sulphur Halides, or by Acid Anhydrides.* Acid halides, most commonly benzoyl or benzene (or toluene) sulphonyl chlorides, or acid anhydrides, react with quinoline *N*-oxides to give acyloxyquinolinium salts, which in some cases have been isolated. In most reported reactions the acylating agent and the nucleophilic reagent are used together, and a wide range of 2-substituted quinolines have been obtained. Henze reported[542] in 1936 that quinoline *N*-oxide could be converted by treatment with benzoyl chloride and sodium hydroxide into carbostyril, and by using potassium cyanide and benzoyl chloride 2-cyanoquinoline (**353**) could be obtained. There are now many examples of the synthesis of carbostyrils and of 2-cyanoquinolines using this method (or simple modifications), and these are grouped in Tables 19 and 20.

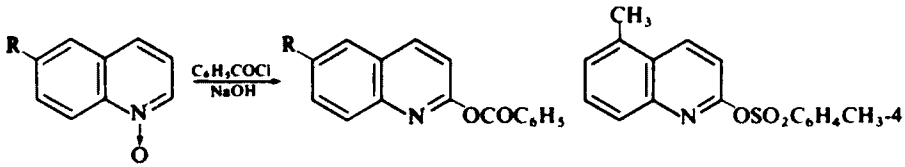
Poor yields of 2- or 4-cyanoquinolines have been obtained when cyanoquinoline *N*-oxides were treated with potassium cyanide in dimethyl sulphoxide,[22] although it had earlier been reported that quinoline *N*-oxide with carbon anions [such as copper(I) cyanide] gave resinous products.[558]



353

In some cases the ester of 2-hydroxyquinoline has been isolated and subsequently hydrolysed, as in the case of the 6-substituted quinoline *N*-oxides (**354** and **355**),[550] or of 5-methylquinoline *N*-oxide, which gave the toluenesulphonate (**356**).[111] More remarkable was the production of the methanesulphonates (**357** or **358**) rather than the cyanides when a number of *N*-oxides were treated with methylsulphonyl chloride and potassium cyanide.[544] Two mechanisms were advanced, shown in Scheme 13, of which the second was thought to make the main contribution.

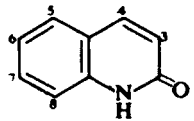
There are a number of cases where substitution has occurred in positions other than 2 or 4, particularly when a substituent is already present in one or both of these positions.



354, R = OCH_3 **356**

355, R = $NHCOCH_3$

TABLE 19. Carbostyrils Obtained by Treatment of *N*-Oxides with Acid Chlorides or Anhydrides BzCl = Benzoyl Chloride; TsCl = *p*-Toluenesulphonyl Chloride; AA = Acetic Anhydride, Sodium Acetate



Substituents in starting material	Substituents in carbostyril	Reagent	Yield (%)	References
None	None	BzCl, NaOH	—	542, 543
None	None	TsCl, $CHCl_3$, H_2O	66	543, 446, 457, 400
None	None	CH_3SO_2Cl, KCN, H_2O	84[a]	544
2-^{14}C	2-^{14}C	TsCl, $CHCl_3$, boil, then HCl	44	106
3-Trifluoromethyl	3-Trifluoromethyl	AA, boil	77	9
3-Phenyl	3-Phenyl	AA, boil	44	102
3-(*p*-Nitrophenyl)	3-(*p*-Nitrophenyl)	AA, boil	66	102
4-Methyl	4-Methyl	CH_3SO_2Cl, KCN, aq.	87[a]	544
4-Phenyl	4-Methyl	TsCl, $CHCl_3$, H_2O	—	545
4-Trifluoromethyl	4-Trifluoromethyl	AA, boil	74	9
4-Styryl	4-Styryl	BzCl, aq. dioxan, KOH	65	110
5-Methyl	5-Methyl	TsCl, Na_2CO_3 aq.	60	111
6-Methyl	6-Methyl	BzCl, NaOH	—	547
6-Methyl	6-Methyl[b]	TsCl, $CHCl_3$, boil, then aq. base	—	547
6-Methyl	6-Methyl	AA, boil	65	548
7-Methyl	7-Methyl[b]	TsCl, $CHCl_3$, boil, then aq. base	—	547
3-Chloro	3-Chloro	AA	75	125
3-Bromo	3-Bromo	CH_3SO_2Cl, KCN, aq.	66[c]	544
3-Bromo	3-Bromo	AA, boil	~70	549
4-Chloro	4-Chloro	CH_3SO_2Cl, KCN, aq.	74[c]	544
4-Bromo	4-Bromo	AA, boil	~70	549
5-Bromo	5-Bromo	AA, boil	~70	549

[a] Mixture of carbostyril and the methanesulphonyl derivative.
[b] With some 1-tosyloxy-2-hydroxy-1,2-dihydroquinoline.
[c] Mixture of carbostyril and the methansulphonyl derivative.

TABLE 19 (*cont.*)

Substituents in starting material	Substituents in carbostyril	Reagent	Yield (%)	References
6 Chloro	6-Chloro	CH_3SO_2Cl, KCN, aq.	75[c]	544
6-Bromo	6-Bromo	CH_3SO_2Cl, KCN, aq.	65[c]	544
6-Bromo	6-Bromo	AA, boil	~70	549
7-Chloro	7-Chloro	CH_3SO_2Cl, KCN, aq.	75[c]	544
7-Bromo	7-Bromo	AA, boil	~70	549
3-Nitro	3-Nitro	TsCl, H_2O	83	171
5-Nitro-3-*p*-nitrophenyl	5-Nitro-3-*p*-nitrophenyl	AA, boil	72	102
6-Nitro	6-Nitro	CH_3SO_2Cl, KCN, aq.	39[c]	544
4-Acetyl	4-Acetyl	TsCl, $CHCl_3$, then NaOH	70	140, 139
4-Benzoyl	4-Benzoyl	TsCl, $CHCl_3$, then NaOH	84	140, 141
4-Methoxy	4-Methoxy	CH_3SO_2Cl, KCN, aq.	65[c]	544
4-Methoxy	4-Methoxy	BzCl, NaOH	43	65
6-Methoxy	6-Methoxy	CH_3SO_2Cl, KCN, aq.	60[c]	544
6-Methoxy	6-Methoxy	BzCl, NaOH	70	546, 550
6-Methoxy	6-Methoxy	AA, boil	—	548
6,7-Methylenedioxy	6,7-Methylenedioxy	AA, boil	63	153
6-Methoxy-4-A[d]	6-Methoxy-4-A[d]	AA, 120-130°C	—	47 (and dihydro)
3-Cyano	3-Cyano	CH_3SO_2Cl, KCN, aq.	51[c]	544
4-Cyano	4-Cyano	CH_3SO_2Cl, KCN, aq.	58[c]	544
4-Cyano	4-Cyano	$(CF_3CO)_2O$	20[f]	53
6-Cyano	6-Cyano	CH_3SO_2Cl, KCN, aq.	80[c]	544
6,7-Dimethoxy-3-carboxy	6,7-Dimethoxy-3-carboxy	AA, boil	—	189
4-Phenylazo	4-Phenylazo	BzCl, NaOH	33	50
4-Amino	4-Benzoylamino	BzCl, NaOH	Small	551
6-Acetamido	6-Acetamido[g]	BzCl, NaOH	8	550
6-Ethoxycarbamoyl	6-Ethoxycarbamoyl	TsCl, K_2CO_3 aq.	2.8	45
5,7-Dichloro-8-hydroxy	5,7-Dichloro-8-hydroxy	AA, boil	—	29

[d] A = quinuclidinyl residues, i.e. quinine.
[c] Mixture of carbostyril and 2-methanesulphonyloxyquinoline.
[f] Plus some 4-cyano-3-hydroxyquinoline.
[g] As 2-benzyloxyquinoline.

TABLE 20. Cyanoquinolines Prepared by the Action of Cyanides on Quinoline *N*-Oxides BzCl = benzoyl chloride; TsCl = *p*-toluene sulphonyl chloride

Substituent(s) in *N*-oxide	Substituent(s) in product	Reagent	Yield (%)	References
None	2-Cyano	KCN, BzCl, H_2O	90	542, 552, 162
None	2-Cyano	KCN, TsCl, −10°C	Good	553
2-Phenyl	4-Cyano-2-phenyl[a]	KCN, BzCl	10	92
2-(*p*-Methoxyphenyl)	4-Cyano-2-(*p*-methoxyphenyl) (A) and 1-benzoyloxy-4-cyano-1,4-dihydro-2-(*p*-methoxyphenyl) (B)	KCN, BzCl, $CHCl_3$, H_2O	1 (A) 10 ((B)	94
2-(*p*-Nitrophenyl)	1-Benzoyloxy-4-cyano-[b] 1,4-dihydro-2-(*p*-nitrophenyl)	KCN, BzCl, $CHCl_3$, H_2O	5	94
3-Trifluoromethyl	2-Cyano-3-trifluoromethyl	BzCl, KCN, $CHCl_3$, H_2O	69	9
4-Methyl	2-Cyano-4-methyl	BzCl, KCN	78	162
4-Trifluoromethyl	2-Cyano-4-trifluoromethyl	BzCl, KCN, $CHCl_3$, H_2O	51	9
4-Styryl	2-Cyano-4-styryl	KCN, BzCl, $CHCl_3$, H_2O	75	110
4-Phenyl	2-Cyano-4-phenyl	KCN, BzCl	100	92
6-Methyl	2-Cyano-6-methyl	BzCl, KCN, H_2O	—	546
4-Chloro	4-Chloro-2-cyano	BzCl, KCN	95	162
4-Chloro	4-Chloro-2-cyano	BzCl, AgCN, $CHCl_3$, H_2O	30	554
4-Bromo	4-Bromo-2-cyano	BzCl, AgCN, $CHCl_3$, H_2O	66	554
6-Chloro	6-Chloro-2-cyano	BzCl, KCN, H_2O	70	148
7-Chloro	7-Chloro-2-cyano	BzCl, KCN, H_2O	70	148
3-Nitro	2-Cyano-3-nitro	BzCl, AgCN, $CHCl_3$, H_2O	80	554
3-Nitro	4-Cyano-3-methoxy	KCN, CH_3OH, boil	38	168
4-Nitro	4-Chloro-2-cyano	BzCl, KCN, H_2O	—	552
6-Nitro	2-Cyano-6-nitro	BzCl, AgCN, H_2O	89	554
4-Methoxy	2-Cyano-4-methoxy	BzCl, KCN, H_2O	84	162, 555, 556
4-Ethoxy	2-Cyano-4-ethoxy	BzCl, KCN, H_2O	80–90	555, 556, 162
4-(*n*-Propoxy)	2-Cyano-4-(*n*-propoxy)	BzCl, KCN, H_2O	—	555, 556
4-(*n*-Butoxy)	4-(*n*-Butoxy)-2-cyano	BzCl, KCN, H_2O	—	555, 556
4-Benzyloxy	4-Benzyloxy-2-cyano	BzCl, KCN, H_2O	90	557

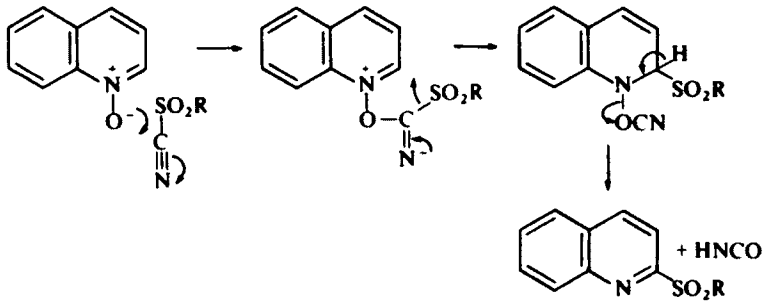
[a] Plus 6-benzoyloxy-2-phenylquinoline (25%) and 8-benzoyloxy-2-phenylquinoline (8%).
[b] Plus 3-benzoyloxy- (29%) and 6-benzoyloxy-2-(*p*-nitrophenyl)quinoline (19%).

TABLE 20 (*cont.*)

Substituent(s) in *N*-oxide	Substituent(s) in product	Reagent	Yield (%)	References
6-Methoxy	2-Cyano-6-methoxy	BzCl, AgCN, $CHCl_3$, H_2O	84	147
6-Methoxy	2-Cyano-6-methoxy	BzCl, KCN, H_2O	85	546
6-Ethoxy	2-Cyano-6-ethoxy	BzCl, KCN, H_2O	70	148
6-Methoxy-4-X[c]	2-Cyano-6-methoxy-4-X[c]	BzCl, KCN (or AgCN), $CHCl_3$, H_2O	75	147
6-Methoxy-4-Y[d]	2-Cyano-6-methoxy-4-Y[d]	BzCl, KCN, $CHCl_3$, H_2O	60	147
2-Cyano	2-Carboxamido-4-cyano *and* 2,4-dicyano	KCN, DMSO, 50 °C	14 *and* 5	22
3-Cyano	3,4-Dicyano	KCN, DMSO, room temp.	14	22
4-Cyano	2,4-Dicyano	KCN, DMSO, room temp.	14	22
5-Methoxycarbonyl	2-Cyano-4-methoxycarbonyl	BzCl, KCN, H_2O, ice	86	873
6-Cyano	2,6-Dicyano	KCN, DMSO, room temp.	8	22

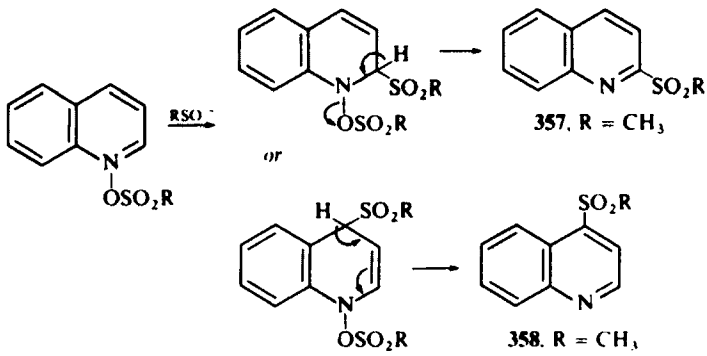
[c] X = dihydroquinuclidinylmethanol≡dihydroquinine.
[d] Y = Quinuclidinylmethanol≡quinine.

(1) $RSO_2Cl + CN^- \rightarrow RSO_2CN + Cl^-$



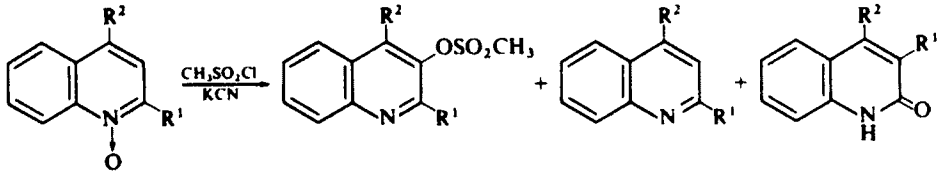
357, R = CH_3

(2) $RSO_2CN + CN^- \rightarrow R{-}SO_2{-}\underset{CN}{\underset{|}{C}}{=}N^- \rightarrow RSO_2^- + CN{-}CN$



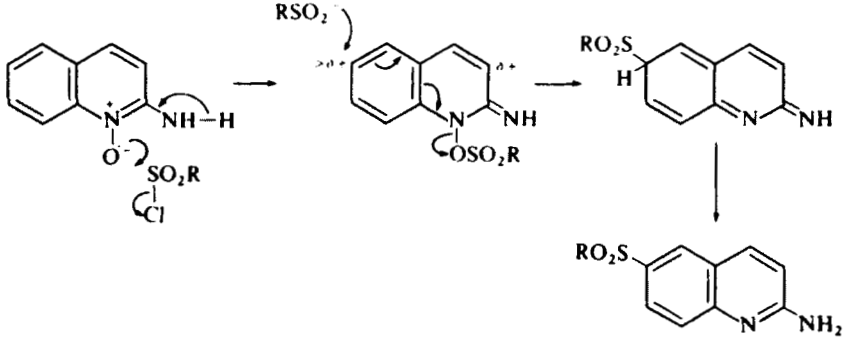
SCHEME 13

Thus, in the reaction between 2,4-disubstituted quinoline *N*-oxides, methanesulphonyl chloride and potassium cyanide variable yields of 3-sulphonyloxyquinolines (**359–362**) were obtained together with substantial amounts of deoxygenated products (**363–365**) and, remarkably, in some cases rearrangement products, such as (**366** and **367**).[559]



$R^1 = R^2 = CH_3$	**359**; 19%	**363**; 11%	**366**; 5%
$R^1 = CH_3$, $R^2 = C_6H_5$	**360**; 3%	**364**; 54%	—
$R^1 = C_2H_5$, $R^2 = CH_3$	**361**; 10%	**365**; 15%	**367**; 3%
$R^1 = C_6H_5$, $R^2 = CH_3$	**362**; 36%		

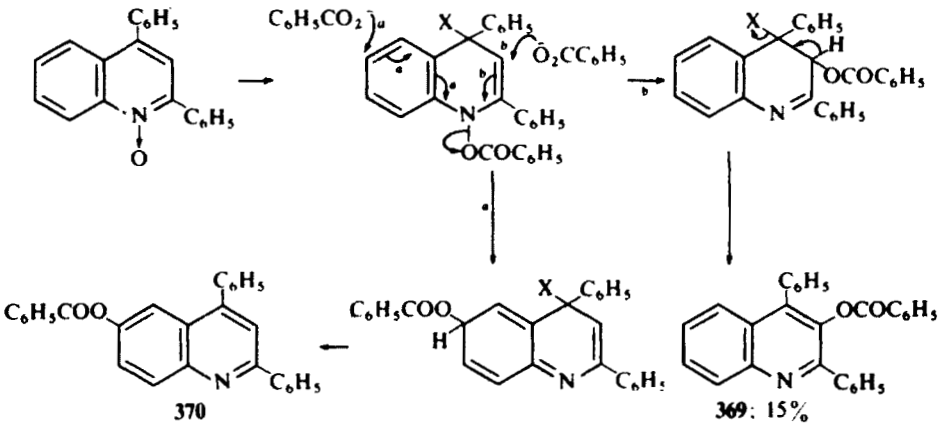
In many other cases the presence of a 2- or 4-substituent capable of loss of a proton to give an 'anhydro base' is associated with substitution at positions 3, 6 or 8 or in a side-chain (for the mechanism of the last reaction type see p. 548). The classic work on such abnormal nucleophilic substitutions was done by Tanida using 2-aminoquinoline *N*-oxide, when 2-amino-6-tosyloxyquinoline (**368**) was obtained after hydrolysis.[560] The mechanism is



368

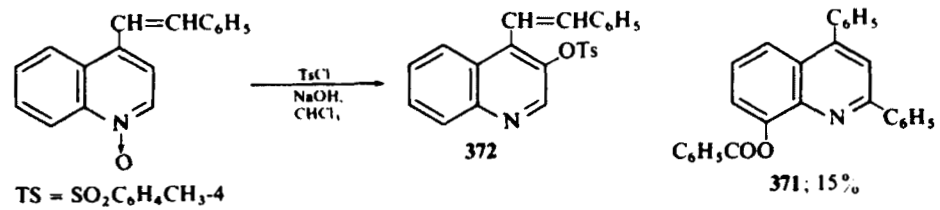
The mechanism has been studied using ^{18}O-labelled tosyl chloride and shown to proceed through a solvent-separated ion pair.[816]

In a similar manner it is possible to account for the production of 3-benzoyloxy-4-methylquinoline from lepidine *N*-oxide and benzoyl chloride[561] or benzoyl nitrate[461] and 3-tosyloxy-4-quinolone from 4-hydroxyquinoline *N*-oxide, tosyl chloride and pyridine.[562] A slightly different mechanism, illustrated for the reaction between 2,4-diphenylquinoline *N*-oxide, potassium cyanide and benzoyl chloride, giving products (**369**–**371**),[92] can also be applied to the production of 3-tosyloxy-4-styrylquinoline



370

369: 15%



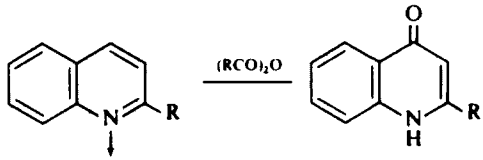
TS = $SO_2C_6H_4CH_3$-4

372

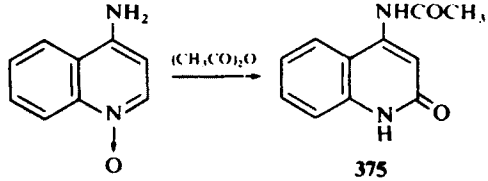
371: 15%

(372),[110] but here it should be noted that with benzoyl chloride and potassium hydroxide 4-styrylquinoline *N*-oxide gave 4-styrylcarbostyril.

Other products isolated from reactions between quinoline *N*-oxides and toluenesulphonyl chloride include 4-chloroquinolines (also obtained when acetyl chloride is used) and bis(2-quinolyl) ethers.[563,501] Quinoline *N*-oxide and tosyl chloride were shown to give *N*-tosyloxyquinolinium chloride;[815] after boiling, 2-tosyloxyquinoline, 4-chloroquinoline and *N*-(2-quinolyl)carbostyril were obtained. The 2-hydroxy-1-tosyloxy-1,2-dihydroquinoline (the intermediate in the normal reaction) has been isolated from 6-methyl- and from 7-methylquinoline *N*-oxide, toluenesulphonyl chloride and chloroform.[547] The treatment of quinoline *N*-oxides with hot acetic anhydride (or occasionally benzoic or trifluoroacetic anhydride) and sodium acetate has provided good yields of carbostyrils, and these are recorded in Table 19 (p. 491). Quinoline *N*-oxide itself was reported to give a poor yield of carbostyril,[549] although later workers recorded a high yield.[548] The mechanism of the reaction has been studied by ^{18}O labelling, and found to show solvent dependence between intermolecular and intramolecular rearrangements; the rearrangement–recombination step is fast.[564] There are a few examples where a 2-substituted quinoline *N*-oxide gave a 4-quinolone, such as compound (373)[9] or (374);[53] in the latter case trifluoroacetic anhydride was used at a lower temperature than is necessary with acetic anhydride. The trifluoroacetate, which is the product, was said to be more easily hydrolysed than the corresponding acetate. If an amino group is present the acetic anhydride reaction gives the acetamidocarbostyril, as in example (375),[551] whereas at low temperatures the amino group can be converted into



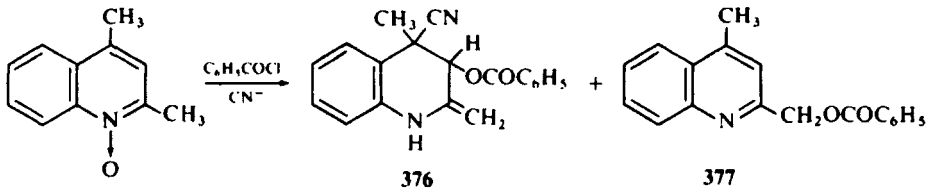
373, R = CF_3; 33%
374, R = CN; 82%



375

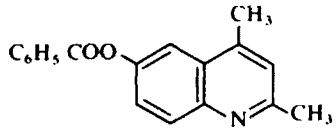
an amide[551] or sulphonamide[565] without rearrangement. The synthesis of 2-cyanoquinolines from *N*-oxides gives good yields when benzoyl chloride and potassium cyanide in aqueous solution are used. Improved yields have been claimed by using *p*-toluenesulphonyl chloride and an aqueous chloroform mixture, and sometimes silver cyanide gives better yields than potassium cyanide.[554] When a substituent is present in the 2-position of the *N*-oxide, benzoyloxy or tosyloxy groups can be introduced into position 3, 6 or 8 (see p. 496) and can provide the major products.[92,121] Treatment of 2,4-dimethylquinoline *N*-oxide with benzoyl chloride and a cyanide was reported to give the anhydro base (**376**), a most unusual structure,[121] in addition to the more conventional products (**377** and **378**). Similar products were obtained from methyl 2-ethyl-3-methylcinchoninate *N*-oxide.

The mechanism of formation of compounds of type (**377**) is discussed later (p. 496). The intermediate 1-benzyloxy-4-cyano-1,4-dihydroquinolines (**379** and **380**) have been



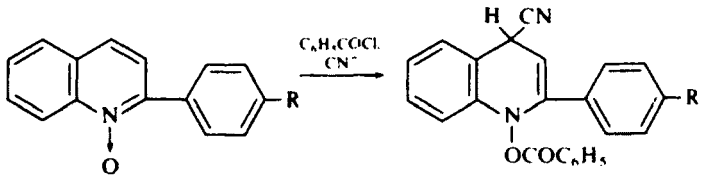
376 377

+



378

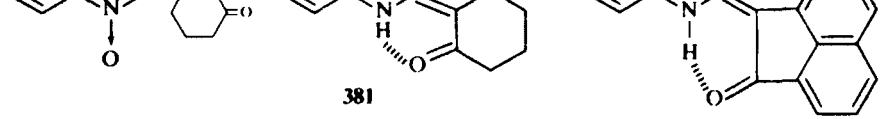
isolated from the corresponding 2-arylquinoline *N*-oxides after treatment with benzoyl chloride and cyanide.[94]



[with some 3- and 6-benzoyloxyquinolines]

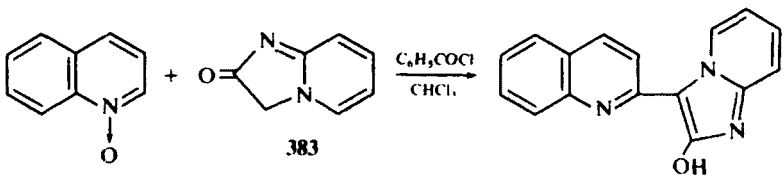
379, R = OCH_3
380, R = NO_2

The reaction of *N*-oxides with acid chlorides or anhydrides and active methylene derivatives, or enamines, can lead to alkylation. Cyclohexanone reacted with quinoline *N*-oxide and benzoyl chloride to give 2-(2-quinolinyl)cyclohexanone (**381**);[566] the more reactive ketone acenaphthenone gave the quinoline (**382**), and the pyridoimidazolone (**383**) gave the compound (**384**).[566]



381

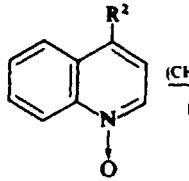
382: 15%



383

384: 65%

The reaction between quinoline *N*-oxide and the oxindoles (**385** and **386**) provided an opportunity for a study of the relative effectiveness of acetic anhydride, benzoyl chloride and *p*-toluenesulphonyl chloride in promoting the condensation.[566,567] Of these three reagents, acetic anhydride was the most and *p*-toluenesulphonyl chloride the least effective,[567] in agreement with the results obtained, using other active methylene compounds.



385, $R^1 = H$
386, $R^1 = CH_3$

387a, $R^1 = R^2 = H$
388a, $R^1 = CH_3$, $R^2 = H$
390a, $R^1 = CH_3$, $R^2 = Cl$

387b, $R^1 = R^2 = H$
388b, $R^1 = CH_3$, $R^2 = H$
390b, $R^1 = CH_3$, $R^2 = Cl$

387c, $R^1 = R^2 = H$
388c, $R^1 = CH_3$, $R^2 = H$
390c, $R^1 = CH_3$, $R^2 = Cl$

389

391

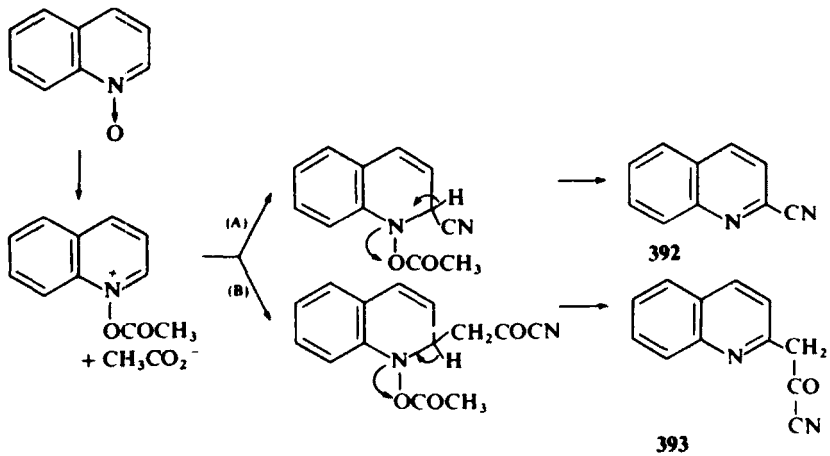
The major product from oxindole (**385**) or the *N*-methyl derivative (**386**) was red, and of the various possible tautomeric forms (**387a–387c**) and (**388a–388c**) the 'exomethylene' tautomers (**387b** and **388b**) seem preferable. The reaction between quinoline *N*-oxide, *N*-methyloxindole (**386**) and acetic anhydride gave a considerable amount of the bis(2-quinolyl)oxindole (**389**); such a product was not observed when

benzoyl chloride was used. A similar reaction took place with 4-chloroquinoline *N*-oxide, benzoyl chloride and *N*-methyloxindole to give compound (**390**), but 2-chloroquinoline failed to react when benzoyl chloride was used as acylating agent. These results are summarized in Table 21. A small yield of the 4-substituted 2-chloroquinoline (**391**) was

TABLE 21. Condensation Products from *N*-Oxides and Oxindoles

Substituent in *N*-oxide	Substituent in oxindole	Reagent	Temperature (°C)	Product(s) and yield(s) (%)
None	H	C_6H_5COCl	Boiling $CHCl_3$	(**386**), 60
None	CH_3	$(CH_3CO)_2O$	75–80	(**387**), 60; (**388**), 28
None	CH_3	C_6H_5COCl	Boiling $CHCl_3$	(**387**), 63
None	CH_3	p-$CH_3C_6H_4SO_2Cl$	Boiling $CHCl_3$	Carbostyril, 63
4-Chloro	CH_3	C_6H_5COCl	Boiling $CHCl_3$	(**389**), 65

obtained on using acetic anhydride. Another condensation for which the conditions have been thoroughly studied was that between quinoline *N*-oxide and pyruvonitrile, which gave 2-cyanoquinoline (**392**) and 2-quinolylpyruvonitrile (**393**).[568] Acetic anhydride was

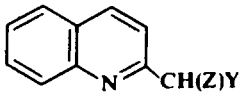


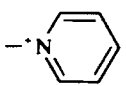
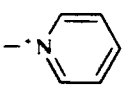
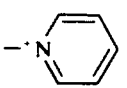
used as the acylating agent and the yield of compound (**392**) could be maximized (36%, with 33% of unreacted *N*-oxide) in neat acetic anhydride, whereas compound (**393**) was obtained (55%) in dioxan as solvent. It was suggested that the pyruvonitrile could ionize to give cyanide ions or pyruvonitrile anions, giving the two products

$$(CH_3CO)_2O + CN^- \xrightarrow[(A)]{} CH_3CO_2^- + CH_3COCN \longrightarrow CH_3CO_2H + {}^-CH_2COCN \quad (B)$$

A wide range of products has been obtained from quinoline *N*-oxides and compounds containing active methylene groups. These are listed in Table 22; most reactions go best using acetic anhydride as solvent and acylating agent. The range of substituents X and Y in the active methylene component is large and the high colour of the products suggests that they should be formulated as shown in (**394**), although no stereoisomers have been reported.

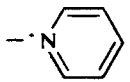
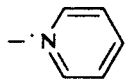
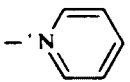
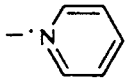
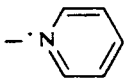
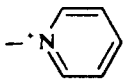
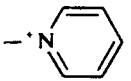
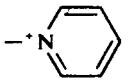
TABLE 22. Compounds Formed from *N*-Oxides and Active Methylene Derivatives, $CH_2(X)Y$



Substituent in *N*-oxides	X	Y	Z[a]	Acylating agents[b] and temperature (°C)	Yield (%)	References
None	$COCH_3$	$COCH_3$	—	AA	68	569
None	$COCH_2C(CH_3)_2CH_2CO$		—	AA	52	569
None	COC_6H_4CO-*o*		—	AA, room	73	570, 571
None	Acenaphthen		—	BzCl, $CHCl_3$, boil	15	566
None	CO_2CH_3	CN	—	AA, 35–40	78	39
None	$CO_2C_2H_5$	CN	—	AA, 30–40	88	570
None	$CO_2C_2H_5$	CN	—	BzCl, dioxan, 30–40	<20	570
None	CO_2Bu^t	CN	—	AA, 35–40	65	39
None	$CONH_2$	CN	—	AA, room	90	39, 864
None	CN	CN	—	AA	70–80	571
None	$CO_2C_2H_5$	$COCH_3$	—	AA, 35–40	86	39, 571
None	$CO_2C_2H_5$	COC_6H_5	—	AA, 40	—	571
None	COC_6H_5		—	AA, CH_3CN, boil	76	572
None	COC_6H_5		—	BzCl, then AA	73	572
None	$COCH_3$		—	AA, CH_3CN, boil	85	572

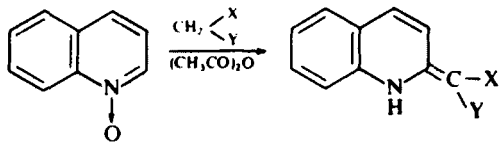
[a] If different from X.
[b] AA = acetic anhydride; BzCl = benzoyl chloride.

TABLE 22 (*cont.*)

Substituent in *N*-oxide	X	Y	Z[a]	Acylating agent[b] and temperature (°C)	Yield (%)	Refs.
None	COC_6H_4Cl-*p*		—	AA, CH_3CN, boil	93	572
None	COC_6H_4Br-*p*		—	AA, CH_3CN, boil	81	572
None	$COC_6H_4CH_3$-*p*		—	AA, CH_3CN, boil	62	572
None	$COC_6H_4OCH_3$-*p*		—	AA, CH_3CN, boil	57	572
None	$COC_6H_4NO_2$-*p*		—	AA, CH_3CN, boil	71	572
None	CO-thienyl-2		—	AA, CH_3CN, boil	78	572
None	CO-furyl-2		—	AA, CH_3CN, boil	83	572
None	$COC_{10}H_7(\alpha)$		—	AA, CH_3CN, boil	76	572

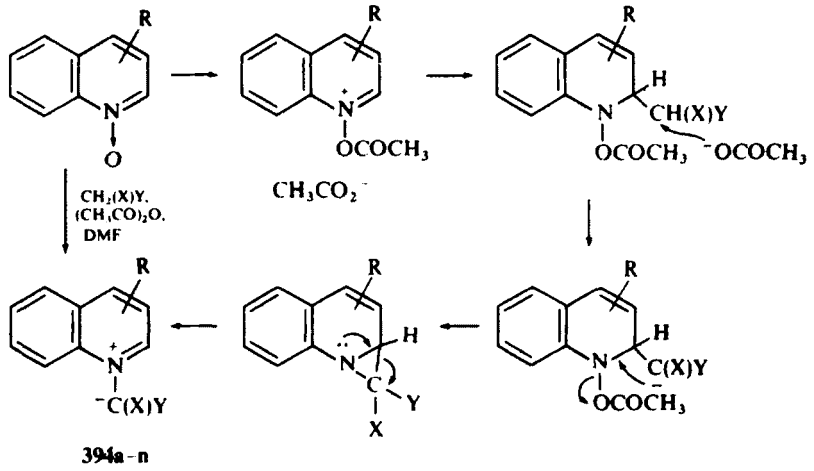
None	$COC_{10}H_7(\beta)$		—	AA, CH_3CN, boil	73	572
None	CO_2Et	NO_2	—	AA, 40	58	570
None		$COON{=}C(CH_3)$	—	AA, $CHCl_3$, room	44	865
None		$CONHC_6H_4$-*o*[c]	—	BzCl, boiling $CHCl_3$	60	567, 566
None		$CON(CH_3)C_6H_4$-*o*[c]	—	AA, 75–80	60[e]	567, 566
None		$CON(CH_3)C_6H_4$-*o*[c]	—	BzCl, $CHCl_3$, boil	63	567, 566
None		$OCOC(CONH_2){=}C(SMe)$	—	AA, ice	60[f]	575
2-CH_3	CN	$CO_2C_2H_5$[d]	—	AA, DMF, ice	49	864
4-CH_3		COC_6H_4CO-*o*	—	AA, 40	55	570
4-CH_3	$CO_2C_2H_5$	CN	—	AA, 40	40	570
4-Cl	CN	$CO_2C_2H_5$	—	AA, DMF, ice	59	864
4-Cl		$CON(CH_3)C_6H_4$-*o*[c]	—	BzCl, $CHCl_3$, boil	65	567
4-OH	CN	$CO_2C_2H_5$	—	AA, DMF, ice	84	864
4-OH	CN	CN	—	AA, DMF, ice	77	864
4-CH_3O	$COCH_3$		—	AA, CH_3CN, $NaClO_4$	66	574
4-CH_3O	COC_6H_5		—	AA, CH_3CN, $NaClO_4$	55	574
4-CH_3O	$COC_6H_4CH_3$-*p*		—	AA, CH_3CN, $NaClO_4$	61	574
8-OH		$COC_6H_4CO(o)$	—	AA	62	573
5,7-Cl_2-8-OH		$COC_6H_4CO(o)$	—	AA	62	573
	Reactions with trisubstituted methanes, CH(X)(Y)Z					
None	NO_2	$CO_2C_2H_5$	$CO_2C_2H_5$	AA, 30–40	63	570
None	$CO_2C_2H_5$	$COCH_2CH_2CH_2$		AA, room	87	39
None	CO_2Bu^t	$COCH_2CH_2CH_2$		AA, room	69	39
None	CN	$COCH_2CH_2CH_2$		AA, ice, then room	68	39

[a] If different from X.
[b] AA = acetic anhydride; BzCl = benzoyl chloride.
[c] Oxindole and *N*-methyloxindole.
[d] 4-Substituted product.
[e] With 28% of bis(2-quinolyl) derivative.[567]
[f] Bis-(2-quinolyl) derivative.



394

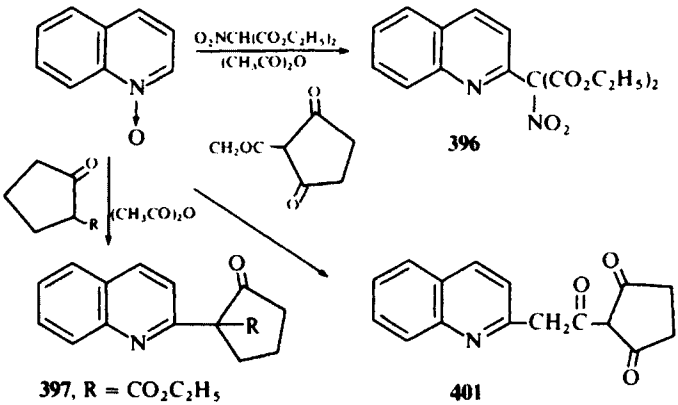
The major product can be a quinolinium methylide when acetic anhydride is used as the acylating agent and the solvent is DMF or DMSO.[864] Such compounds (**394a–394n**) have been obtained from quinoline *N*-oxide and methyl or ethyl cyanoacetate, malonitrile or benzoylacetonitrile; lepidine *N*-oxide, 4-methoxyquinoline *N*-oxide, and 4-aminoquinoline *N*-oxide were also used. From 4-hydroxyquinoline *N*-oxide and 4-chloroquinoline *N*-oxide good yields of the 2-substituted quinolines were obtained (see Table 21) but no ylides were isolated. Quinaldine *N*-oxide likewise gave only 4-substituted products.



394a–n

	R	X	Y	%
394a	H	CN	CO_2CH_3	16.8
394b	H	CN	$CO_2C_2H_5$	53.6
394c	H	CN	CN	11.6
394d	H	CN	COC_6H_5	61
394e	4-CH_3	CN	$CO_2C_2H_5$	24.5
394f	4-CH_3	CN	COC_6H_5	66
394g	4-CH_3	CN	CN	11.6
394h	4-CH_3O	CN	$CO_2C_2H_5$	39
394j	4-CH_3O	CN	CN	43.2
394k	4-CH_3O	CN	COC_6H_5	16.4
394l	4-NH_2	CN	$CO_2C_2H_5$	90
394m	4-NH_2	CN	CN	35.9
394n	4-NH_2	CN	COC_6H_5	82.3

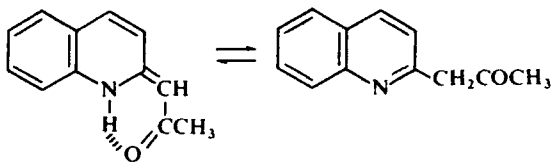
Hamana and Yamazaki[570] reported that diethyl malonate gave not the normal adduct of type (**394**), but the bis(2-quinolyl) adduct (**395**). Trisubstituted methanes have been used successfully, as in the synthesis of the nitromalonate (**396**)[570] and the cyclopentyl derivatives (**397–399**).[39] Hamana and Yamazaki were unable to obtain reaction between quinoline *N*-oxide and acetone, acetophenone or phenylacetonitrile in the presence of acetic anhydride[570] although, as mentioned previously, cyclohexanone reacted with quinoline *N*-oxide and benzoyl chloride.[566] In this context a surprising discovery was that 2-acetylcyclopentan-1,3-dione reacted via the anion from the methyl group, and not via the far more acidic anion (**400**), giving a high yield of compound (**401**).[39] Acetylacetone gave 2-quinolylacetone (**402**), with the loss of one acetyl group; the proportions of the tautomers (**402a** and **402b**) were as shown.[569]



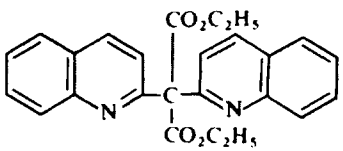
396

397, R = $CO_2C_2H_5$
398, R = $CO_2C_4H_9$-*t*
399, R = CN

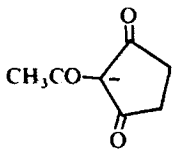
401



402a 73 : 27 **402b**

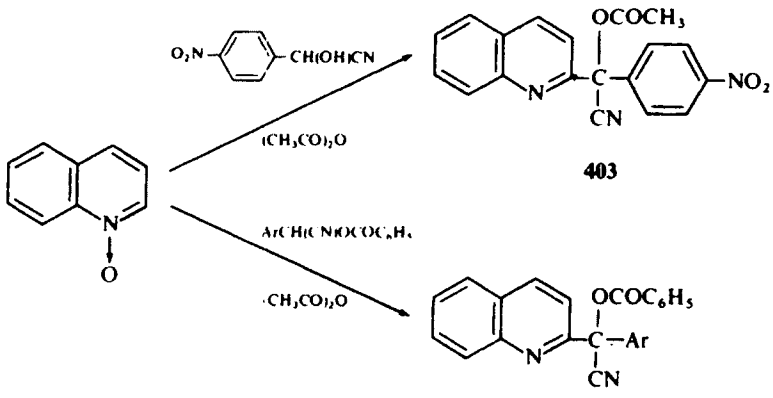


395



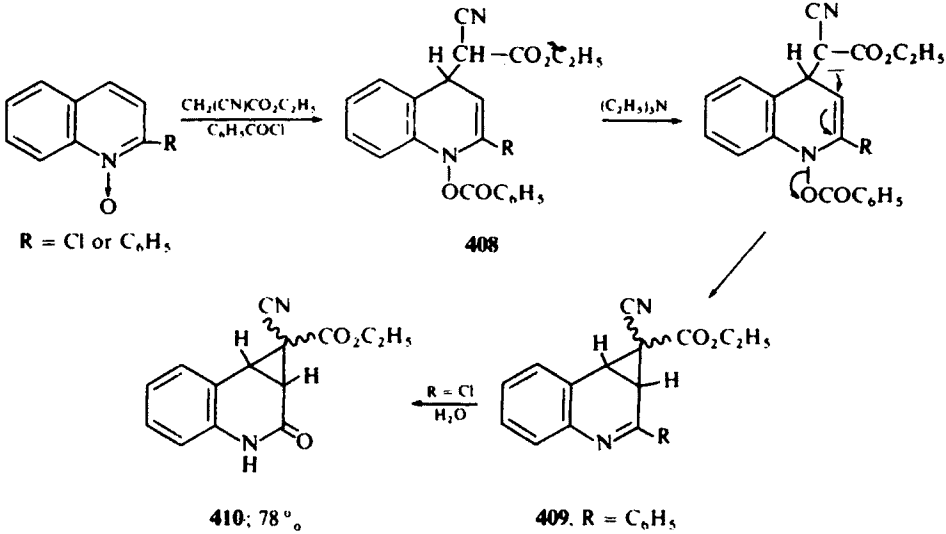
400

An example of 'umpolung' is provided by the reaction between quinoline *N*-oxide and the cyanohydrins of an aromatic aldehyde, under the influence of acetic anhydride.[576] The product was the acetoxycyanomethyl derivative (**403**). Better yields were achieved by using the cyanohydrin benzoates, and compounds (**404–407**) were thus obtained.

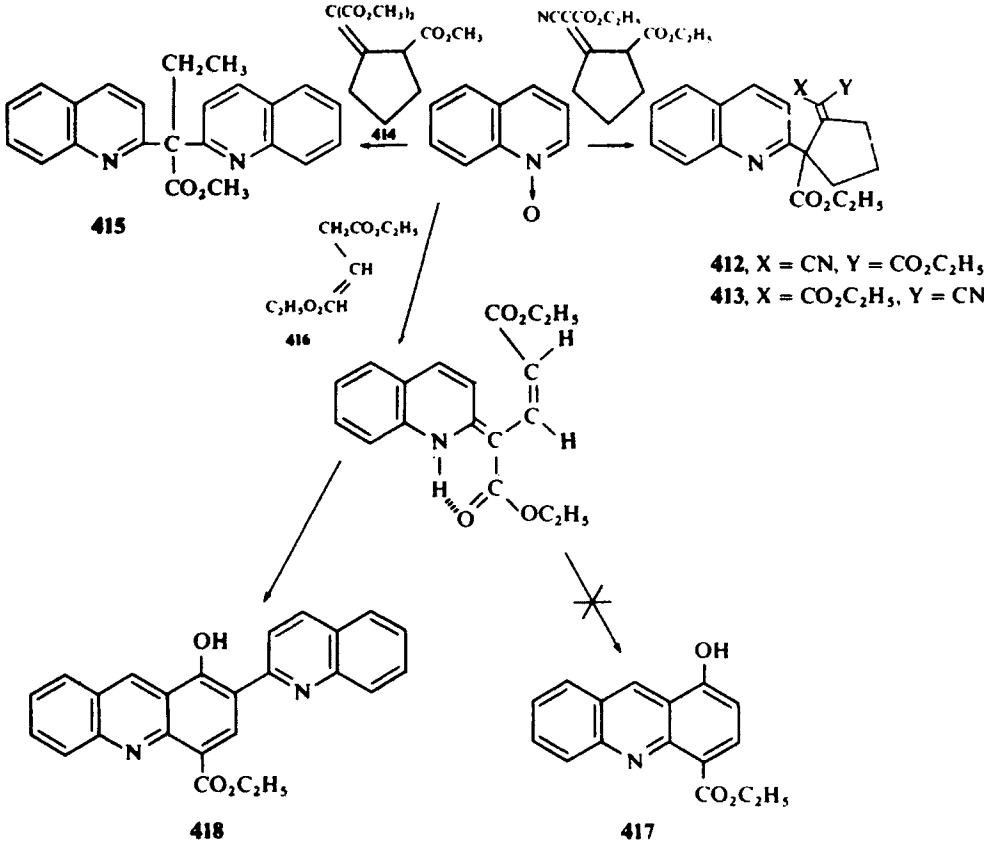


404, Ar = *p*-$O_2NC_6H_4$; 75%
405, Ar = *o*-$O_2NC_6H_4$; 11.4%
406, Ar = *p*-$HO_2CC_6H_4$; 44%
407, Ar = 2-pyridyl; 74%

A very unusual type of product has been obtained from 2-chloro- or 2-phenylquinoline *N*-oxides with ethyl cyanoacetate and benzoyl chloride with triethylamine.[13] The initial adduct (**408**) must re-ionize and cyclize to the enamine carbon, giving a cyclopropane (**409** or **410**).



Success with condensation of active methylene compounds led to the use of compounds of general form $XCH_2CH{=}CHY$, with only one satisfactory result, the cyclopentylidenecyanoacetate (**411**) giving the geometric isomers (**412** and **413**).[39] In the case of the cyclopentylidene malonate (**414**), a reverse aldol reaction presumably formed dimethylmalonate, since the product was the bis(2-quinolyl) derivative (**415**).[39] The vinylogous malonate (**416**) gave the quinolylacridine (**418**); this reaction was not thought to go via the acridine (**417**), since quinoline *N*-oxide does not react with phenols.[577]



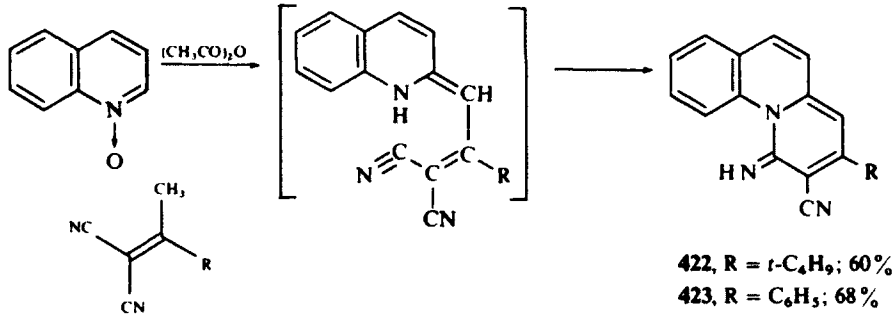
415

412, X = CN, Y = $CO_2C_2H_5$
413, X = $CO_2C_2H_5$, Y = CN

418 **417**

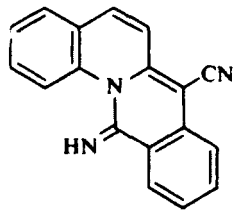
Similarly, the dicyanoethylenes (**419** and **420**) formed the cycloadducts (**422** and **423**), presumably via the general intermediate (**421**).[578] More surprisingly, *o*-cyanobenzyl cyanide gave the tetracycle (**424**).

Gogte *et al.* reported on the reaction between quinoline *N*-oxide or 7-methoxy-4-phenylquinoline *N*-oxide and dimethylsulphoxonium methylide.[579] Without additional



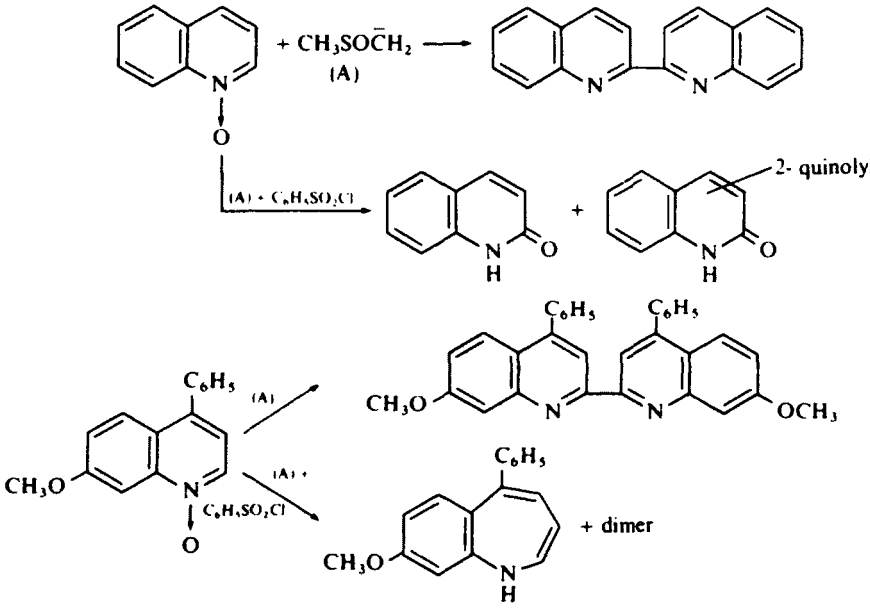
419, R = *t*-C_4H_9
420, R = C_6H_5

422, R = *t*-C_4H_9; 60%
423, R = C_6H_5; 68%



424

reagents the only product in either case was the biquinolyl. With added benzenesulphonyl chloride, however, quinoline *N*-oxide gave 2-quinolone and a quinolylquinolone; the methoxyphenylquinoline *N*-oxide was reported to give the benzazepine (**424a**). This structure seems unlikely in view of the known instability of the 1H tautomer in azepines without a substituent on the nitrogen atom.

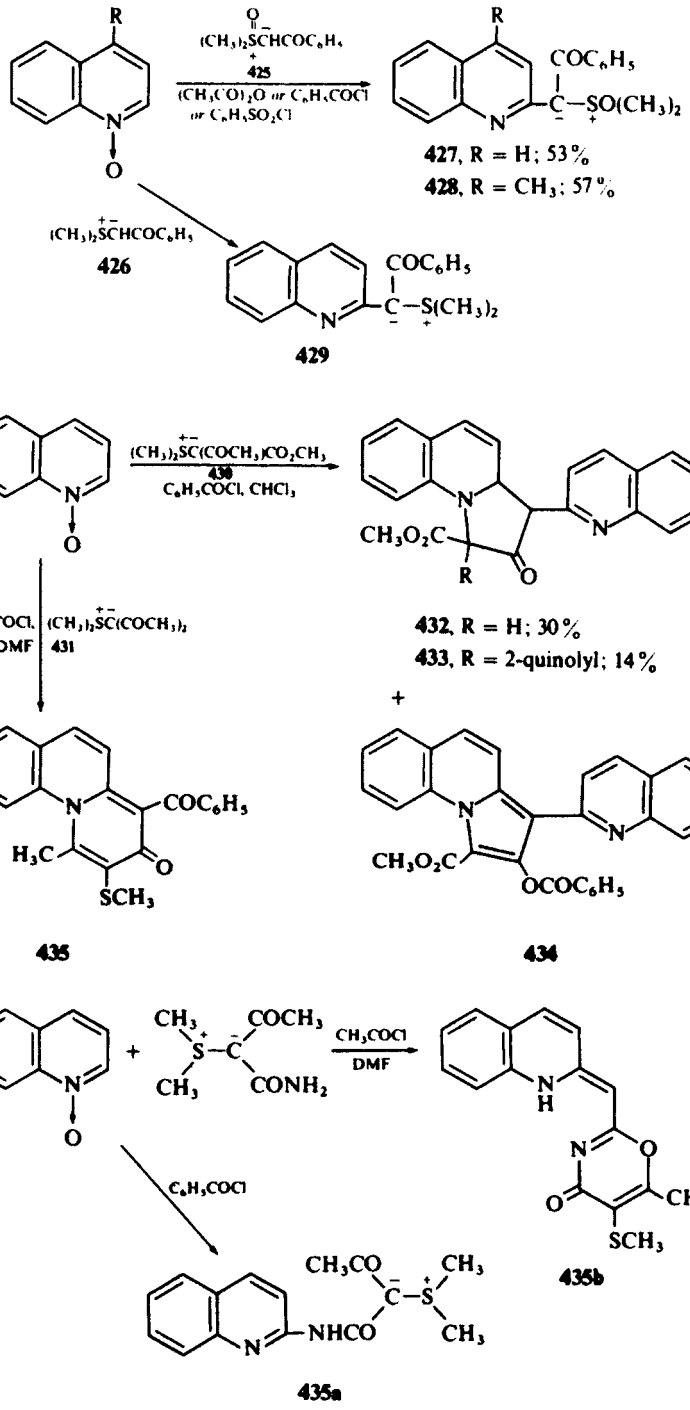


424a

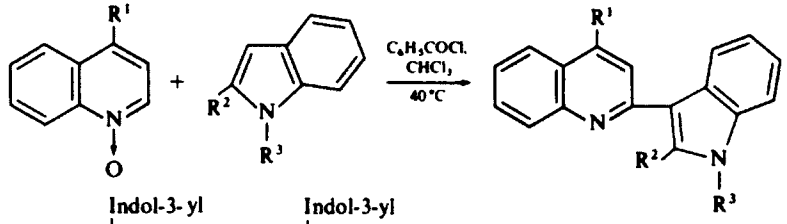
Quinoline *N*-oxide and 4-methylquinoline *N*-oxide reacted with the sulphur ylids (**425** or **426**) and an acylating agent (toluenesulphonyl chloride is best) to give the 2-quinolyl ylids (**427–429**).[580]

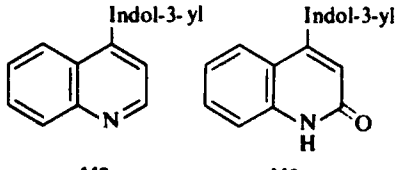
The more stabilized sulphur ylides (**430** and **431**) gave tricyclic products.[581] With the acetoacetate (**430**) two or three molecules of the *N*-oxide were involved, and the pyrroloquinolinones (**432** and **433**) plus a trace of pyrroloquinoline (**434**) were obtained. With the acetylacetone derivative the product was a pyridoquinolinone (**435**). The acetoacetanilide sulphonium ylide gave the quinoline (**435a**) and the oxazine (**435b**).[1400]

The indole β-position is sufficiently strongly nucleophilic to allow the preparation of 3-(2-quinolyl)indoles. Benzoyl chloride was found to be the most generally satisfactory acylating agent; indole, 1-methylindole and 2-phenylindole were used,[582–584] giving


R
O
(CH3)2SCHCOC6H5
425
(CH3CO)2O or C6H5COCl
or C6H5SO2Cl
COC6H5
C—SO(CH3)2
427, R = H; 53%
428, R = CH3; 57%
(CH3)2SCHCOC6H5
426
COC6H5
C—S(CH3)2
429
(CH3)2SC(COCH3)CO2CH3
430
C6H5COCl, CHCl3
CH3O2C
R
O
C6H5COCl, DMF
(CH3)2SC(COCH3)2
431
432, R = H; 30%
433, R = 2-quinolyl; 14%
+
COC6H5
H3C
SCH3
435
CH3O2C
OCOC6H5
434
CH3
S
C
COCH3
CONH2
CH3COCl
DMF
C6H5COCl
NHCO
CH3CO
435a
NH
CH3
SCH3
435b

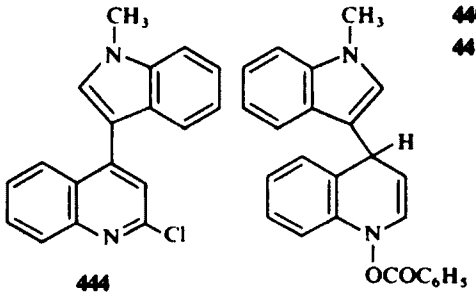
with various quinoline *N*-oxides the quinolylindoles (**436–441**). Small amounts of 3-(4-quinolyl)indole (**442** or 3-(4-carbostyril)indole (**443**) were also isolated.[584] Skatole failed to react;[582–584] 2-chloroquinoline *N*-oxide gave the 3-(4-quinolyl)indole (**444**) and the dihydroquinoline (**445**).[584]





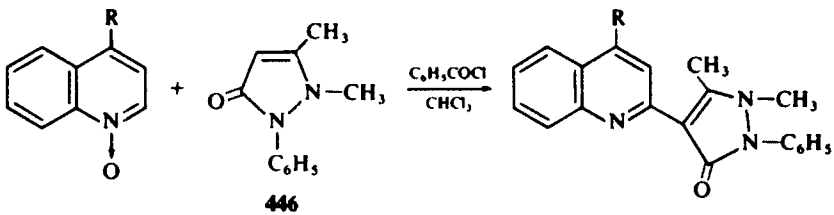
442 **443**

436, $R^1 = R^2 = R^3 = H$; 67%[584]
437, $R^1 = R^2 = H$, $R^3 = CH_3$; 56%[584]
438, $R^1 = Cl$, $R^2 = H$, $R^3 = CH_3$; 54%[584]
439, $R^1 = CH_3$, $R^2 = R^3 = H$; 27%[582,583]
440, $R^1 = R^3 = H$, $R^2 = C_6H_5$; 40%[584]
441, $R^1 = H$, $R^2 = C_6H_5$, $R^3 = CH_3$; 18%[582,583]



444 **445**

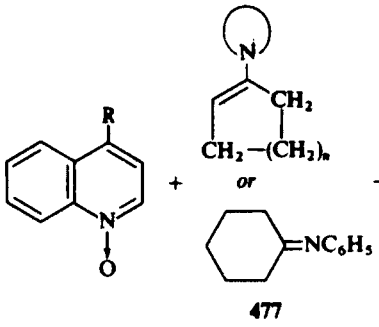
Indoles and pyrazolones can be regarded as enamines, as also can dimethylaminobenzene. Pyrazolones, notably antipyrine (**446**), react with quinoline *N*-oxides to give 4-(2-quinolyl)antipyrines.[582,585] Yields of compounds (**447** and **448**) are satisfactory only when benzoyl chloride is used;[585] with toluenesulphonyl chloride a mixture of 4-chloroquinoline and carbostyril was obtained. Dimethylaniline with quinoline *N*-oxide and benzoyl chloride gave 2-(*p*-dimethylaminophenyl)quinoline in 58% yield.[586]



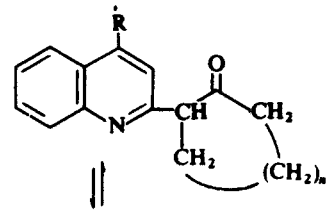
446

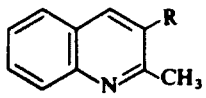
447, R = H; 63%
448, R = Cl; 88%

Hamana and Noda reported the reaction between quinoline *N*-oxide and enamines of cyclohexanone (reactivity: morpholine > piperidine > pyrrolidine) using various acylating agents, of which benzoyl chloride was marginally the best.[587] A more detailed study[38] of this reaction showed that the best yield of 2-(2-quinolyl)cyclohexanone (**449**)

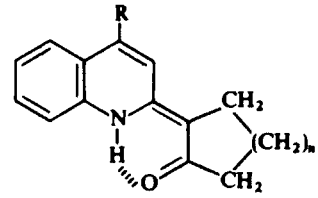


477

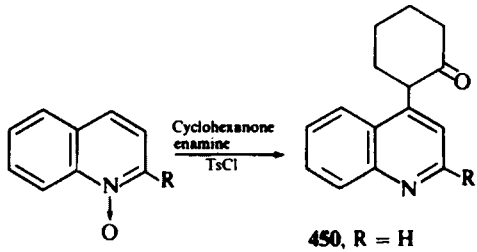




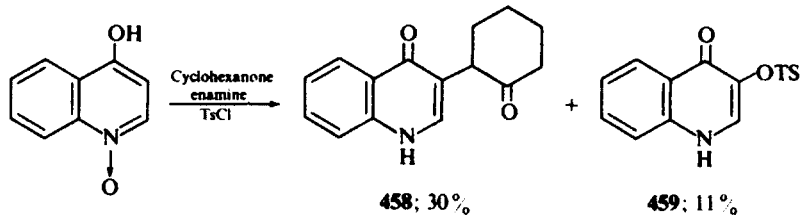
454, R = Cl; 2%
455, R = TsO; 47%



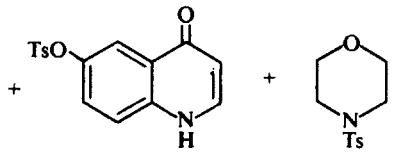
449, R = H, n = 2; 73% [from (**477**), 40%]
451, R = H, n = 1; 80%
452, R = CH_3, n = 2; 79%
456, R = Cl, n = 2; 78%



450, R = H
453, R = CH_3; 37%
454, R = Cl



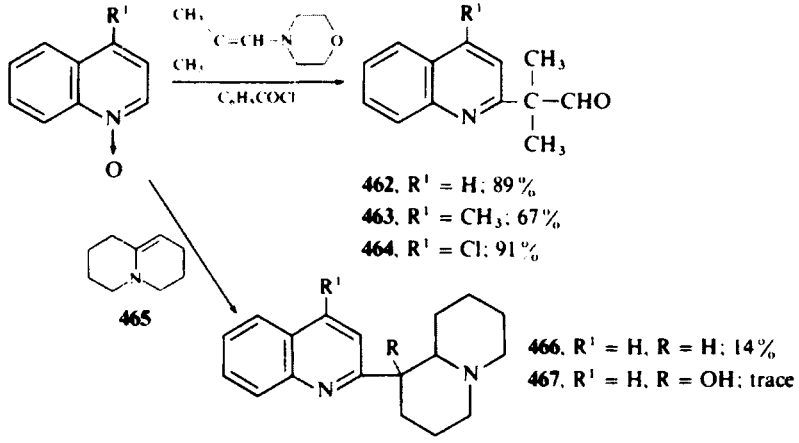
458; 30%
459; 11%

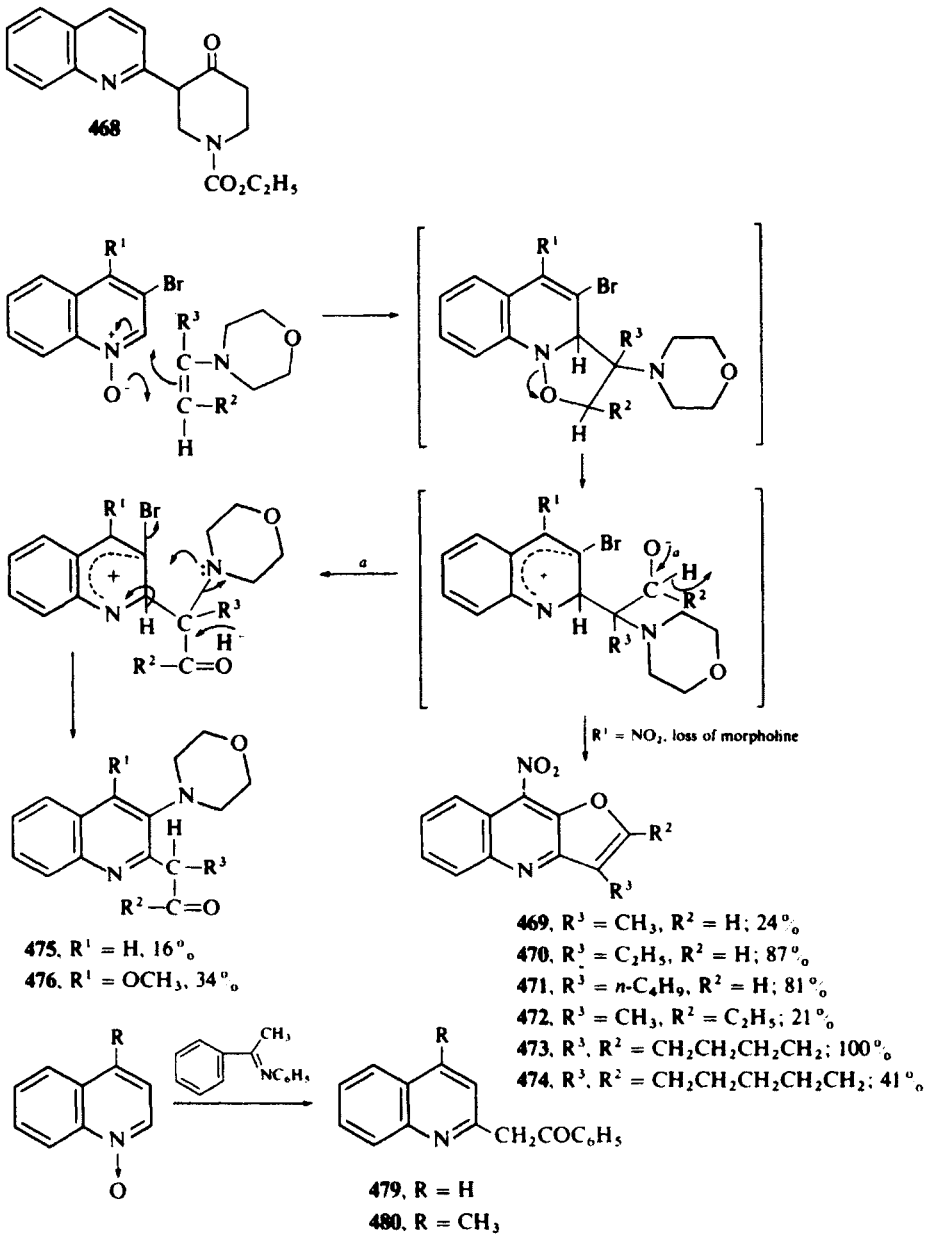


460; 13%
461; 10%

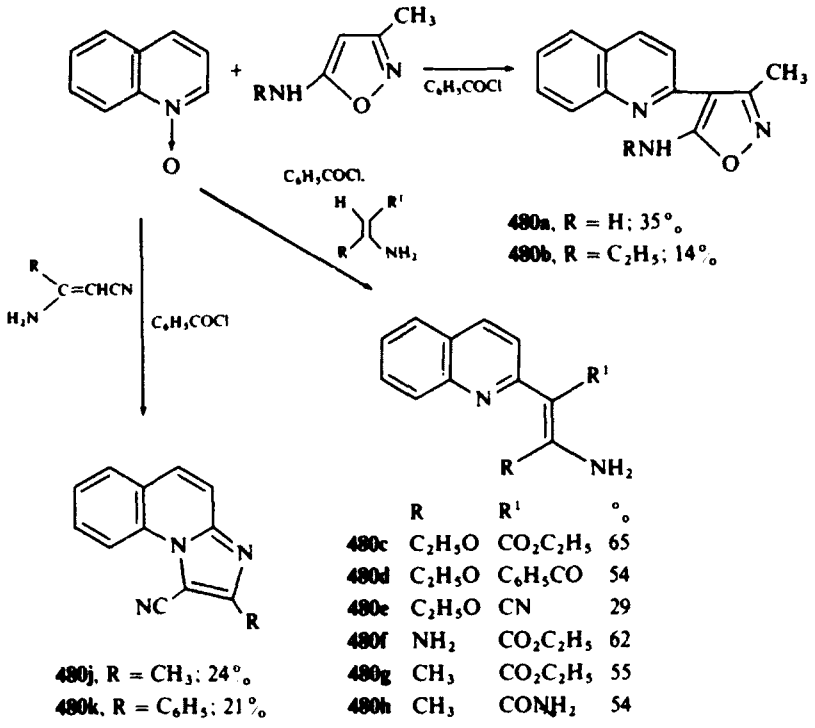
was obtained with a ratio of *N*-oxide, benzoyl chloride and enamine of 1 : 1 : 2. As in most alkylation reactions, traces of the product of reaction at position 4, in this case 2-(4-quinolyl)cyclohexanone (**450**), were obtained. A similar reaction using the morpholine enamine of cyclopentanone gave 2-(2-quinolyl)cyclopentanone (**451**) in 82% yield.[39] Surprisingly, *p*-toluenesulphonyl chloride proved better than benzoyl chloride when 4-methylquinoline *N*-oxide was reacted with cyclohexanone enamines to give the ketone (**452**); 2-methylquinoline *N*-oxide gave a mixture of 2-(2-methyl-4-quinolinyl)-cyclohexanone (**453**) and its *p*-toluenesulphonate, a small amount of 3-chloro-2-methylquinoline (**454**) and a substantial amount of 2-methyl-3-toluenesulphonyl-oxyquinoline (**455**).[164] Such 3-substituted quinolines are common by-products in reactions using toluenesulphonyl chloride. Very similar results were achieved from 4-chloroquinoline *N*-oxide [product (**456**)] and 2-chloroquinoline *N*-oxide [product (**457**)];[588] 4-hydroxyquinoline *N*-oxide, however, gave mainly the 3-quinolyl-cyclohexanone (**458**) with smaller amounts of compounds (**459**–**461**).[588] Hamana and co-workers have also achieved condensation between quinoline *N*-oxides and the morpholine enamine of isobutyraldehyde giving quinolylisobutyraldehydes (**462**–**464**) (using benzoyl chloride),[589] and with the hexahydroquinolizine (**465**), giving a small yield (after borohydride reduction) of the quinolylquinolizidines (**466** and **467**).[590] The synthesis of a number of 3-(2-quinolyl)-4-piperidones, such as compound (**468**), has been reported in a Japanese patent.[591] Abnormal reaction was observed when 3-bromo-4-nitroquinoline *N*-oxide was treated with morpholine enamines. Initial dipolar addition was followed by displacement of the bromine atom from position 3, giving furo-quinolines (**469**–**474**).[592] The mechanism shown was supported by the isolation of the 3-morpholino-2-(2-cyclohexanonyl)quinolines (**475**) and (**476**) in 16% and 34% yields, respectively, when 3-bromoquinoline *N*-oxide or 3-bromo-4-methoxyquinoline *N*-oxide was used. Bruni and Strocchi have used the anils of cyclohexanone and of acetophenone, (**477**) and (**478**), to react with quinoline and 4-methylquinoline *N*-oxides, with benzoyl chloride as acylating agent, to give the quinolyl acetophenones (**479**) and (**480**) and the quinolyl cyclohexanones (**449**) and (**452**).[593] Imines and azines of the ketones were also used.

Other compounds that reacted like enamines were the 2-aminoisoxazoles, which gave 2-substituted quinolines (**480a**) and (**480b**) from quinoline *N*-oxide and benzoyl chloride.[865] The isoxazoles could be hydrogenolysed to give 2-quinolylacetamides. A range of primary enamines have also been used to provide 2-quinolylacetamidates



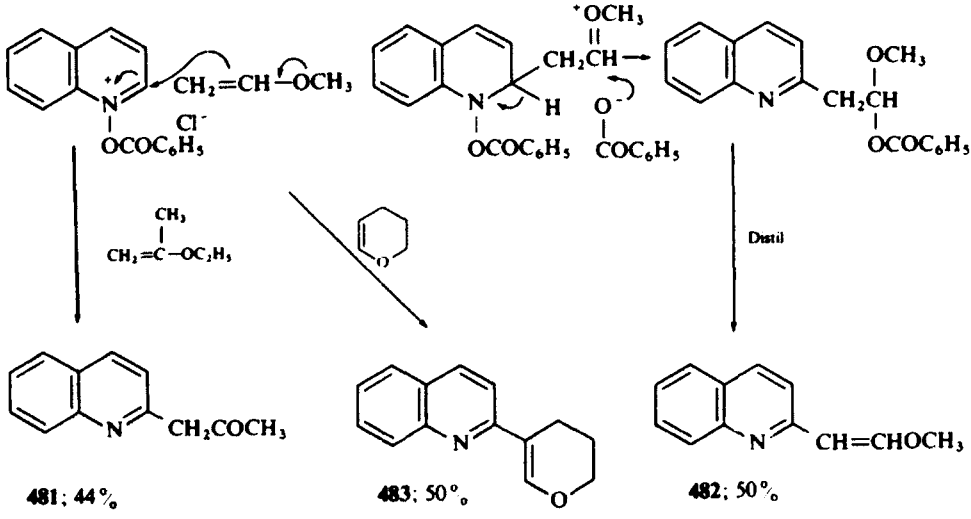


(**480c–e**) and ethyl 2-(2-diaminomethylene)quinolyl acetate (**480f**).[866] While ethyl β-aminocrotonate and β-aminocrotonamide behaved similarly, giving the unsaturated amines (**480g**) and (**480h**), 3-aminocrotononitrile and 3-aminocinnamonitrile gave as major products, with quinoline *N*-oxide and benzoyl chloride, the imidazoles (**480j**) and (**480k**).[867]



	R	R^1	%
480c	C_2H_5O	$CO_2C_2H_5$	65
480d	C_2H_5O	C_6H_5CO	54
480e	C_2H_5O	CN	29
480f	NH_2	$CO_2C_2H_5$	62
480g	CH_3	$CO_2C_2H_5$	55
480h	CH_3	$CONH_2$	54

Vinyl ethers react with *N*-oxides under acylation conditions to provide another route to α-(2-quinolyl) ketones.[594] By direct reaction, with hydrolytic work-up, the cyclohexanones (**449**) and (**456**) were obtained in 58 and 73% yields, respectively, and 2-quinolylacetone (**481**). By prior preparation of the *N*-benzoylquinolinium chloride, and then treating it with methyl vinyl ether and *p*-toluenesulphonic acid in chloroform, a



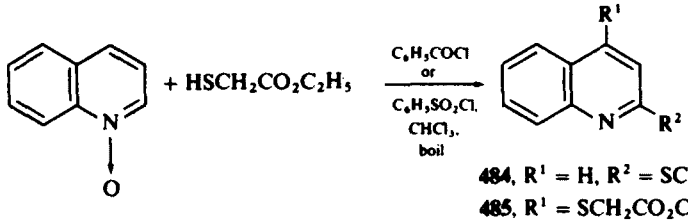
481; 44%

483; 50%

482; 50%

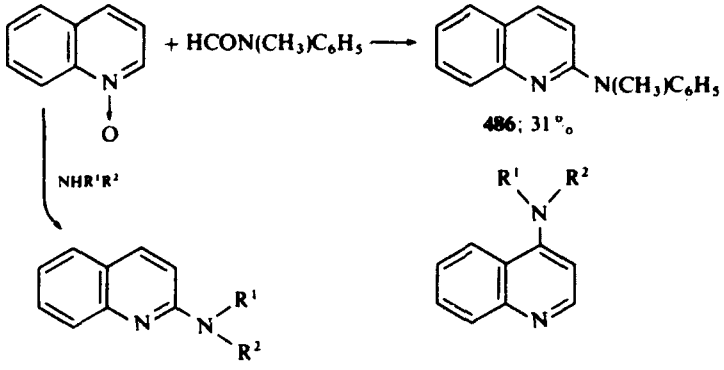
mixture of methyl benzoate and the quinolyl vinyl ether (**482**) was obtained; dihydropyran gave 3-(2-quinolyl)dihydropyran (**483**). Furan, quinoline *N*-oxide and benzoyl chloride gave only carbostyril (94%) after 4 days at room temperature; thiophen and anisole failed to react. The proposed mechanism is shown above.

There are a few examples of attack on *N*-oxides by sulphur or nitrogen nucleophiles under acylating conditions; others which involve transfer from the oxygen are dealt with among 1,3-dipolar additions (p. 519). Quinoline *N*-oxide, ethyl thioglycolate and benzoyl chloride gave a 55 : 45 mixture of 2-quinolyl- (**484**) and 4-quinolylthioglycolate (**485**).[595] When benzenesulphonyl chloride was used only compound (**484**) was obtained.



484, $R^1 = H$, $R^2 = SCH_2CO_2C_2H_5$
485, $R^1 = SCH_2CO_2C_2H_5$; $R^2 = H$
Total yield = 46%

Quinoline *N*-oxide has been reported to react with *N*-methylformanilide, oluenesulphonyl chloride and boron trifluoride to give a mixture of amines (**486**) and (**487**).[596] Later workers claimed reaction with ammonia,[586, 597, 598] ammonium chloride,[597, 598] acid amides[451, 597–599] or aromatic and aliphatic amines[586] to give compounds of general formula (**488**);[597, 598] in the case of aniline[586] and dimethylformamide[451, 599] 4-anilinoquinoline (**489**) and 4-dimethylaminoquinoline (**490**) were also formed.



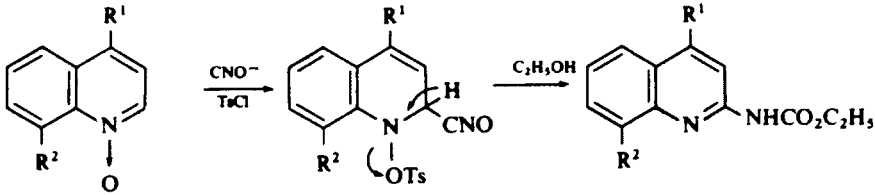
486; 31%

488, $R^1 = H$, $R^2 = C_6H_5$; 57%
$R^1 = H$, $R^2 = CH_3$; 12%
$R^1 = R^2 = CH_3$; 30%
$R^1R^2 = CH_2CH_2OCH_2CH_2$; 27%
$R^1 = R^2 = H$; 71%
$R^1 = R^2 = CH_3$; 14%
(All yields from ref. 586)

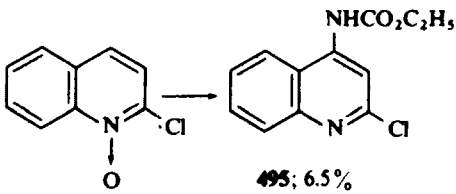
487, $R^1 = CH_3$, $R^2 = C_6H_5$; 20%
489, $R^1 = H$, $R^2 = C_6H_5$
490, $R^1 = R^2 = CH_3$

Quinolyl carbamates have been obtained by two routes. The later published, but mechanistically simpler, route used potassium cyanate and *p*-toluenesulphonyl chloride

in cold ethanol.[600] Thus were obtained the 2-quinolyl carbamates (**491–494**). With boiling ethanol the yield of 2-quinolylcarbamate (**491**) was much decreased, the major products being 2-ethoxyquinoline (54%) and carbostyril (29%), presumably by competitive substitution of the dihydroquinoline intermediate. Less successful reaction was obtained with 4-ethoxyquinoline *N*-oxide (2,4-diethoxyquinoline was formed), and 4-hydroxyquinoline *N*-oxide gave a mixture of 3-, 6- and 8-tosyloxy-4-hydroxyquinolines. No reaction was observed with 4-nitroquinoline *N*-oxide. A very small yield of 2-chloro-4-quinolylcarbamate (**495**) was obtained from 2-chloroquinoline *N*-oxide, but 2-methylquinoline *N*-oxide gave a mixture of 3-ethoxy- and 3-tosyloxy-2-methylquinoline, with very small amounts of 6- and of 8-tosyloxy-2-methylquinolines.



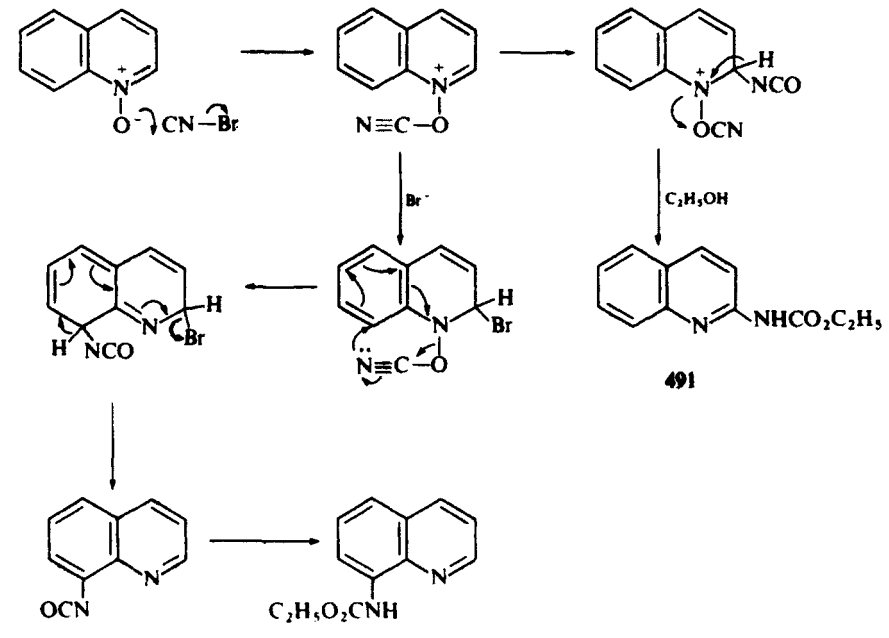
491, $R^1 = R^2 = H$; 70%
492, $R^1 = CH_3$, $R^2 = H$; 39%
493, $R^1 = Cl$, $R^2 = H$; 59%
494, $R^2 = NHCO_2C_2H_5$, $R^1 = H$; 15%



495; 6.5%

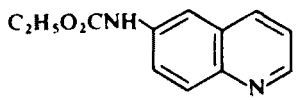
A more complex series of reactions has been observed between cyanogen bromide and quinoline *N*-oxides.[601,45] It seems clear that the cyanogen bromide acts as an electrophile, attacked by the *N*-oxide to give an intermediate of type (**496**). With quinoline *N*-oxide the major carbamate formed was the 8-substituted compound (**497**), with smaller amounts of 2-quinolylcarbamate (**491**) and 6-quinolylcarbamate (**498**), unless potassium cyanate was added, when the 2-substituted derivative predominated, although carbostyril was almost always the product isolated in highest yield.[601] These observations led Hamana and Kumadaki to suggest a number of mechanisms; the most plausible of these, in view of the later work with cyanate,[600] involves an intramolecular attack to give 8-substitution, and a bimolecular reaction to give 2-substitution. Substantial amounts of *N*-(2-quinolyl)carbostyril (**499**) were obtained unless sodium acetate or sodium benzoate was added; the role of the base was thought to be the removal of bromide ion and thus prevention of formation of the dihydroquinoline intermediate (**500**). Variation in the alcohol used as solvent made little difference to the product composition or yield, but the use of solvents other than alcohols gave resins.

In a second paper Hamana and Kumadaki reported the reactions between substituted quinoline *N*-oxides and cyanogen bromide.[45] The results were similar to those obtained with quinoline *N*-oxide itself; *N*-oxides carrying reactive substituents in position 4 (chlorine, bromine, nitro) underwent some substitution at this position to give 4-ethoxyquinolylcarbamates. The major differences were observed with 4-hydroxyquinoline *N*-oxide and 2-aminoquinoline *N*-oxide. In the former case the main product was 4-hydroxy-3-quinolylcarbamate (**501**), and in the latter the product was the oxadiazolo[2,3-*a*]quinoline derivative (**502**), probably formed by intramolecular attack by the amino group on the intermediate *N*-isocyanato compound. Products and yields are summarized in Schemes 14 and 15 (pages 518 and 519).

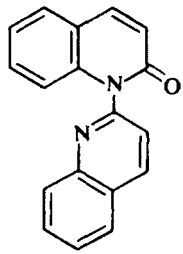


491

497



498



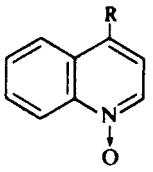
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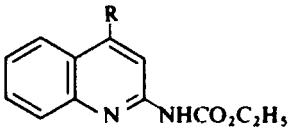
When quinoline *N*-oxides carrying substituents on the benzene ring were reacted with cyanogen bromide the yields of 8-quinolylcarbamates (**503**) and (**504**) were among the best recorded. From the *N*-oxide of 8-quinolylcarbamate only a small yield of 2,8-dicarbamate (**505**) could be obtained; more forcing conditions caused bromination of the *N*-oxide in position 5, with subsequent deoxygenation.

Quinoline *N*-oxides have been shown to react with pyridine in the presence of *p*-toluenesulphonyl chloride to give 2-quinolyl- or 4-quinolylpyridinium salts;[602,562,92] examples are shown in compounds (**506–511**) (p. 520).

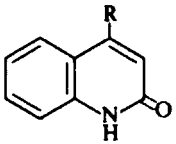
The hydroxyquinoline *N*-oxides were again abnormal; from 2-hydroxyquinoline *N*-oxide, toluenesulphonyl chloride and pyridine the main product was 8-tosyloxycarbostyril (**512**), with some *N*-(6-carbostyryl)pyridinium chloride (**513**),[562] and from 4-hydroxypyridine *N*-oxide the products were 3-tosyloxy-4-quinolone (**514**) and *N*-(4-quinolinon-6-yl)pyridinium perchlorate (**515**).[562]

There are a few cases in which an acid halide with a second reactive centre can first react with the oxygen atom of the *N*-oxide and then intramolecularly substitute position

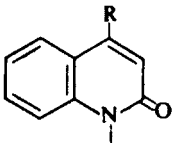
SCHEME 14. Products from 4-Substituted Quinoline *N*-Oxides  and Cyanogen Bromide.

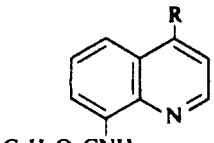


(A)

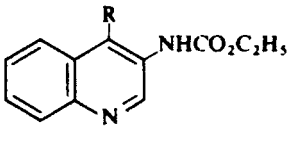


(B)

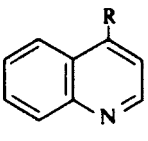




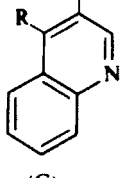
(D)



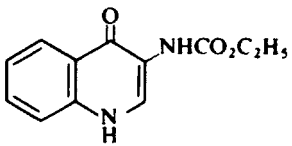
(E)



(F)



(C)



501

R in *N*-oxide	Products (%) (A)	(B)	(C)	(D)	(E)	(F)	(501)
Cl	–	26.7	3.5	10.9	–	10.9	15.8
Br		69.6	3.7	4.1	—	—	4.6
OC_2H_5	11.2	–	5.0	17.2	—	10.5	—
NO_2[a]	—	–	–	—	—	—	3.1
CH_3	7.4	–		9.1[b]	3.0	—	—
OH	–	–	–	21.6[c]	—	—	—
NH_2	–	—	–	36.0	—	—	—

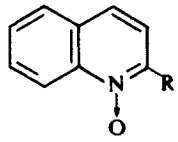
[a]At 90–100 °C; some 4-bromoquinolyl-8-carbamate formed (8.8%).

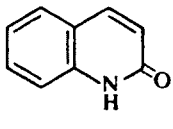
[b]Some 4-Br_2CH-quinolyl-8-carbamate formed (1.5%).

[c]Some 4-hydroxyquinoline-3-carbamate (47.4%) (**501**) and 3-bromo-4-hydroxyquinoline-8-carbamate (3.2%) formed.

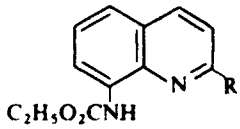
2. Thus *N*-phenylbenzimidoyl chloride reacted with quinoline *N*-oxide in boiling 1,2-dichloromethane to give 2-(*N*-benzoylanilino)quinoline (**516**),[119,603] benzanilide, 2-anilinoquinoline (**517**)[603] and 3-quinolylbenzoate (**518**).[603] Reaction of 2,4-dimethylquinoline under similar conditions gave the *N*-phenylbenzimidate (**519**);[119] the cyclophane (**520**) was chlorinated by *N*-phenylbenzimidoyl chloride, possibly via an anhydro base (**521**).[119] Abramovitch *et al.* suggested that a 1,5-sigmatropic shift could account for the formation of the anilinoquinoline and the 3-quinolylbenzoate; their mechanism is shown in Scheme 16.[603] Similar products were obtained from 4-nitroquinoline *N*-oxide.[603]

A similar reaction has been reported with *NN*-diethylthiocarbamoyl chloride,[604] giving the *S*-(2-quinolyl)thiocarbamate (**522**) and the *O*-(3-quinolyl)thiocarbamate

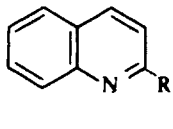
SCHEME 15. Products from 2-Substituted Quinoline *N*-Oxides  and Cyanogen Bromide.



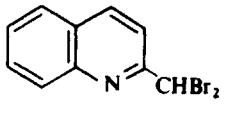
(A)



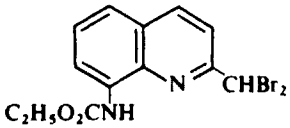
(B)



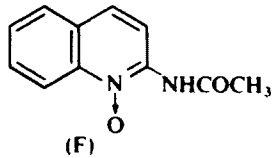
(C)



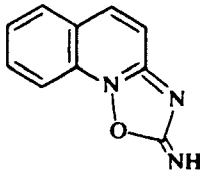
(D)



(E)



(F)



502

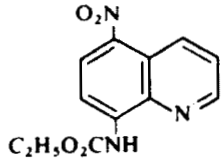
	Products (%)						
R in *N*-oxide	(A)	(B)	(C)	(D)	(E)	(F)	(**502**)
Cl	52	—	—	—	—	—	—
CH_3	—	3.5	12.6	9.6	3.9	—	—
OH	—	39	—	—	—	—	—
NH_2	—	—	—	—	—	19.8[a]	65[b]

[a]With sodium acetate.

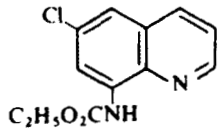
[b]Without sodium acetate.

(**523**). The production of these two products can be rationalized by a mechanism similar to that given in Scheme 16. Addition of triethylamine to the reaction mixture gave the *S*-(3-quinolyl)- (**524**) and *S*-(8-quinolyl)thiocarbamates (**525**); the yield of compound (**525**) was sometimes as high as 27%.

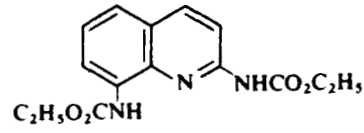
(iv) *Reactions Involving 1,3-Dipolar Additions.* A number of the reactions in Section III.2.D.b(iii) were thought to proceed, at least in part, by formation of a new ring between positions 1 and 2. The simplest reactions where a three-carbon chain is involved are those between *N*-oxides and acrylic acid derivatives,[434,605] or diketene,[489] or



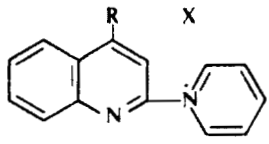
503: 34%



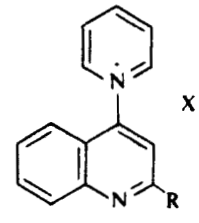
504: 37%



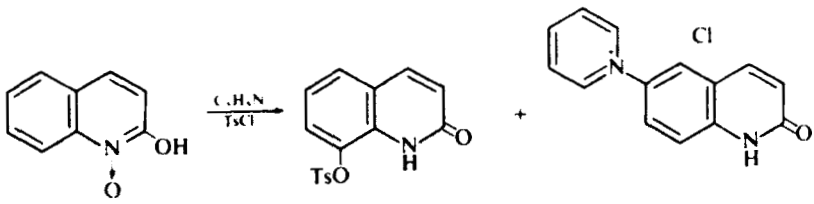
505: 11% maximum



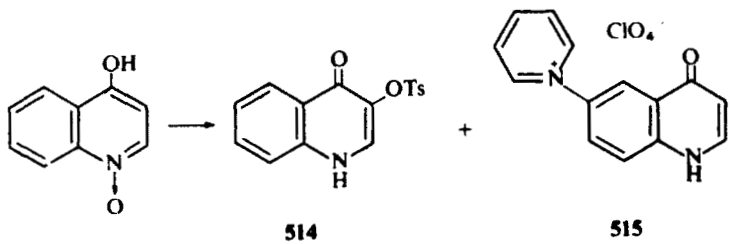
506. R = H, X = ClO_4, picrate[602]
507. R = CH_3, X = ClO_4, picrate[602]
508. R = Cl, X = Cl; 95%[562]
509. R = C_6H_5, X = OTs; 78%[92]



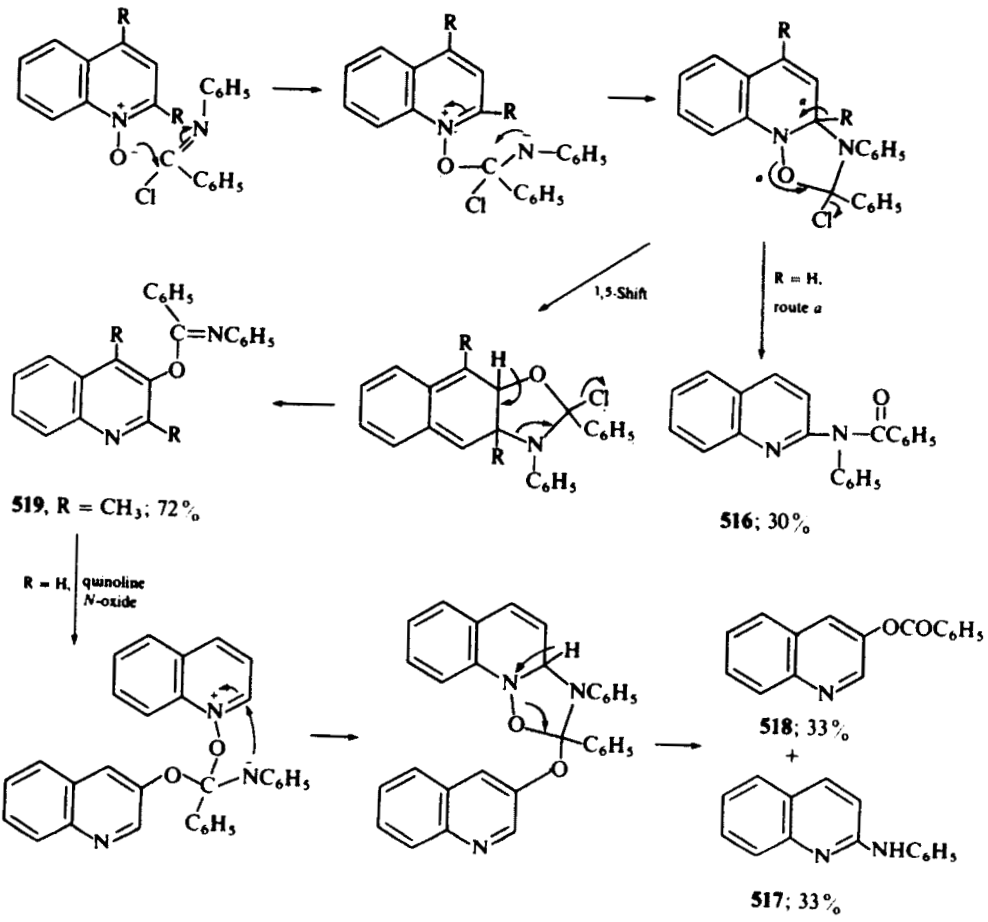
510. R = H, X = ClO_4, picrate[602]
511. R = C_6H_5, X = OTs; 90%[92]



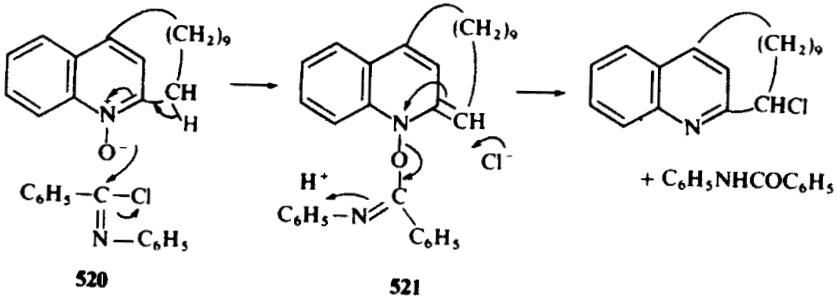
512 **513**

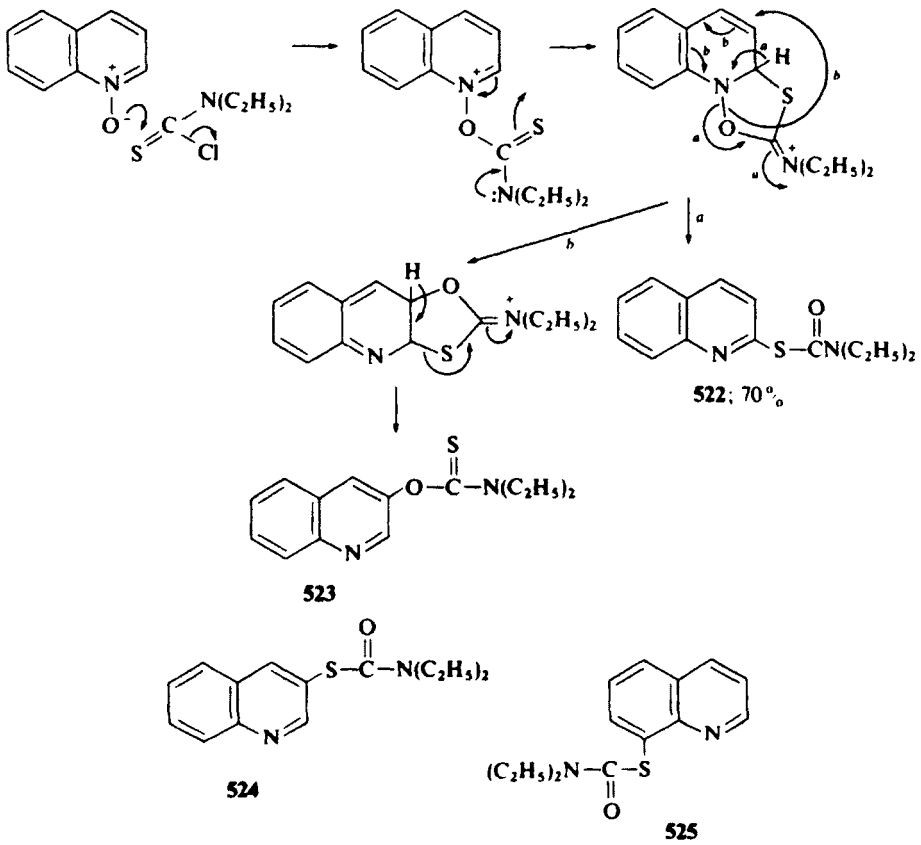


514 **515**


1,5-Shift
R = H, route a
519, R = CH3; 72%
516; 30%
R = H, quinoline N-oxide
518; 33%
+
517; 33%

SCHEME 16


520
521
+ C6H5NHCOC6H5



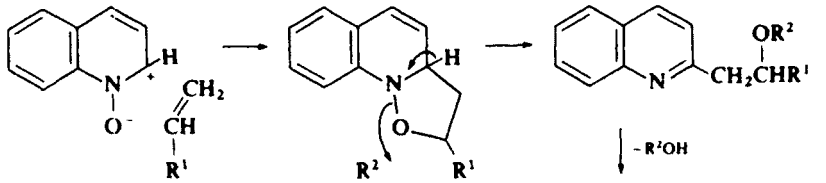
522; 70%

523

524

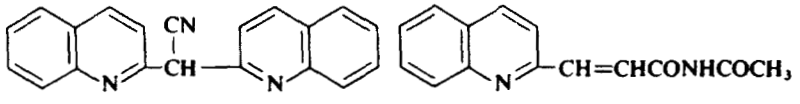
525

acetylenes.[605-609] Although the acrylic acid derivatives reacted in acetic anhydride, Hamana and co-workers regarded the formation of 2-quinolylacrylic acid derivatives (**526**–**528**) as a 1,3-dipolar reaction.[434] Other products obtained were (a) di(2-quinolyl)acetonitrile (**529**) and carbostyril from acrylonitrile and (b) the compound (**529**)



531, $R^1 = CN$
532, $R^1 = CONH_2$
533, $R^1 = CO_2C_2H_5$

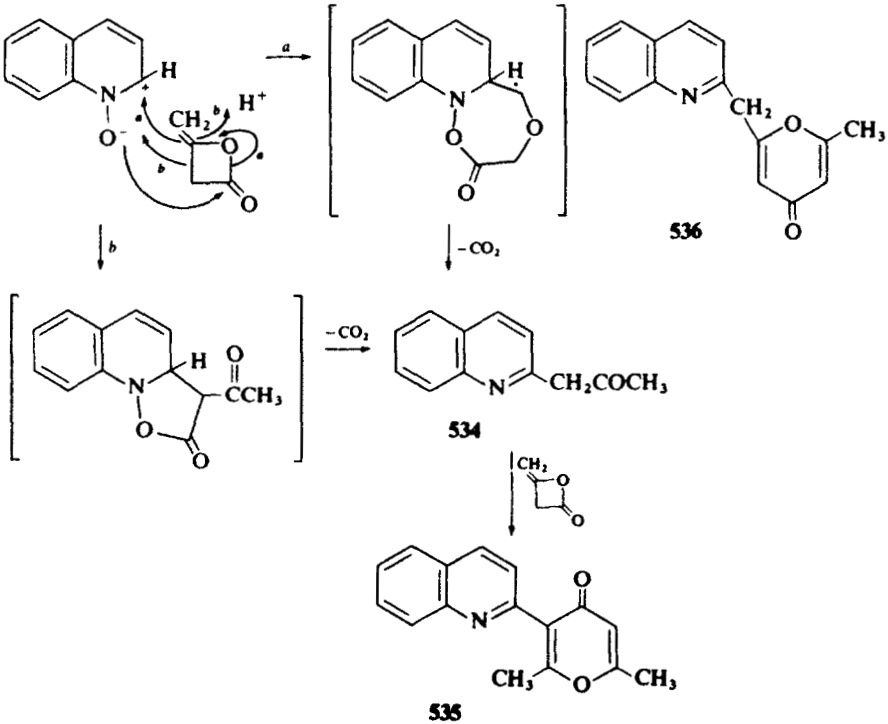
526, $R^1 = CN$; 34%
527, $R^1 = CONH_2$; 12%
528, $R^1 = CO_2C_2H_5$; 5%



529 530

and the *N*-acetyl-β-(2-quinolyl)acrylamide (**530**) from acrylamide. Some reaction occurred between quinoline *N*-oxide and the acrylic acid derivatives in dioxan without acetic anhydride if hydroquinone was added; the most notable feature of these reactions was the isolation of the hydroxypropionic acid derivatives (**531**–**533**), of which the hydroxyamide (**532**) was obtained in 50% yield. Methacrylonitrile gave the methyl derivative of compound (**531**), and 2-quinolylacetone, the latter possibly from the cyanohydrin by loss of hydrogen cyanide.[605]

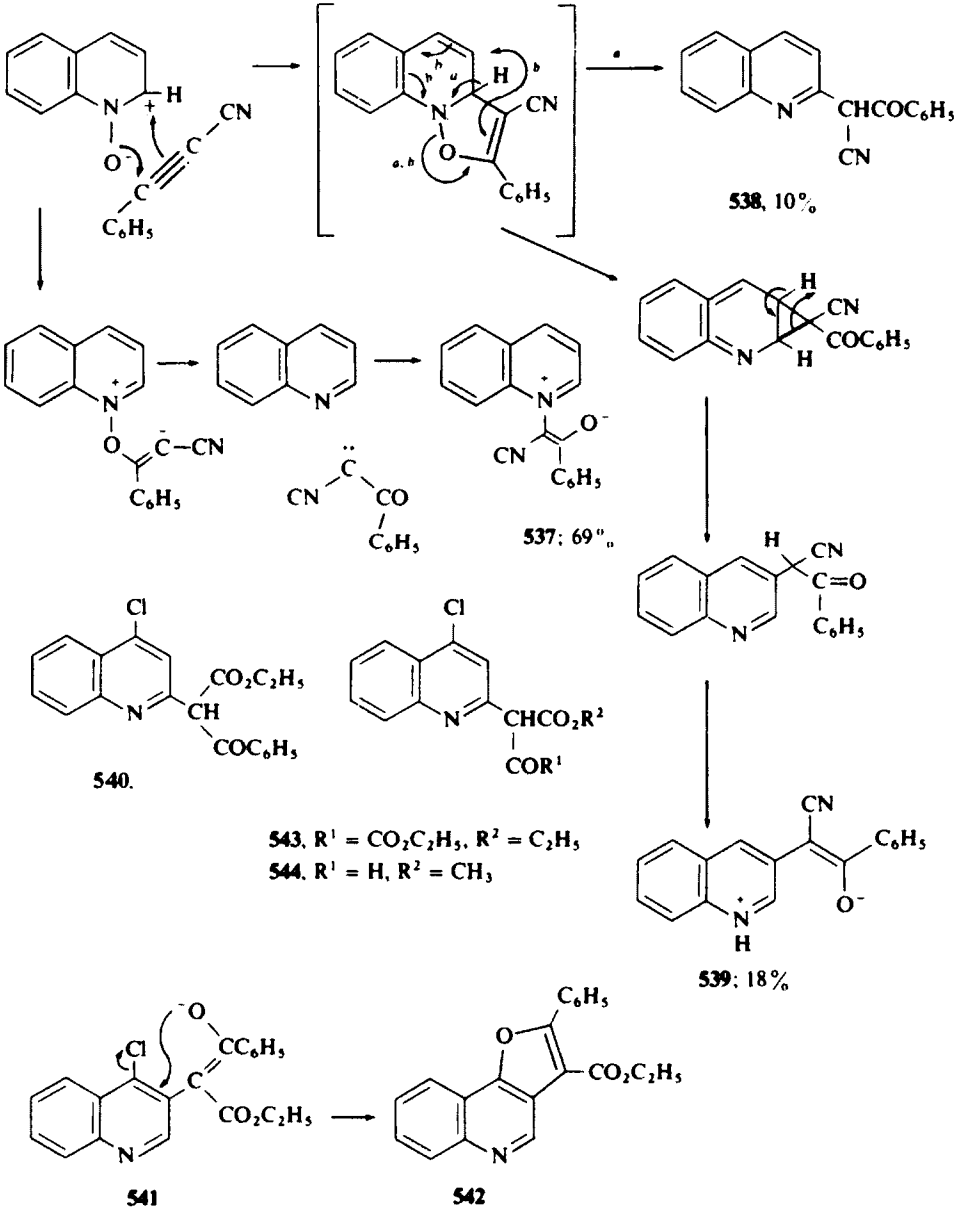
Quinoline *N*-oxide reacted with diketene to give a 2-quinolyl-γ-pyrone (**535**)[489] [incorrectly formulated as (**536**) in an earlier paper[802]]. Two possible mechanisms were advanced; the intermediate (**534**) could be isolated when an excess of quinoline *N*-oxide was used, and then converted into compound (**535**) by further diketene.



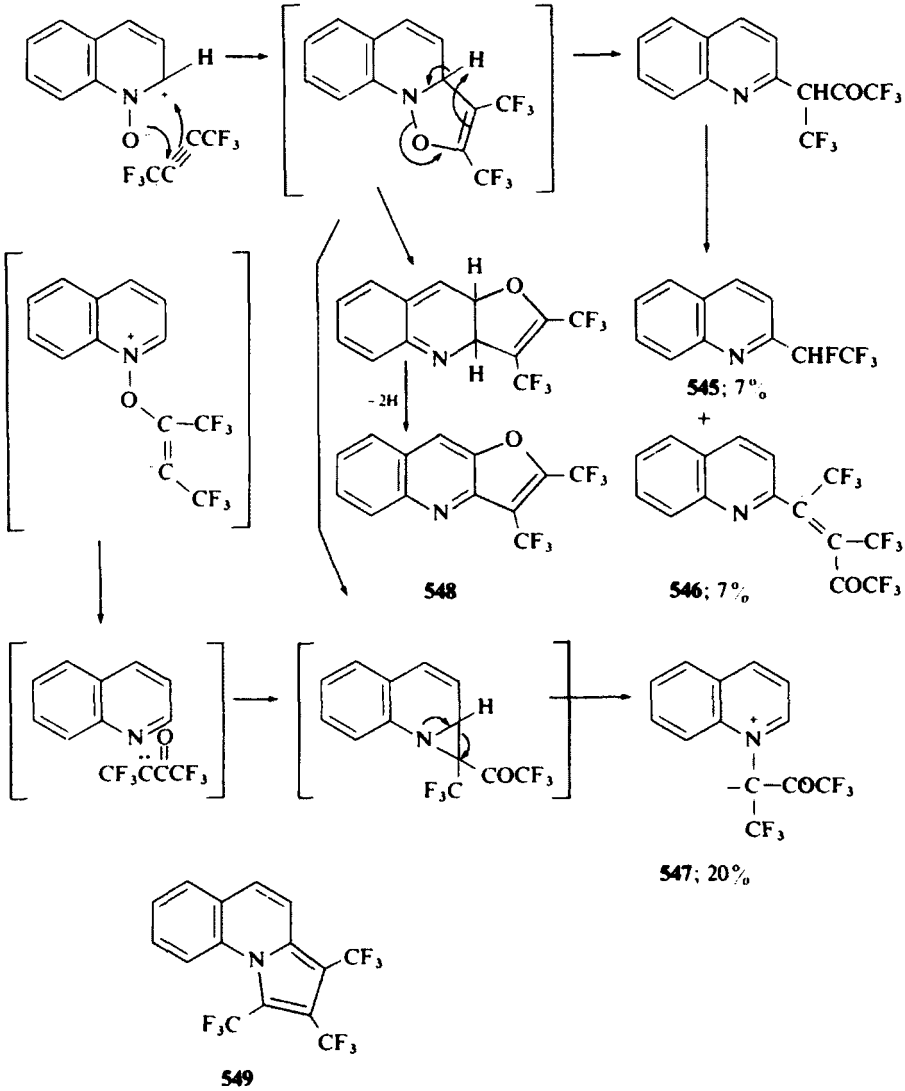
536

Reaction between quinoline *N*-oxide and phenylpropiolonitrile gave an ylid (**537**) formed from a carbene, the 2-substituted compound (**538**) formed via the normal five-membered ring and a 3-substituted product (**539**).[608] The mechanism of the closely related rearrangement of pyridine *N*-oxide has been thoroughly discussed in a review.[610] The more favoured candidate is a $_{\sigma}2_{s}+{}_{\pi}2_{a}+{}_{\pi}4_{s}$ process, as shown; a diradical mechanism is not ruled out. A similar pair of products (**540**) and (**541**) has been reported to be formed from 4-chloroquinoline *N*-oxide and ethyl phenylpropiolate with the additional,

easily explained, tricyclic compound (**542**), formed by nucleophilic displacement from compound (**541**).[609] Diethyl acetylenedicarboxylate gave the product (**543**); all of the yields reported were very low. Methyl propiolate gave, with quinoline *N*-oxide and acetic anhydride, the formyl derivative (**544**) and carbostyril.[605] In the absence of acetic anhydride, but with hydroquinone, the yield of compound (**544**) was slightly higher, and no carbostyril was observed. Ethyl propiolate provided a low yield of the ethyl ester corresponding to compound (**544**).

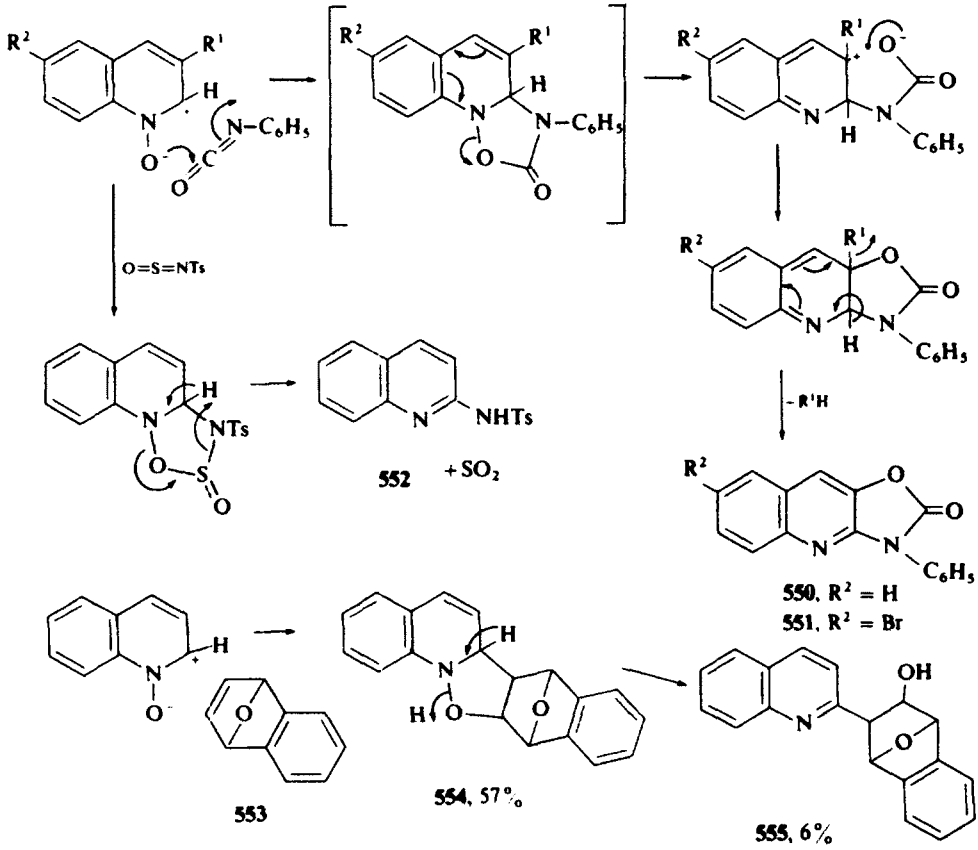


Quinoline *N*-oxide was reported to react with hexafluorobut-2-yne to give the 2-(tetrafluoroethyl)quinoline (**545**) and carbonyl fluoride.[606] Kobayashi and co-workers reported three additional products, the vinylquinoline (**546**), the ylid (**547**) and the tricyclic compound (**548**).[611,607] Mechanisms advanced to account for the products were similar to those suggested by Abramovitch for other acetylenes. When 3-bromoquinoline *N*-oxide was treated with hexafluorobutyne the products were the furoquinoline (**548**) (13%) and a very small amount of the pyrroloquinoline (**549**).[607]



In two other reactions in which quinoline *N*-oxides function as 1,3-dipolar species, phenyl isocyanate[612] and *N*-sulphinyl-*p*-toluenesulphonamide[613] were used. Phenyl isocyanate reacted with 3-nitro-, 3-bromo- and 3,6-dibromoquinoline *N*-oxides to give

the oxazoloquinolin-2-ones (**550**) and (**551**).[612] The sulphinyl derivative gave 2-(*p*-toluenesulphonamidyl)quinoline (**552**).[613] Wittig and Steinhoff reported a 1,3-dipolar addition between naphthalene endoxide (**553**) and quinoline *N*-oxide to give the adduct (**554**), which with acid gave the compound (**555**).[614]



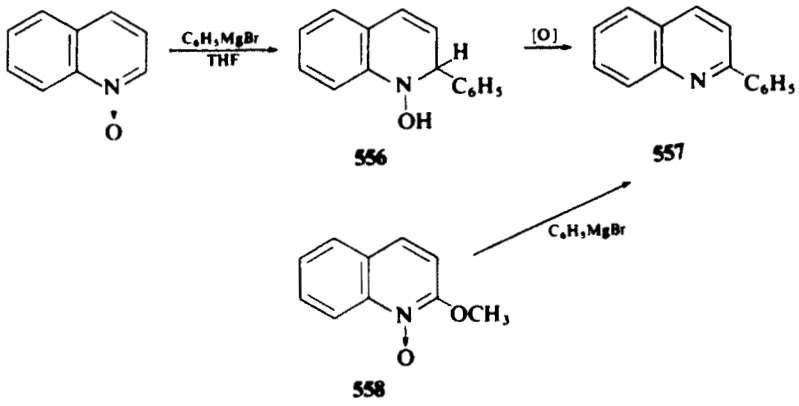
(v) *Reactions with Grignard Reagents.* Reactions between quinoline *N*-oxides and Grignard reagents with oxygen retention have been already described (p. 456). Colonna reported that 2-phenylquinoline (**557**) could be prepared from quinoline *N*-oxide and phenylmagnesium bromide;[615,62] by using 5-molar equivalents of phenylmagnesium bromide in tetrahydrofuran a yield of 95% was obtained.[488] It was subsequently reported that by using oxygen-free tetrahydrofuran the intermediate (**556**) could be isolated in 60% yield.[616] Alkylmagnesium halides have provided 2-alkylquinolines in reasonable yields,[531,617] although sometimes accompanied by the 2-alkylquinoline *N*-oxide and quinoline.[617] The only unusual reaction was observed when 2-methoxyquinoline *N*-oxide (**558**) was treated with phenylmagnesium bromide to give 2-phenylquinoline, with displacement of the methoxyl group. Reactions between quinoline *N*-oxides and Grignard reagents giving deoxygenated products are grouped in Table 23.

(vi) *Reactions with 2- or 4-Halogenopyridines or -quinolines.* Quinoline *N*-oxide has been reported to react with 2-bromopyridine to give 1-(2-quinolyl)-2(1*H*)-pyridone (**559**)

TABLE 23. Deoxygenative Alkylation and Arylation of Quinoline *N*-Oxides by Grignard Reagents

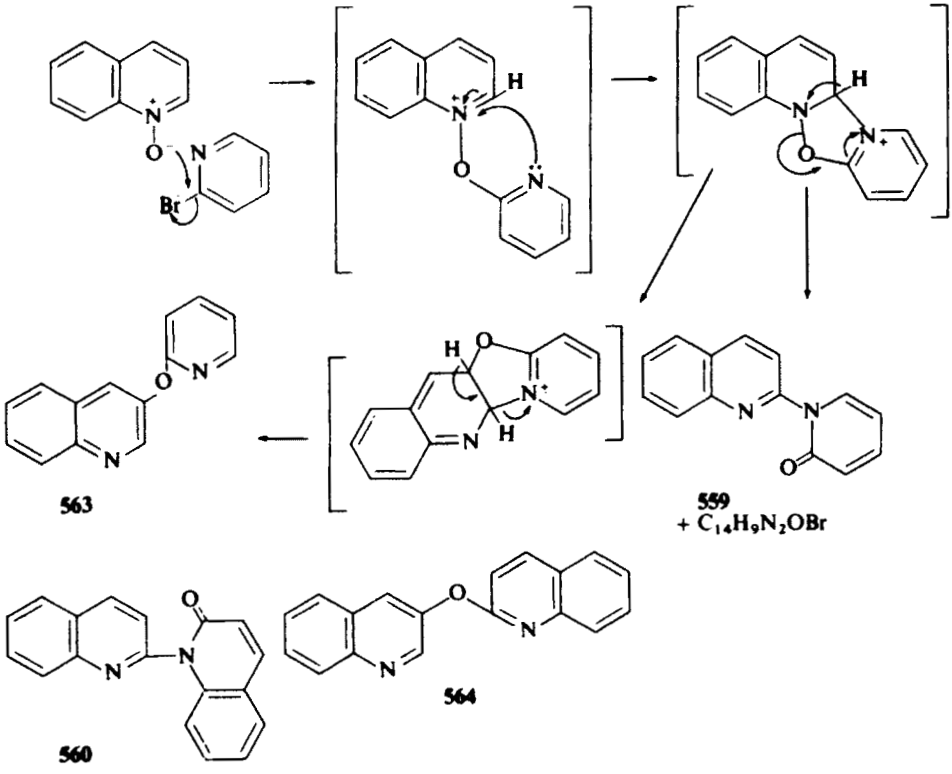
Substituent(s) in *N*-oxide	Grignard reagent	Substituents in quinoline	(Yield (%)	Other products	References
None	CH_3MgX, ether	2-Methyl	66	2-Methylquinoline *N*-oxide, quinoline[617]	531, 617
None	C_2H_5 MgBr, THF	2-Ethyl	72		617, 531
None	n-C_3H_7MgBr, ether	2-*n*-Propyl	85		617, 531
None	i-C_3H_7MgBr, ether	2-*i*-Propyl	36	2-Isopropylquinoline *N*-oxide, quinoline[617]	617
None	n-C_4H_9MgX, ether	2-*n*-Butyl	51		531
None	Cyclohexyl-MgBr, ether	2-Cyclohexyl	32	2-Cyclohexylquinoline *N*-oxide, quinoline	617
None	$C_6H_5CH_2MgBr$, ether	2-Benzyl	65		617
None	$C_6H_5CH_2CH_2MgBr$	2-Phenethyl	13	2-Phenethylquinoline *N*-oxide, quinoline	617
None	C_6H_5MgBr, THF	2-Phenyl	95	1-Hydroxy-2-phenyl-1,2-hydroquinoline;[a] 2-phenylquinoline *N*-oxide[488]	616, 62, 488
2-Methoxy	C_6H_5MgBr, ether	2-Phenyl	—		618
4-Methyl	CH_3MgX, ether	2,4-Dimethyl	73		531
4-Methyl	C_2H_5MgX, ether	2-Ethyl-4-methyl	69		531
4-Methyl	C_6H_5MgBr, THF	4-Methyl-2-phenyl	30	4-Methyl-2-phenylquinoline *N*-oxide (45%)	488
4-Chloro	C_6H_5MgBr, THF	4-Chloro-2-phenyl	low	4-Chloro-2-phenylquinoline *N*-oxide (63%)	488
4-Methoxy	C_6H_5MgBr, THF	4-Methoxy-2-phenyl	13	4-Methoxy-2-phenylquinoline *N*-oxide (64%)	488, 618
4-Ethoxy	C_6H_5MgBr, THF	4-Ethoxy-2-phenyl	16	4-Ethoxy-2-phenylquinoline *N*-oxide (65%)	488
6-Methyl	C_6H_5, MgBr, ether	6-Methyl-2-phenyl	—		62
6-Methoxy	C_6H_5MgBr, ether	6-Methoxy-2-phenyl	40		62
—[b]	C_6H_5MgBr, 70 °C	2-Phenylquinine	36		619
—[c]	C_6H_5MgBr	2-Phenylquinidine	35		619

[a] In the cold; oxygen-free THF.[616]
[b] Quinine.
[c] Quinidine.

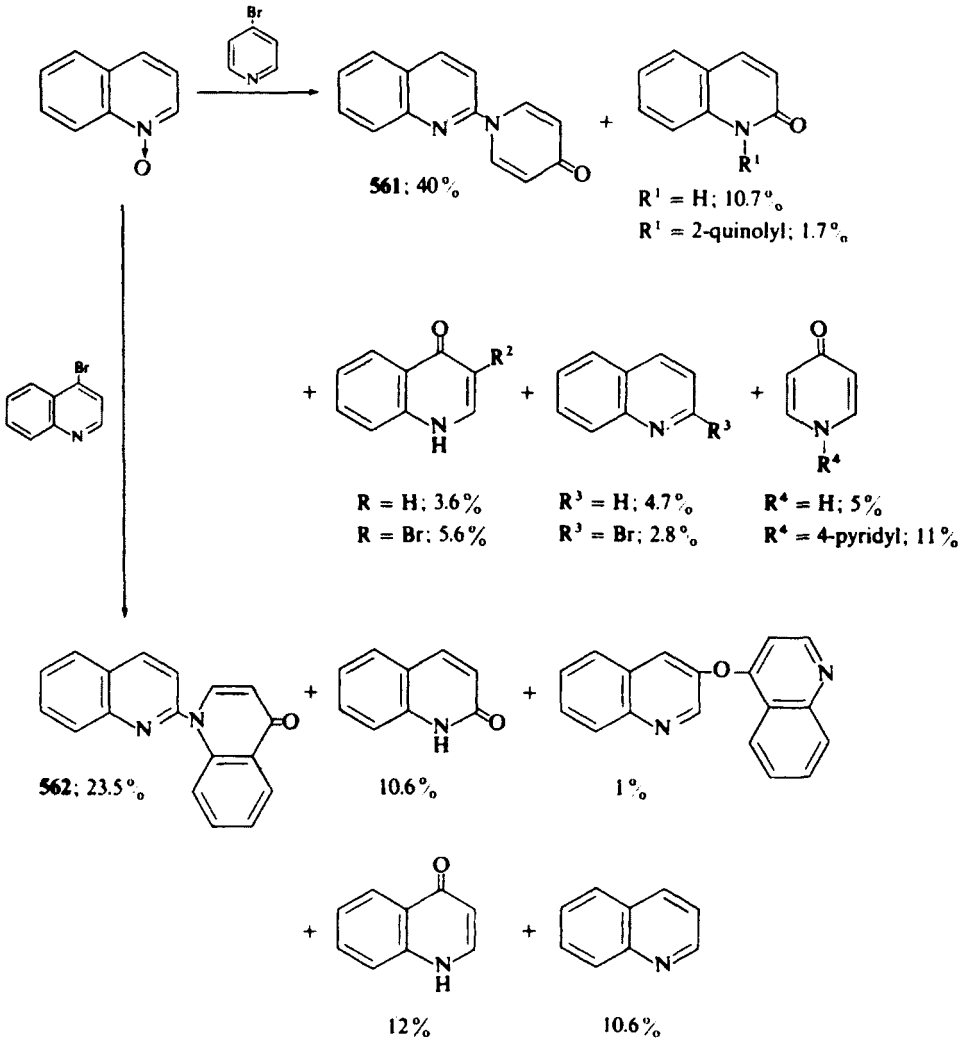


556 557 558

and a monobromo derivative, while 2-bromoquinoline gave 1-(2-quinolyl)carbostyril (**560**).[620] A later study, using dioxan as solvent and a temperature of 110–120 °C, showed that 4-bromopyridine gave a large number of products, that in largest yield being the 4-(1*H*)-pyridone (**561**); 4-bromoquinoline similarly gave the 4-(1*H*)-quinolone (**562**).[621] The chloroheterocycles were less reactive. The mechanism advanced for the reaction involving 2-bromopyridine or 2-bromoquinoline invoked a tricyclic intermediate, which also accounts for formation of ethers (**563**) and (**564**).[621] It is difficult to extend this mechanism to the reaction with 4-substituted pyridine or quinoline.

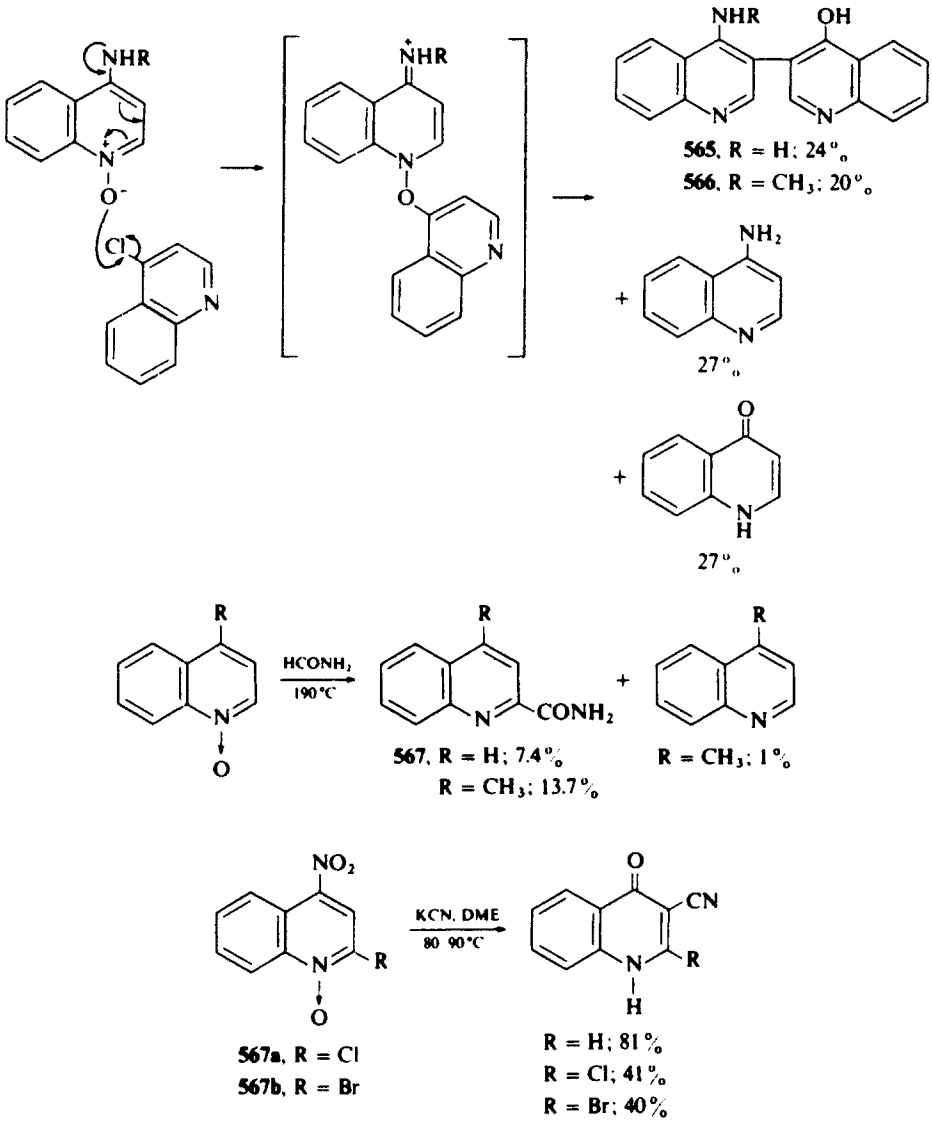


563 559 + $C_{14}H_9N_2OBr$ 564 560



An interesting variation of this reaction occurred when 4-aminoquinoline *N*-oxide reacted with 4-chloroquinoline; here, rearrangement competed with O—N cleavage and the products were the biaryl (**565**), 4-aminoquinoline and 4-(1*H*)-quinolone. The *N*-methylamino derivative gave the *N*-methyl biaryl (**566**).[622]

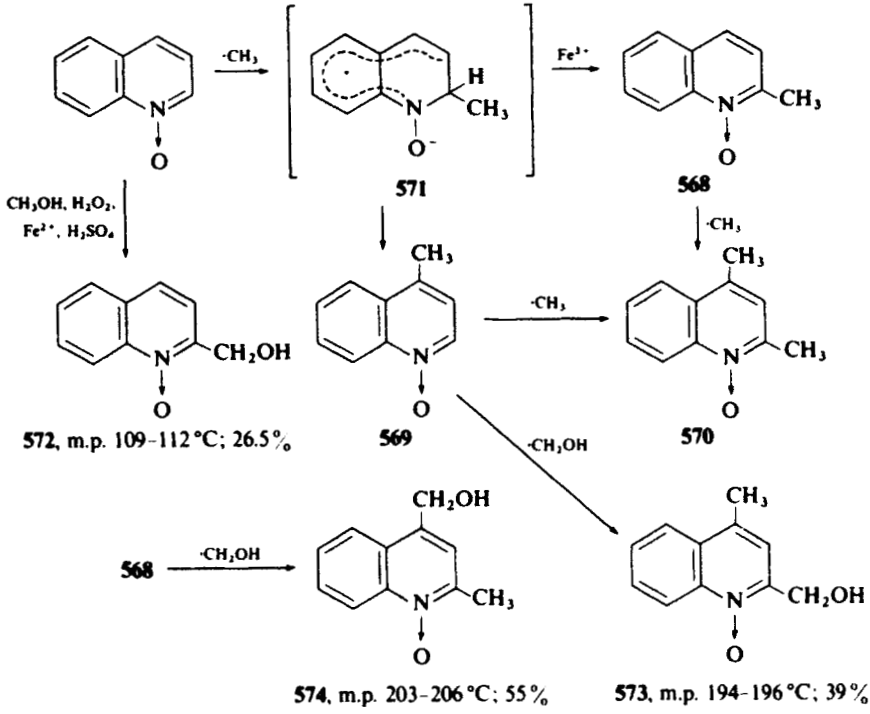
(vii) *Miscellaneous Reactions.* Formamide reacts with quinoline *N*-oxide at 195–205 °C to give 2-carboxamidoquinoline (**567**); a similar reaction occurs with 4-methylquinoline *N*-oxide.[795] Potassium cyanide in DMF reacts with 4-nitroquinoline *N*-oxide and the substituted *N*-oxides (**567a**) and (**567b**) to give 3-cyano-4-quinolones.[862] The same reaction was observed with potassium cyanide and 4-nitroquinoline; neither the mechanism of the substitution nor that of the deoxygenation has been established. Potassium cyanate gave 4-ethoxyquinoline *N*-oxide.



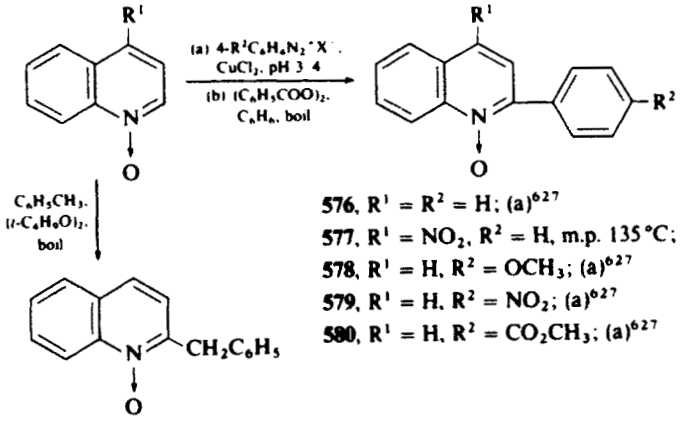
E Homolytic Substitution

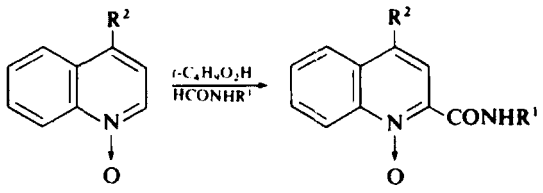
There are relatively few substitutions on quinoline *N*-oxides by free radicals; there seems to be a preference for 2-substitution over 4-substitution with alkyl and aryl radicals. Methyl radicals generated from *t*-butyl hydroperoxide in sulphuric acid gave 2-methylquinoline *N*-oxide (**568**) (37.7%), 4-methylquinoline *N*-oxide (**569**) (3.0%) and 2,4-dimethylquinoline *N*-oxide (**570**) (3.6%).[623] Methylation of 2-methylquinoline *N*-oxide gave poor yields of the dimethyl compound (**570**) (7.7%), but methylation of 4-methylquinoline *N*-oxide gave good yields of the dimethyl compound (**570**), (57.7%). The suggested mechanism involved attack by the methyl radical to give the intermediate

(**571**), oxidized by Fe^{3+} to give products.[330] Radical hydroxymethylation showed a similar product distribution of compounds (**572–574**).[623]



Hydroxylamine *O*-sulphonic acid in methanol gave, with 4-methylquinoline *N*-oxide, a mixture said to contain compound (**573**);[624] quinoline *N*-oxide and toluene with di-*t*-butyl peroxide gave 2-benzylquinoline *N*-oxide (**575**).[625] Phenyl radicals generated from dibenzoyl peroxide[626] or from diazonium salts with copper salt catalysis[627] also react to give 2-phenylquinoline *N*-oxides (**576**) and (**577**). Other aryldiazonium salts have also

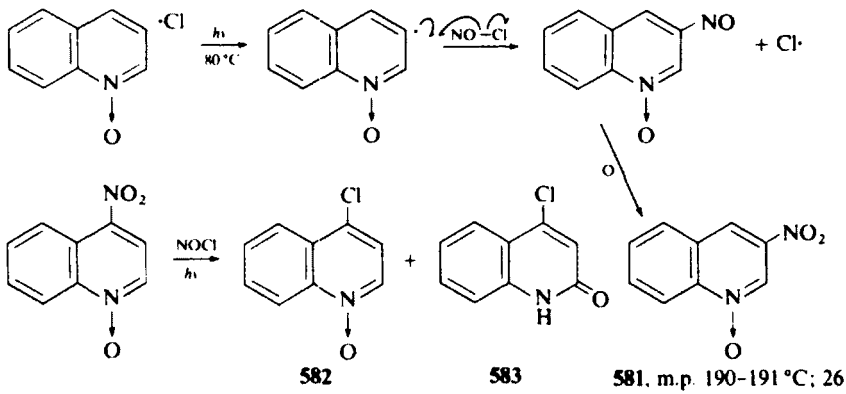




	R¹	R²	m.p. (°C)		R¹	R²	m.p. (°C)
580a	H	H	221–223	**580f**	CH_3	H	133–135
580b	H	CH_3	245–247	**580g**	CH_3	CH_3	108–110
580c	H	Cl	253–255	**580h**	CH_3	Cl	117–119
580d	H	OCH_3	240–241	**580j**	CH_3	OCH_3	181–183
580e	H	NO_2	258–261				

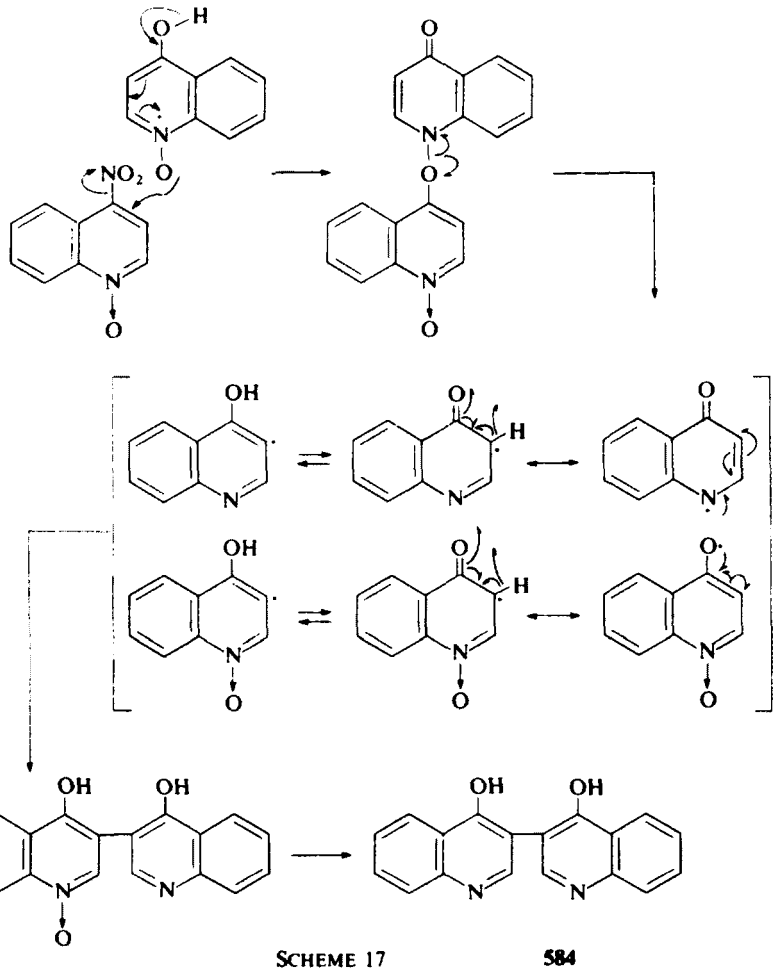
been used[627] to give 2-phenylquinoline *N*-oxides (**578**–**580**). A number of 4-substituted quinolines were converted into 2-carboxamidoquinoline *N*-oxides (**580a**–**j**) by homolytic attack; the reagent used was *t*-butyl hydroperoxide and an amide.[811]

In contrast, nitrosyl chloride gave, with quinoline *N*-oxide, 3-nitroquinoline *N*-oxide (**581**).[628] The reaction was thought to be free radical because of an observed increase in yield (acceleration of reaction) on irradiation. In this case the mechanism suggested involved hydrogen abstraction from position 3 by chlorine radicals, with subsequent substitution by nitroso radicals, and oxidation. The production of 3-nitroquinoline *N*-oxide from butyl nitrite was also thought to be by radical substitution, in spite of the observation of better yields in the dark than under irradiation. Nitrosyl chloride and 4-nitroquinoline *N*-oxide gave, under irradiation, 4-chloroquinoline *N*-oxide (**582**) and 4-chlorocarbostyril (**583**), indicating radical replacement to be a possible route for

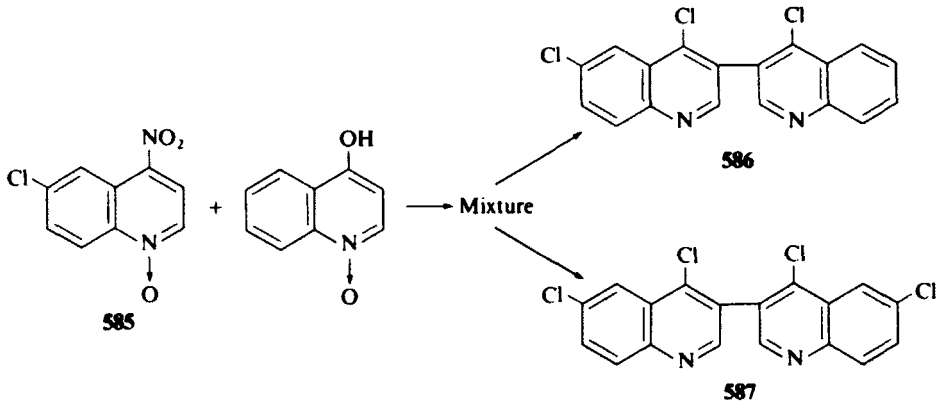


582 **583** **581**, m.p. 190–191 °C; 26%

interconversions from 4-nitroquinoline *N*-oxide.[629] A reaction for which a free radical mechanism was suggested was that between 4-nitroquinoline *N*-oxide and 4-hydroxyquinoline *N*-oxide in boiling methanol. The products were 4-quinolone and the biquinoline (**584**).[630] The suggested mechanism is shown in Scheme 17. From 6-chloro-4-nitroquinoline *N*-oxide (**585**) and 4-hydroxyquinoline *N*-oxide a mixture was obtained, which gave, with phosphorus pentachloride and phosphoryl chloride, a 19 : 1 mixture of the trichloro derivative (**586**) and tetrachloro derivative (**587**). The isolation of compound (**587**) seemed to indicate that some of the biquinoline was formed from 4-nitroquinoline *N*-oxide alone.



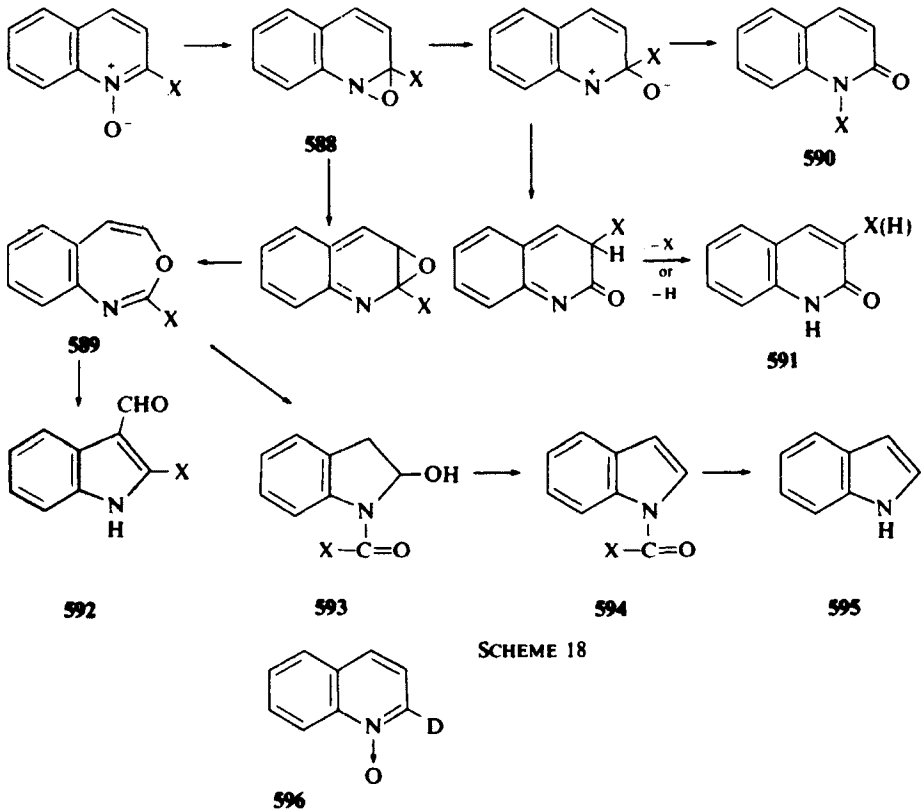
SCHEME 17 **584**



585 **586** **587**

F. Photochemical Reactions

In this section photochemical reactions which involve the quinoline *N*-oxide skeleton are considered. Other photochemical reactions, such as photochemically induced substitution, or photochemical transformation of a substituent group, are dealt with elesewhere. The knowledge of photochemical rearrangement up to 1970 has been dealt with in a good review; the results to that date are summarized in Scheme 18.[631]

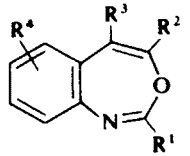


SCHEME 18

From Scheme 18 it can be seen that the principal products are carbostyrils (**590** and **591**) and indoline derivatives (**593**) with some products of further reaction, such as indoles (**594** and **595**), or carbostyril $_{\pi}2_s + _{\pi}2_s$ photodimers. The crucial intermediates are the oxazirine (**588**) and the benzoxazepine (**589**), and there are now a number of examples where benzoxazepines have been obtained (Table 24). The parent compound (**589**, X = H) was isolated after irradiation of quinoline *N*-oxide in cyclohexane with rigid exclusion of moisture; addition of water or purification by chromatography gave secondary products.[871]

When first isolated the benzoxazepines (**589**) were described as oxaziridines (**588**);[634] there is virtually no direct evidence for the oxaziridine intermediates. Scheme 18 was supported by photolysis of [2-^{2}H]quinoline *N*-oxide (**596**).[631] The indoline (**593**), X = ^{2}H was formed, and the *N*-formylindole (**594**), X = ^{2}H; the indole (**595**) showed no deuterium labelling. Thus the route suggested for the photolysis in non-protic solvents, via intermediates (**588**) and (**589**), seems fully confirmed. Measurements of quantum

TABLE 24. Benzo[*d*]-1,3-oxazepines from Quinoline *N*-Oxides



Substituent(s) in *N*-oxide	Photochemical conditions[a]	R^1	R^2	R^3	R^4	Yield (%)	References
None	HP, Pyrex, cyclohexane	—	—	—	—	60	871
2-Trifluoromethyl	HP, Pyrex, ether	CF_3	—	—	—	70	632
2-Styryl	—	$C_6H_5CH{=}CH$	—	—	—	—	638
2-Phenyl	MP, Pyrex, ethanol or acetone	C_6H_5	—	—	—	80	633, 353, 634, 635
2-(*p*-Bromophenyl)	MP, Pyrex, acetone	*p*-BrC_6H_4	—	—	—	85	633
2-(*p*-Chlorophenyl)	MP, Pyrex, acetone	*p*-ClC_6H_4	—	—	—	70	633
4-Methyl-2-trifluoromethyl	HP, Pyrex, ether	CF_3	—	CH_3	—	50	632
3-Methyl-2-phenyl	MP, Pyrex, acetone	C_6H_5	CH_3	—	—	90	633, 635
4-Methyl-2-phenyl	MP, Pyrex, acetone	C_6H_5	—	CH_3	—	90	633, 635
6-Bromo-2-phenyl	MP, Pyrex, acetone	C_6H_5	—	—	7-Br	65	633
6-Bromo-2-(*p*-bromophenyl)	MP, Pyrex, acetone	*p*-BrC_6H_4	—	—	7-Br	80	633
4-Methoxy-2-trifluoromethyl	HP, Pyrex, ether	CF_3	—	OCH_3	—	65	632
4-Carbomethoxy-2-phenyl	HP, Pyrex, acetone (20 min)	C_6H_5	—	CO_2CH_3	—	80	636
4-Carbomethoxy-3-methyl-2-phenyl	HP, Pyrex, acetone	C_6H_5	CH_3	CO_2CH_3	—	83	636
2-Cyano	HP, Pyrex, acetone	CN	—	—	—	90	637, 634, 872
2-Cyano-3-methyl	MP, Pyrex, acetone	CN	CH_3	—	—	70	633
2-Cyano-3-trifluoromethyl	HP, Pyrex, benzene	CN	CF_3	—	—	91	101
2-Cyano-4-methyl	MP, Pyrex, acetone	CN	—	CH_3	—	90	633, 634
2-Cyano-4-trifluoromethyl	HP, Pyrex, benzene	CN	—	CF_3	—	97	101
2-Cyano-4-chloro	MP, Pyrex, CH_2Cl_2	CN	—	Cl	—	80	639, 640

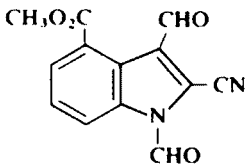
[a] MP = medium-pressure, HP = high-pressure mercury lamp.

TABLE 24 (*cont.*)

Substituent(s) in *N*-oxide	Photochemical conditions[a]	R^1	R^2	R^3	R^4	Yield (%)	References
2-Cyano-4-methoxy	MP, Pyrex, CH_2Cl_2	CN	—	OCH_3	—	80 (100)	639, 641
2-Cyano-6-methoxy	MP, Pyrex, acetone	CN	—	—	7-OCH_3	75	633, 642
4-Cyano-2-trifluoromethyl	HP, Pyrex, ether	CF_3	—	CN	—	75	632
2-Cyano-5-methoxycarbonyl	HP, Pyrex, acetone[b]	CN	—	—	6-CO_2CH_3	94	873

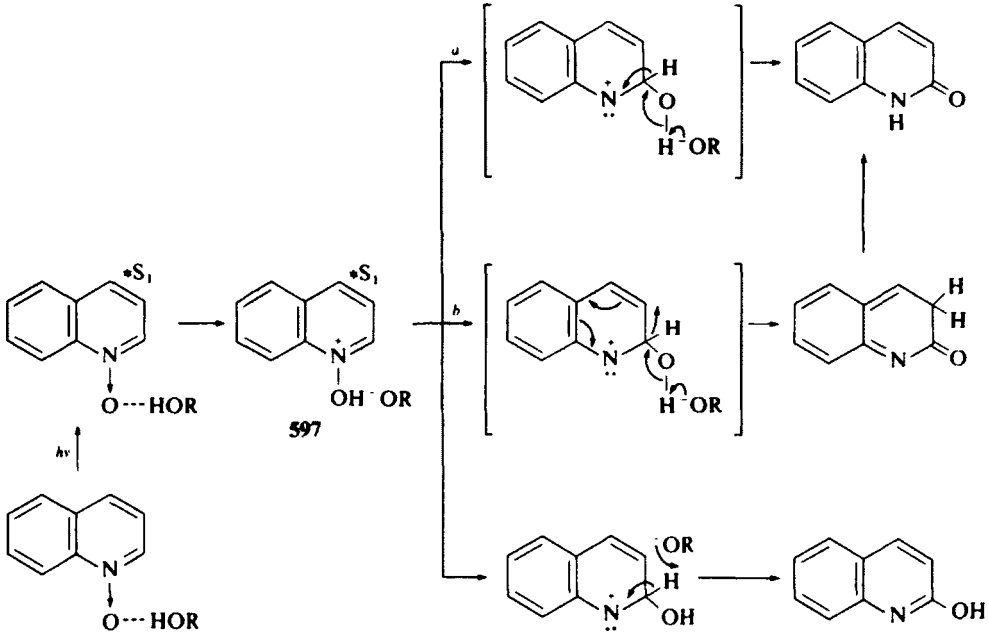
[a] MP = medium-pressure, HP = high-pressure mercury lamp.

[b] Irradiation through quartz gave



yield for the two major processes have shown that both come from an excited singlet; deoxygenation (dealt with on p. 425) occurs from an excited triplet.[643,644,812] When iodide ion was added to the solution of 2-cyanoquinoline *N*-oxide before photolysis there was quenching of the photoisomerization and liberation of iodine.[63] Since the 2-cyanoquinoline *N*-oxides form benzoxazepines, even in hydroxylic solvents, the formation of iodine represents the best evidence available for the intermediate formation of oxaziridines, which are known to be strong oxidizing agents. It has been shown[637] that 2-cyanoquinoline *N*-oxides do not form strong hydrogen bonds with hydroxylic solvents; Hata and Oguro also examined the change in photochemical reaction of 4-methylquinoline *N*-oxide in 95% ethanol with added iodide ion, observing a decrease in quantum yield of formation of carbostyril and an increase in quantum yield for deoxygenation.[644]

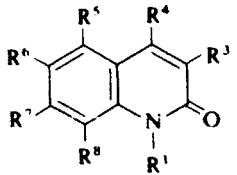
These observations were clearly explained by a deactivation of an excited singlet, and a modified mechanism (Scheme 19) was advanced for the formation of carbostyril. The hydrogen-bonded excited singlet–solvent complex does not rearrange to the oxaziridine (no liberation of iodine), but directly to species (**597**) which can proceed to carbostyril by path *a* or path *b* but not by path *c* in view of the observation[631] that [2-^{2}H]quinoline *N*-oxide gives [1-^{2}H]carbostyril or [3-^{2}H]carbostyril. Carbostyrils prepared by photochemistry are listed in Table 25.



SCHEME 19

The less commonly observed products of photochemical reaction are those due to migration of substituents (usually from position 2 in the *N*-oxide) and those due to further reaction of primary photo-products. Thus, in the first category, irradiation of 2-methylquinoline *N*-oxide or of 2,4-dimethylquinoline *N*-oxide in protic solvents gave a mixture of 3-methylcarbostyrils (**598**) or (**599**), with 1-methylcarbostyrils (**600**) or (**601**),

TABLE 25. Carbostyrils from Quinoline *N*-Oxides by Irradiation



Substituent(s) in *N*-oxide	Irradiation conditions[a]	R^1	R^3	R^4	R^5	R^6	R^7	R^8	Yield (%)	References
None	MP, Pyrex, H_2O	—							91	645, 646
None	HP, Pyrex, methanol	—	—	—	—	—	—	—	60–70	647
2-Methyl	MP, Pyrex, H_2O or ethanol	—	CH_3	—	—	—	—	—	17	645, 209
2-Methyl	HP, Pyrex, methanol	—	CH_3	—	—	—	—	—	22	633, 634, 635, 647
		CH_3	—	—	—	—	—	—	16	
2-Phenyl	MP, Pyrex, ethanol	—	C_6H_5	—	—	—	—	—	8	633, 634, 635
3-Methyl	MP, Pyrex, H_2O	—	CH_3	—	—	—	—	—	90	645, 209
3-Ethyl	MP, Pyrex, H_2O	—	C_2H_5	—	—	—	—	—	90	646
3-Phenyl	MP, Pyrex, ethanol	—	C_6H_5	—	—	—	—	—	98	648
3-Bromo	MP, Pyrex, ethanol or acetone	—	Br	—	—	—	—	—	50–60	646
4-Methyl	HP, Pyrex, H_2O or methanol	—	—	CH_3	—	—	—	—	70–80	209, 645, 647
4-Phenyl	MP, Pyrex, ethyl acetate	—	—	C_6H_5	—	—	—	—	83	648
4-Chloro	HP, Pyrex, methanol	—	—	Cl	—	—	—	—	75–80	647
4-Bromo	MP, Pyrex, H_2O or ethanol	—	—	Br	—	—	—	—	50	646
4-Nitro	HP, Pyrex, ethanol	—	—	OH	—	—	—	—	7	649
4-Methoxy	HP, Pyrex, methanol	—	—	OCH_3	—	—	—	—	60–70	647
4-(*p*-Tolylthio)	Ethanol	—	—	*p*-$CH_3C_6H_4S$	—	—	—	—	90	650
5-Methyl	MP, Pyrex, H_2O	—	—	—	CH_3	—	—	—	88	645, 209

6-Methyl	MP, Pyrex, H_2O or ethanol	—	—	—	—	CH_3	—	—	80–90	209, 645, 646
6-Fluoro	MP, Pyrex, H_2O	—	—	—	—	F	—	—	70	646
6-Chloro	Hanau Q-700, Pyrex, H_2O or ethanol	—	—	—	—	Cl	—	—	70–95	646
6-Bromo	Hanau Q-700, Pyrex, H_2O	—	—	—	—	Br	—	—	80	646
6-Methoxy	HP, Pyrex, methanol or ethanol	—	—	—	—	OCH_3	—	—	50–63[b]	647
7-Methyl	Hanau Q-700, Pyrex, H_2O or ethanol	—	—	—	—	—	CH_3	—	70–98	646, 209, 645
7-Chloro	Hanau Q-700, Pyrex, acetone	—	—	—	—	—	Cl	—	31	646
8-Methyl	MP, Pyrex, H_2O	—	—	—	—	—	—	CH_3	80	209, 645
8-Methoxy	Hanau Q-700, Pyrex, H_2O	—	—	—	—	—	—	OCH_3	50[c]	646
3-Methyl-4-nitro	HP, Pyrex, ethanol	—	CH_3	OH	—	—	—	—	30	649
2,4-Dimethyl	HP, Pyrex, methanol	—	CH_3	CH_3	—	—	—	—	15	647
		CH_3	—	CH_3	—	—	—	—	20	
4-Methyl-2-phenyl	MP, Pyrex, ethanol	—	C_6H_5	CH_3	—	—	—	—	12	633, 635
8-Methyl-4-phenyl	MP, Pyrex, ethanol	—	C_6H_5	—	—	—	—	CH_3	9	633, 635
4-Methoxy-2-methyl	HP, Pyrex, methanol	CH_3	—	CH_3O	—	—	—	—	55[d]	874
4-Allyloxy-2-methyl	HP, Pyrex, methanol	CH_3	—	C_3H_5O	—	—	—	—	45[d]	874
4-Methallyloxy-2-methyl	HP, Pyrex, methanol	CH_3	—	C_4H_7O	—	—	—	—	47[d]	874
4-Propargyloxy-2-methyl	HP, Pyrex, methanol	CH_3	—	C_3H_3O	—	—	—	—	48[d]	874

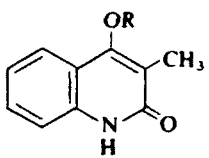
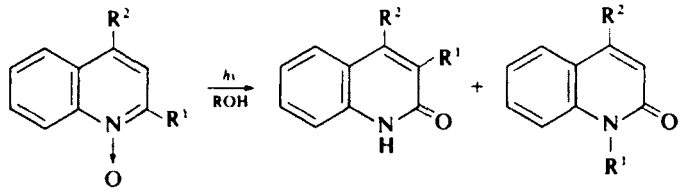
[a] MP = medium-pressure, HP = high-pressure mercury lamp.
[b] Dimer in some experiments.
[c] Dimer.
[d] With small quantities of  and 

TABLE 25. (*cont.*)

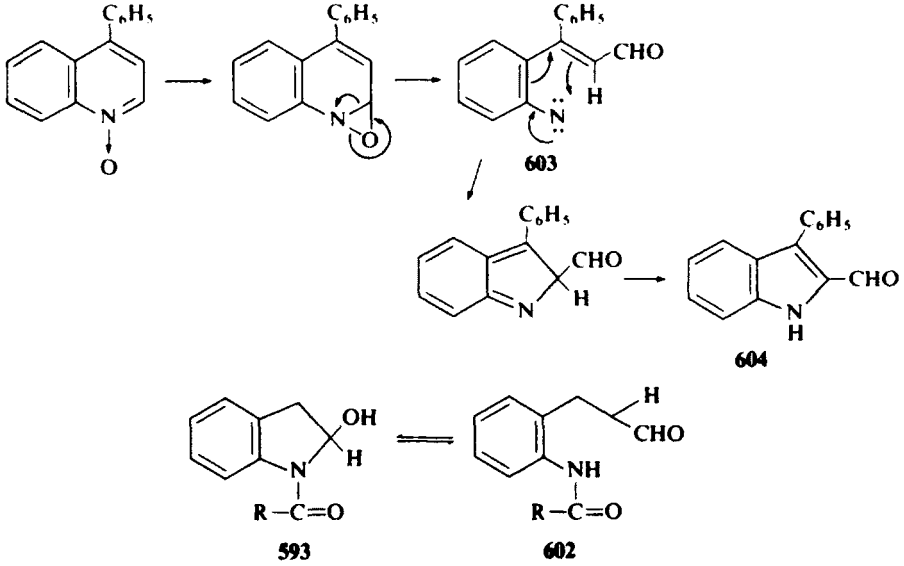
Substituent(s) in *N*-oxide	Irradiation conditions[a]	R^1	R^3	R^4	R^5	R^6	R^7	R^8	Yield (%)	References
2-Cyano-4-methyl	HP, Pyrex, CH_2Cl_2, CH_3NH_2	CH_3NH	—	CH_3	—	—	—	—	35	651
2-Cyano-4-methyl	HP, Pyrex, CH_2Cl_2 $(CH_3)_2NH$	$(CH_3)_2NH$	—	CH_3	—	—	—	—	90	651
2-Cyano-4-methyl	HP, Pyrex, CH_2Cl_2, $C_2H_5NH_2$	C_2H_5NH	—	CH_3	—	—	—	—	25	651
2-Cyano-4-methyl	HP, Pyrex, CH_2Cl_2, $(C_2H_5)_2NH$	$(C_2H_5)_2N$	—	CH_3	—	—	—	—	65	651
5-Methoxycarbonyl	HP, Pyrex, acetone	—	—	—	CO_2CH_3	—	—	—	33	873



598, $R^1 = CH_3$, $R^2 = H$; 22% **600**, $R^1 = CH_3$, $R^2 = H$; 16%
599, $R^1 = R^2 = CH_3$; 15% **601**, $R^1 = R^2 = CH_3$; 20%

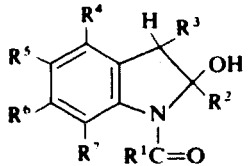
among other products.[652,647,354] Similar compounds were obtained from 2-phenylquinoline *N*-oxide and 4-methyl-2-phenylquinoline *N*-oxide, although here the main products were benzoxazepines.[633] A mechanism has been advanced for the rearrangement of 2-methylquinoline *N*-oxides, involving the separation of a methyl carbonium ion from the oxaziridine intermediate to form a charge-transfer complex.[874] The results of photolysis of 4-alkoxy- or of 4-methoxycarbonyl-2-methylquinoline *N*-oxides were said to support this mechanism. In non-protic solvents the primary products of photochemical reaction are the benzoxazepines (**589**). These have been shown to rearrange to the indolinols (**593**), which are listed in Table 26.

The sequence has been clearly demonstrated with 2-cyano-6-methoxyquinoline *N*-oxide, which gave the benzoxazepine, converted by sulphuric acid in dioxan to the 1-cyanocarbonylindolinol, which with trifluoroacetic acid gave the cyanocarbonylindole.[642] The indolinols have been shown to be in equilibrium with open-chain tautomers (**602**),[115] and to give *N*-acylindoles (**594**) by dehydration.[115] Indoles are formed from *N*-acylindoles by hydrolysis. Among the unusual indole photo-products were 3-phenylindole-2-carboxaldehyde (**604**) from 4-phenylquinoline *N*-oxide,[648] which, it was suggested, was formed via a nitrene intermediate (**603**).



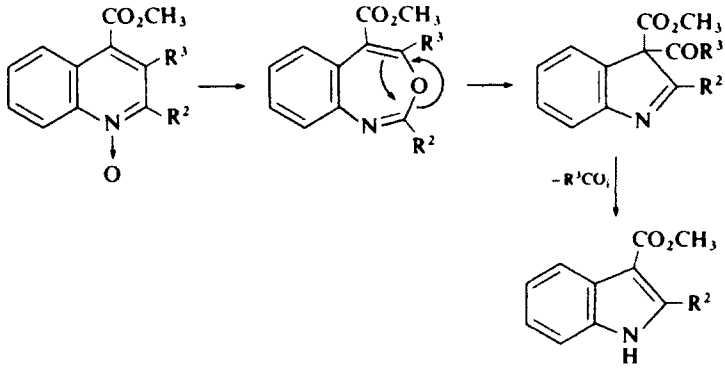
When 4-carbomethoxy-2-phenyl- or 4-carbomethoxy-2-methylquinoline *N*-oxides were irradiated with a high-pressure lamp through Pyrex in acetone solution, 2-phenyl- (**605**) or 2-methylindole carboxylates (**606**) were formed.[636,1399] Brief irradiation

TABLE 26. Indolinols Produced by Irradiation of Quinoline *N*-Oxides

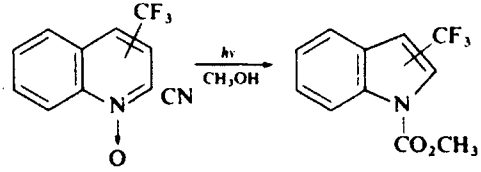


Substituent(s) in *N*-oxide	Irradiation conditions[a]	R^1	R^2	R^3	R^4	R^5	R^6	R^7	Yield (%)	References
None	Hanau Q-700, or Philips HPK 125, Pyrex, ether or acetone	H	—	—	—	—	—	—	40–50	647, 646, 813
2-Methyl	MP, Pyrex, benzene	CH_3	—	—	—	—	—	—	66	354, 115
4-Methyl	Hanau Q-700, Pyrex, benzene	H	—	CH_3	—	—	—	—	25	646
4-Phenyl	MP, Pyrex, cyclohexane	H	—	C_6H_5	—	—	—	—	10[b]	633
4-Chloro	Hanau Q-700, Pyrex, acetone	H	—	Cl	—	—	—	—	0–20	646
6-Methyl	Hanau Q-700, Pyrex, ether	H	—	—	—	CH_3	—	—	33	646, 653
6-Fluoro	Hanau Q-700, Pyrex, acetone	H	—	—	—	F	—	—	45	646
6-Bromo	Hanau Q-700, Pyrex, acetone	H	—	—	—	Br	—	—	33	646
6-Methoxy	Hanau Q-700, Pyrex, benzene	H	—	—	—	OCH_3	—	—	11	646, 653
7-Chloro	Hanau Q-700, Pyrex, acetone	H	—	—	—	—	Cl	—	50	646
8-Methyl	Hanau Q-700, Pyrex, acetone	H	—	—	—	—	—	CH_3	23	646
2,4-Dimethyl	MP, Pyrex, benzene	CH_3	—	CH_3	—	—	—	—	50	115
6-Methoxy-2-methyl	MP, Pyrex, benzene	CH_3	—	—	—	OCH_3	—	—	34	115
4-Methyl-2-phenyl	MP, Pyrex, ethanol	C_6H_5	—	CH_3	—	—	—	—	14	633, 635
5-Methoxycarbonyl	HP, Pyrex, acetone	H	—	—	CO_2CH_3	—	—	—	41	873

[a] MP = medium-pressure, HP = high-pressure mercury lamp.
[b] Plus 3-phenylindole-2-carboxaldehyde (45%).



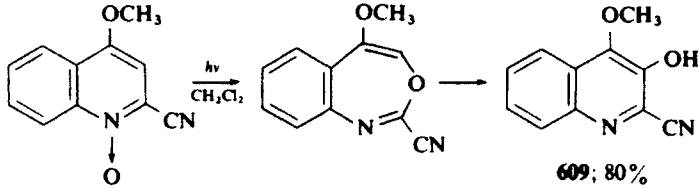
605, $R^2 = C_6H_5$; 82%
606, $R^2 = CH_3$; 68%



607, 2-CF_3; 34%
608, 3-CF_3; 8%

established the presence of a benzoxazepine intermediate; rearrangement to the indolenine was thought to precede deacylation. The same workers reported that 4-carboxyquinoline *N*-oxides, irradiated in methanol at 300 nm, gave indole-3-carboxylic acids.[1399] The loss of one carbon atom during photolysis was also observed with 2-cyano-3-trifluoromethylquinoline *N*-oxide, and to a lesser extent with the 4-trifluoromethyl isomer,[101] the products being *N*-carbomethoxyindoles (**607**) and (**608**).

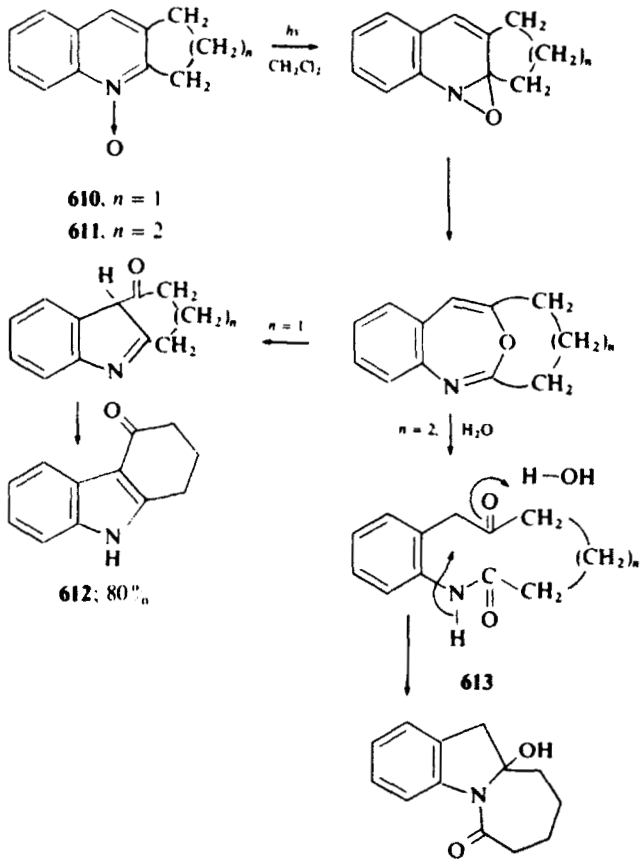
Another escape route for the benzoxazepine is provided by ring contraction to 3-hydroxyquinoline, exemplified by compound (**609**).[639,641] An apparently slight change



609; 80%

in molecular geometry can entirely alter the progress of the photochemical reaction: the homologous pair of compounds (**610**) and (**611**) gave completely different products. The smaller ring in compound (**610**) produced a normal 3-acylindole (**612**), while the larger ring in compound (**611**) led to an intermediate (**613**), which on chromatography rearranged to give predominantly the indolinol (**614**).[654]

Further elaboration of carbostyril products has been achieved by irradiation of quinoline *N*-oxides in propionic acid[655] or with added amines.[651] In the former case irradiation with a high-pressure mercury lamp through quartz gave mixtures of *cis*- and



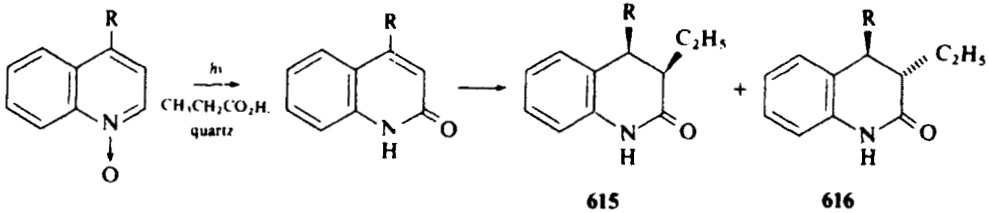
610, $n = 1$
611, $n = 2$

612; 80%

613

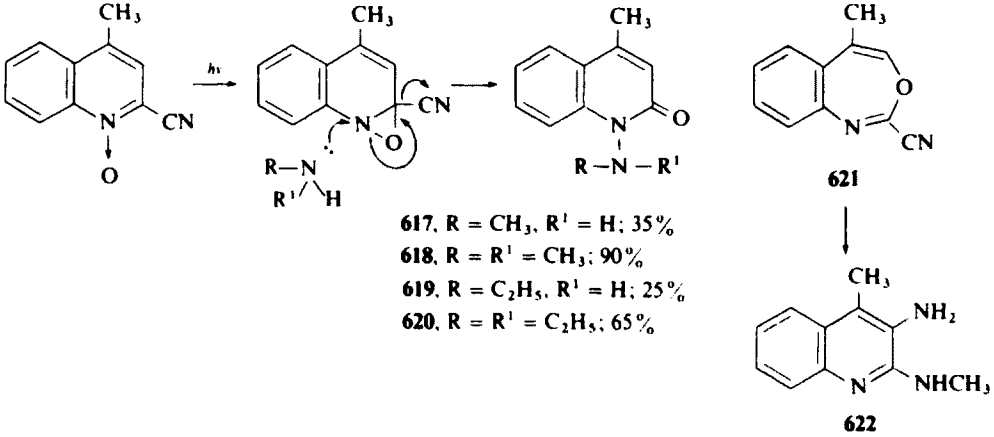
614, 70%

trans-3-ethyl-3,4-dihydrocarbostyrils (**615**) and (**616**), which could also be obtained by irradiation of the carbostyrils in propionic acid. In the second case 1-aminocarbostyrils (**617**–**620**) were formed, possibly by trapping the elusive oxaziridine intermediate. Treatment of the benzoxazepine (**621**) with methylamine gave not compound (**617**), but the diamine (**622**).



615 **616**

R = CN	CO_2CH_3	CO_2H
615 (%) 41	28	50
616 (%) 8	5	12

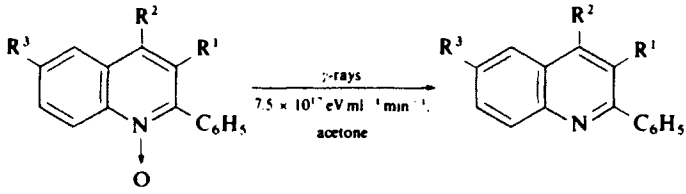


617, R = CH_3, R' = H; 35%
618, R = R' = CH_3; 90%
619, R = C_2H_5, R' = H; 25%
620, R = R' = C_2H_5; 65%

621

622

Photochemical deoxygenation has been dealt with elsewhere; a small amount of deoxygenated material is observed in most photochemical reactions, and increases if the triplet state is favoured. Rosenthal and Buchardt examined the effect of γ-rays on quinoline *N*-oxides in acetone solutions.[356] The 2-phenylquinoline *N*-oxides (**623**–**626**) were deoxygenated with yields of up to 30%; 2-cyanoquinoline *N*-oxides were also deoxygenated, with traces of benzoxazepine observed. These observations indicated that deoxygenation occurred from one excited state (triplet), while benzoxazepine formation occurred from the other (singlet).



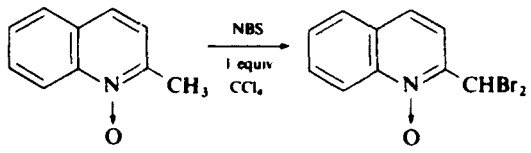
623, R' = R² = R³ = H
624, R' = CH_3, R² = R³ = H
625, R² = CH_3, R' = R³ = H
626, R³ = CH_3, R' = R² = H

G. Reactions Involving Side-chains

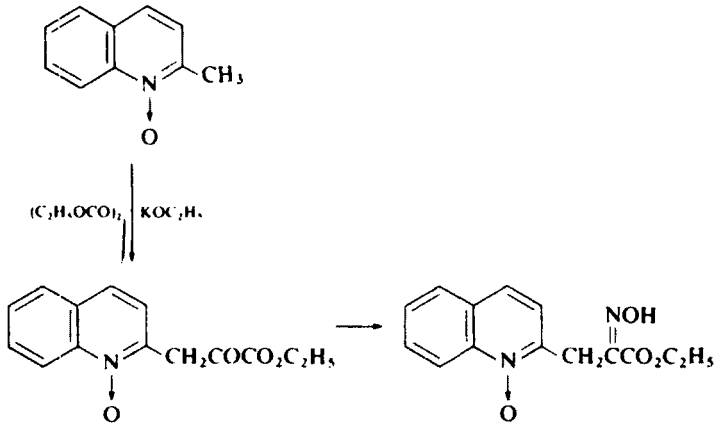
Oxidation and reduction have been mentioned in Sections III.2.A and III.2.B.

a. SUBSTITUTION REACTIONS The hydrogen atoms of methyl substituents can be replaced directly by bromine by the use of *N*-bromosuccinimide but the reaction appears non-selective, a low yield of the dibromomethylquinoline *N*-oxide (**627**) being obtained when one equivalent of *N*-bromosuccinimide was used.[60]

More commonly, substitution occurs via an anion, or by replacement of a halogen atom. Thus quinaldine *N*-oxide reacts with potassium ethoxide and diethyl oxalate to give the quinolylpyruvate (**628**), which was converted via its oxime (**629**) and the oximino acid (**630**) into 1-oxido-2-quinolinylalanine (**631**).[86] More remarkably, quinaldine *N*-oxide with potassium amide and bromobenzene in liquid ammonia was reported to give 2-benzylquinoline *N*-oxide (**632**).[656]

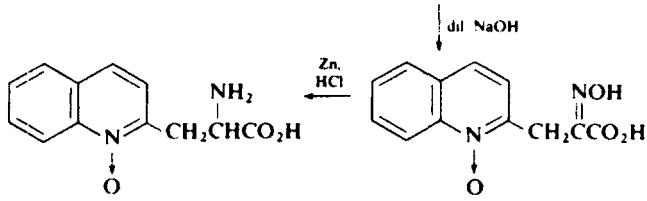


627, m.p. 108–109 °C; 22%



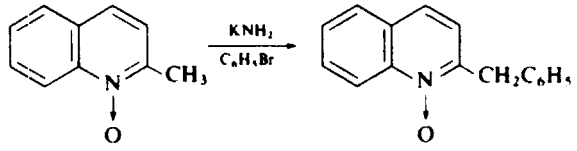
628, m.p. 135–136 °C; 82%

629, m.p. 220–222 °C



631, m.p. 228–229 °C;
picrate, m.p. 199–199.5 °C

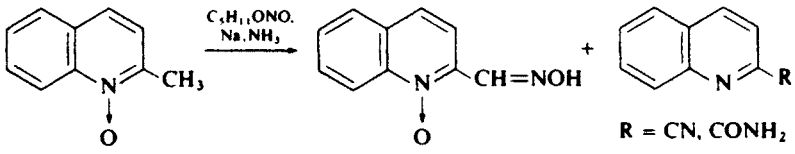
630, m.p. 183–185 °C



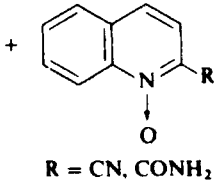
632, m.p. 118–120 °C; 26%

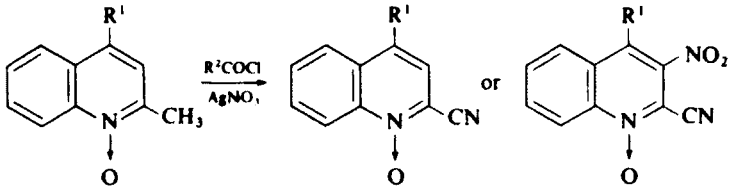
Quinaldine *N*-oxide has also been treated with amyl nitrite and sodamide in liquid ammonia to give the oxime (**633**); lepidine reacted similarly but the products were difficult to separate.[657] Small amounts of quinaldonitrile and its *N*-oxide and of quinaldamide and its *N*-oxide were also obtained in the first case.

Tanida has reported[809] that 2-methylquinoline *N*-oxides, when treated with acid chlorides and silver nitrate in boiling chloroform, can give 2-cyanoquinoline *N*-oxides (**633a–c**), sometimes with nitration in the 3-position (**633c**). With silver nitrite quinaldine *N*-oxide gave the oxime acetate (**633d**).



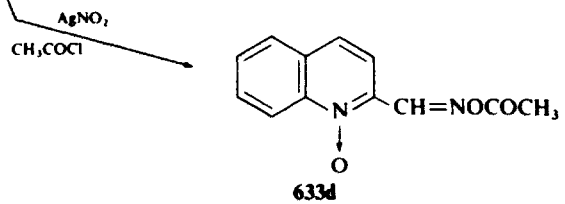
633, m.p. 215 °C; 51 %





When $R^2 = CH_3$:
633a, R^1 = H, m.p. 170.5–171 °C
633b, $R^1 = CH_3$, m.p., 185–187 °C

When $R^2 = C_6H_5$:
633c, R^1 = H, m.p. 249–250 °C

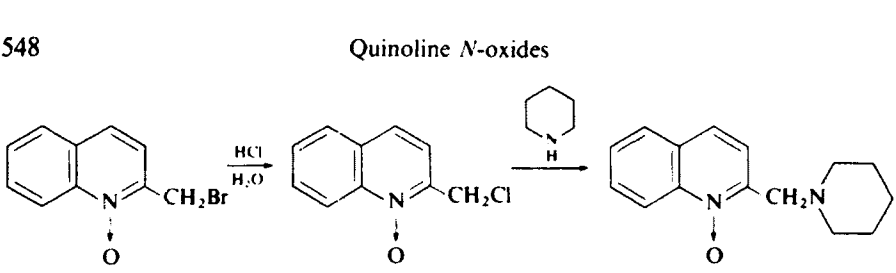


633d

Replacement of halide in side-chains has been achieved to give other halides, or amines. Dilute hydrochloric acid converted 2-bromomethylquinoline *N*-oxide to 2-chloromethylquinoline *N*-oxide (**634**),[60] which has been used to make the amines (**635**)[40] and (**636**).[469] A similar aziridine (**637**) was obtained from 2-chloromethyl-4-nitroquinoline *N*-oxide.[469]

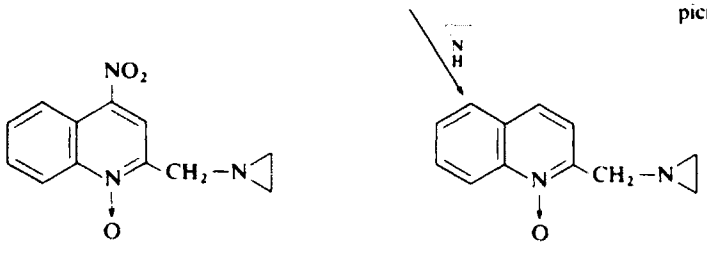
A combination of iodination and nucleophilic displacement is shown in the Ortoleva–King reaction which has been applied to quinaldine and lepidine *N*-oxides.[658] The products from these *N*-oxides and the pyridine–iodine complex were the *N*-(2-quinolylmethyl)pyridinium salt (**638**) and the corresponding 4-quinolylmethyl derivative (**639**). Introduction of an acetoxy group into a side-chain with retention of the *N*-oxide function (by thallium triacetate or lead tetraacetate[430,431]) has been dealt with in Section III.2.A.

A methyl group in position 2 of a quinoline *N*-oxide can be converted into a nitrile group by the action of acetyl chloride and silver nitrate in boiling chloroform.[386] The reaction proceeded via the oximinomethyl intermediate (**640**) and the oxime acetate (**641**). Examples are provided by the synthesis of compounds (**642–644**). The 4-chloro compounds (**645–647**) were obtained from 2-methyl-4-nitroquinoline *N*-oxide.[386]



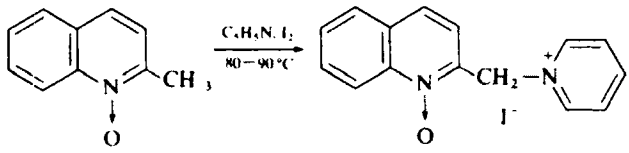
634, m.p. 124–125 °C

635, m.p. 90.5–91.5 °C; picrate, m.p. 158 °C

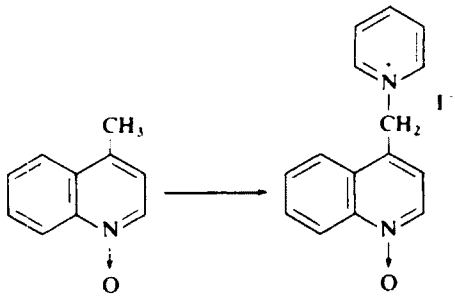


637, m.p. 164–165 °C

636, m.p. 79 °C



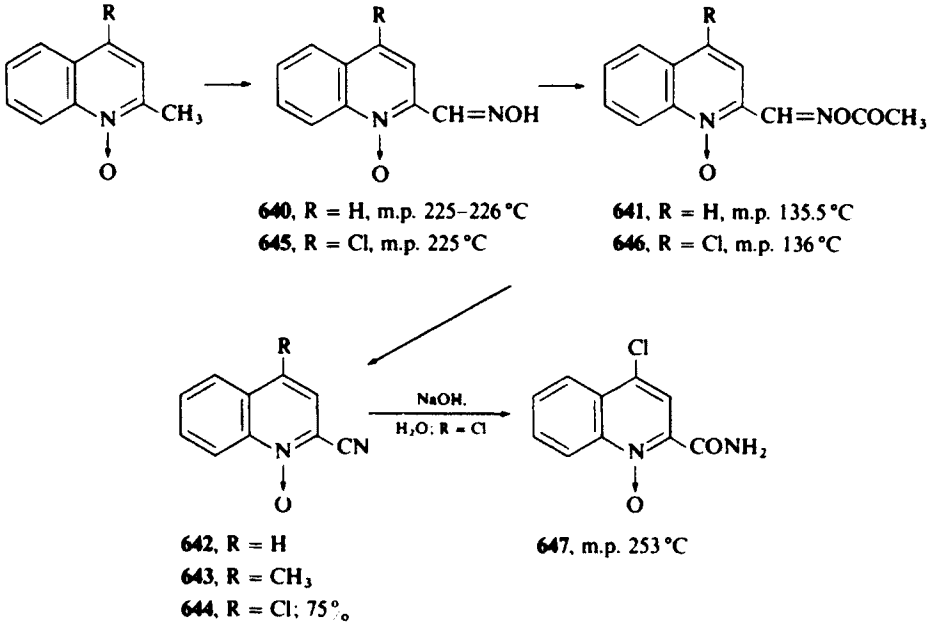
638, m.p. 190 °C; 75%



639, m.p. 196–197 °C;[683] 65%

The intermediate (**641**) was obtained by using silver nitrite and acetyl chloride, and the intermediates (**645**) and (**641**) or (**646**) by working at low temperatures.[386] The nitrile (**644**) was hydrolysed to give the amide (**647**).[386]

When a 2-methyl- or 4-methylquinoline *N*-oxide is heated with acetic anhydride the 2- or 4-acetoxymethylquinoline is formed. The mechanism of the rearrangement has been thoroughly examined in the pyridine series, and a good account of the work has appeared. The suggested mechanism for the quinoline *N*-oxides is shown in Scheme 20, and will be briefly discussed.[659]



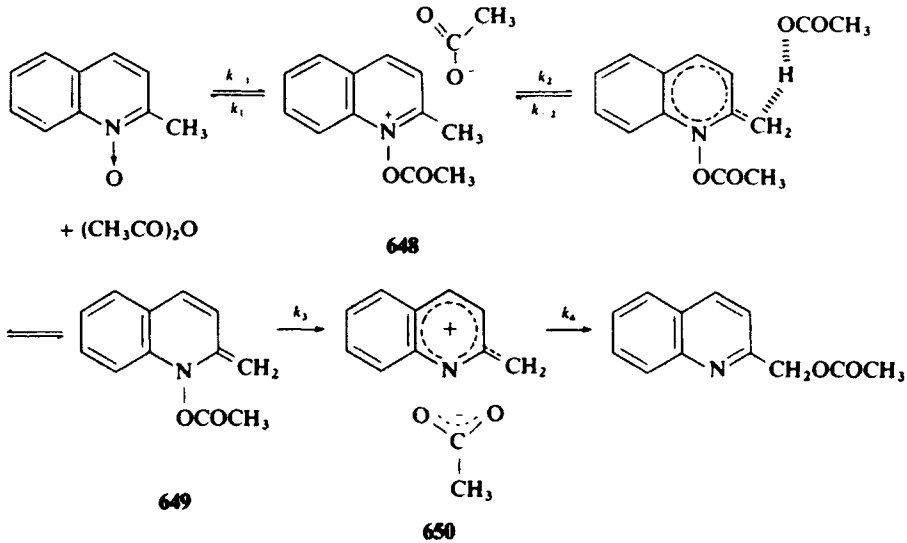
640, R = H, m.p. 225–226 °C
645, R = Cl, m.p. 225 °C

641, R = H, m.p. 135.5 °C
646, R = Cl, m.p. 136 °C

642, R = H
643, R = CH_3
644, R = Cl; 75%

647, m.p. 253 °C

The reaction kinetics have been examined[659-663] in solvents of differing polarity (dioxan, acetonitrile and dimethylformamide) and higher rates were observed with higher polarity of the solvent.[659] The kinetic isotope effect on the rates has been observed by using α,α,α-trideuteriomethylquinoline *N*-oxides, and has been shown to be >7 for lepidine *N*-oxide and for 6-methylquinaldine *N*-oxide, but low (<2) for quinaldine *N*-oxide.[661,659] The isotope effect was thought to indicate a higher stability of the 'anhydro



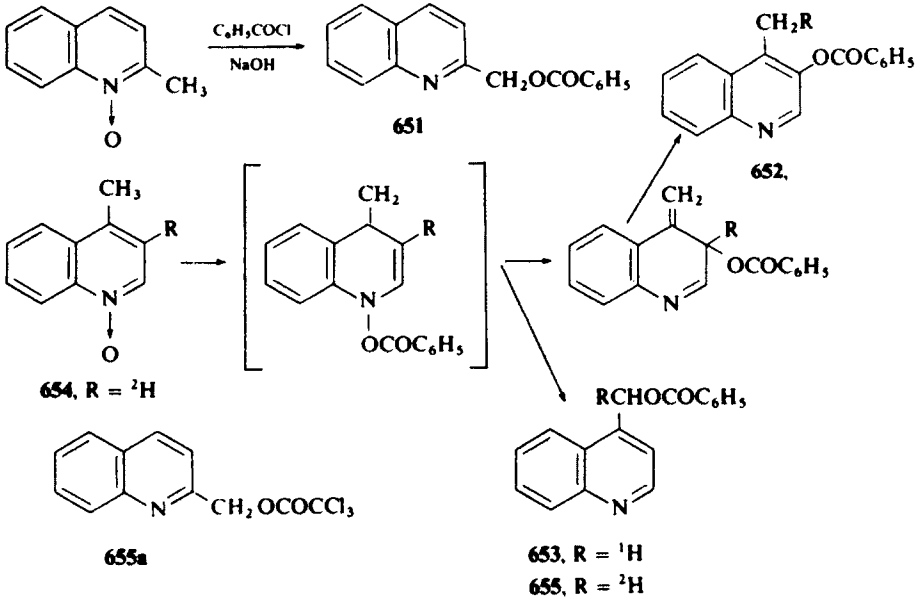
648

649

650

SCHEME 20

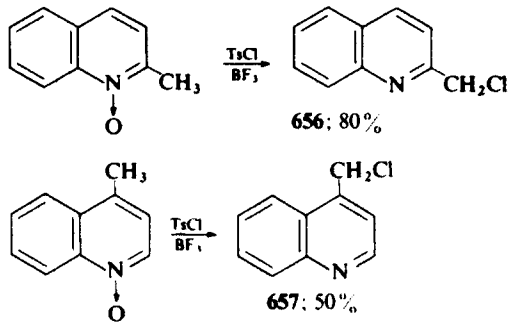
base' (**649**) for quinaldine, so that the importance of the deprotonation step (rate determining in the 'normal' rearrangements) was decreased, while N—O bond cleavage increased in importance. There is no physical evidence for the 'anhydro base' (**649**) in the quinoline series. The equivalence of the oxygen atoms in the acetoxymethyl group has been demonstrated for the pyridine series by the use of ^{18}O-labelled acetic anhydride,[664,665] and this has been interpreted on the basis of an ion pair (**650**) in a solvent cage. Similar labelling experiments with quinaldine *N*-oxide showed scrambling of the oxygen to be lower in a non-polar solvent than in a polar solvent, although still sufficiently high to exclude a non-dissociative rearrangement.[666,659] The first intermediate, the acetoxyquinolinium salt (**648**) has been isolated and the rate of its conversion into 2-acetoxymethylquinoline agreed well with those for reaction between the *N*-oxide and acetic anhydride.[660,667] There is a similar reaction between 2-methylquinoline *N*-oxide and benzoyl chloride in basic medium;[668] the product has been shown[669] to be 2-benzoyloxymethylquinoline (**651**). A mechanism similar to that proposed for the acetoxy migration has been proposed and ^{18}O labelling experiments have confirmed scrambling.[670] The similar reaction with 4-methylquinoline *N*-oxide gave 3-benzoyloxyquinoline (**652**) and 4-benzoyloxymethylquinoline (**653**).[561] The migration was suggested as proceeding via an anhydro base, and this seems to be confirmed by the observation that the 3-deuteriolepidine *N*-oxide (**654**) (50% labelled) gave a benzoyloxymethyl derivative (**655**) labelled in the methylene group.[561]



Reaction between trichloroacetyl chloride and quinaldine *N*-oxide gave 80% of the 2-trichloroacetyloxymethyl compound (**655a**).[818] The slight evolution of carbon dioxide indicated a heterolytic mechanism, and an ion pair was again suggested.

Related reactions, which could also be rationalized via an 'anhydro base' or a tight ion pair, are those in which 2- or 4-chloromethylquinolines (**656**) and (**657**) were obtained by treatment of quinaldine or lepidine *N*-oxide with *p*-toluenesulphonyl chloride and boron trifluoride in dimethylformamide[545] (some 4-chloromethylquinoline was obtained in the

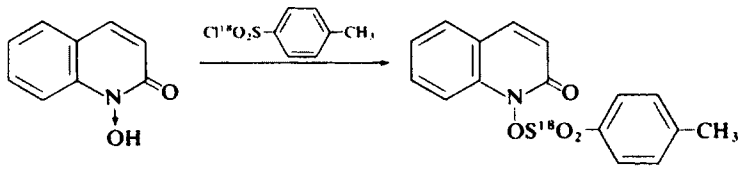
reaction between lepidine *N*-oxide and benzoyl chloride[561]). A series of 2-methylquinoline *N*-oxides when treated with tosyl chloride and other acid chlorides and sodium *p*-toluenesulphinate gave 2-*p*-tolylsulphonylmethylquinolines, as well as ring-substituted derivatives.[870] Some deoxygenation was observed.



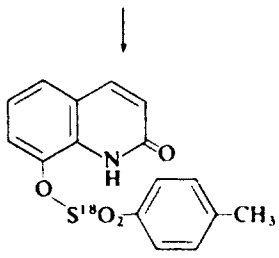
656; 80%

657; 50%

On the preparative scale, a yield of 60% of 2-hydroxymethylquinoline (after hydrolysis of the intermediate acetoxymethyl derivative) has been obtained.[671] The yield of 4-hydroxymethylquinoline was only 4% (most of the product was formed by the competing nuclear hydroxylation). From 2,4-dimethylquinoline *N*-oxide a 70% yield of 2-hydroxymethyl-4-methylquinoline was obtained.[672] Ketene has been used instead of acetic anhydride; quinaldine *N*-oxide gave a low yield of 2-hydroxymethylquinoline, and lepidine *N*-oxide a very small amount of 3-hydroxy-4-methylquinoline.[673] The conversion of 1-hydroxycarbostyril (**658**) into 8-tosyloxycarbostyril (**660**) on treatment with *p*-toluenesulphonyl chloride and pyridine[562] has been investigated by ^{18}O tracer studies on 1-tosyloxycarbostyril (**659**), the presumed intermediate.[674,816] The labelled intermediate (**659**) was heated in nitromethane or acetonitrile to give the labelled product (**660**); the scrambled labelling indicated that the solvent separated ion pair was involved.

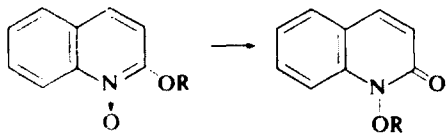


658 **659**



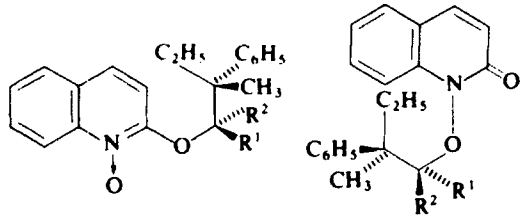
660

In this context it is interesting that the 2-alkyloxyquinoline *N*-oxides (**661**) are unstable; when heated in dimethylaniline all rearrange to the 1-alkyloxycarbostyril (**661a**).[675] The mechanism of this rearrangement has been studied.[676]



661. R = CH_3, C_2H_5, $CH_2C_6H_5$, C_3H_7 **661a**

The *erythro* (**662**) and *threo* (**663**) isomers of an oxide were rearranged at 170 °C and the product ratios (**664**) (**665**) determined by ^{1}H-nmr spectroscopy. By a CIDNP study it was possible to estimate the extent of rearrangement by the radical pair route [75% for compound (**662**), 20% for compound (**663**)], the remainder rearranging by a sigmatropic process. The radical pairs from (**662**) and (**663**) were identical by CIDNP.



662, R^1 = H, R^2 = C_6H_5
663, R^1 = C_6H_5, R^2 = H

664, R^1 = H, R^2 = C_6H_5
665, R^1 = C_6H_5, R^2 = H

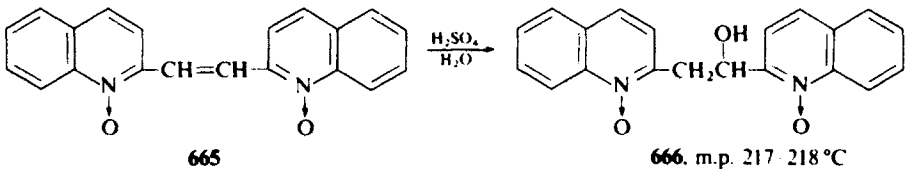
A variant of this reaction was the treatment of 2-ethoxyquinoline *N*-oxide with alkyl halides to give compounds of type (**661a**).[819] The intermediate *N*-alkoxy-2-ethoxyquinolinium salts were attacked by halide ion, with displacement of ethyl bromide.

b. Addition Reactions Hydrogenation of unsaturated side-chains is the commonest addition reaction; this has been treated in Section III.2.B. Dilute sulphuric acid caused the conversion of the diquinolylethene dioxide (**665**) into the alcohol (**666**),[427] which had been obtained as a by-product in the synthesis of the ethene (see next section).

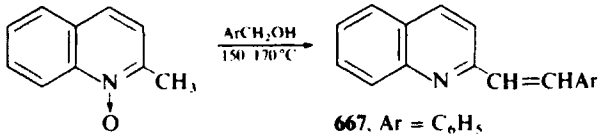
c. Condensation Reactions Methyl groups in positions 2 and 4 are activated towards condensation reactions and the acidity has been estimated by base-catalysed deuterium exchange.[847,849,850] A number of alkenylquinoline *N*-oxides have been prepared by reaction between the appropriate methylquinoline *N*-oxide and an aromatic aldehyde with the basic catalysts sodium or potassium methoxide,[110,35,406,368,677] or piperidine in acetic acid.[433] Alkenylquinolines (**667–669**) have been obtained from quinaldine or lepidine *N*-oxides by the action of benzyl alcohol or 2-pyridylmethanol and potassium hydroxide at 150–170 °C.[404] Other active methylene derivatives can conversely condense with quinoline carboxaldehyde *N*-oxides to give alkenylquinoline *N*-oxides, as illustrated by the preparation of the nitroalkenylquinoline *N*-oxides (**670**) and (**671**).[678,679]

Alkenylquinoline *N*-oxides thus prepared are listed in Table 27.

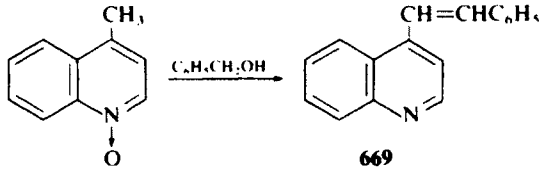
By treatment of quinaldine *N*-oxide with nitrobenzene[681] or nitrosobenzene[90] and base, 1,2-di(2-quinolyl)ethene (**672**) was obtained. Lepidine *N*-oxide and nitrobenzene[681] or nitrosobenzene[682] similarly gave the di(4-quinolyl)ethene (**673**). When *p*-dimethylaminonitrosobenzene was used with lepidine *N*-oxide, the nitrone (**674**) was obtained,[682] which hydrolysed to give the aldehyde *N*-oxide (**675**).



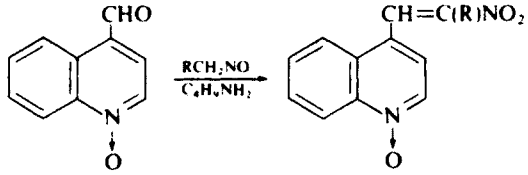
665 666, m.p. 217–218 °C



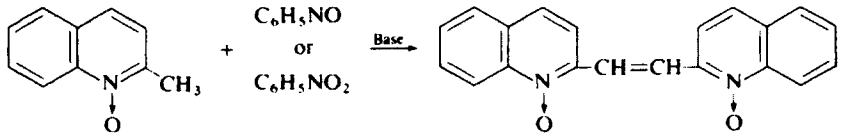
667, Ar = C_6H_5
668, Ar = 2-pyridyl



669



670, R = H, m.p. 215 °C
671, R = CH_3, m.p. 153 °C

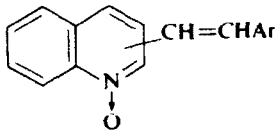


672, m.p. 243 °C

The pyridinium methyl salts mentioned in the previous section are very reactive in condensations. Condensation with *p*-dimethylaminonitrosobenzene has been variously reported to give the anil (**677**)[658] and the nitrone (**678**)[399] from the 2-quinolylmethylpyridinium salt (**676**), but there seems agreement that the 4-quinoline derivative (**679**) gives the nitrone (**680**).[399,658]

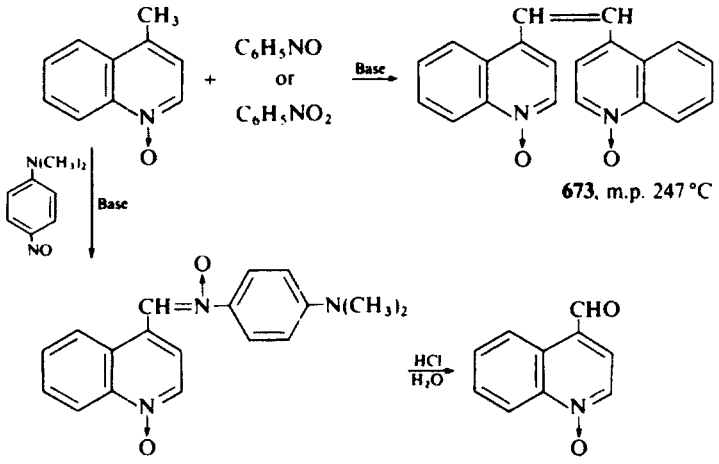
The anil (**677**) and the isomer (**681**) were also prepared from the appropriate quinoline aldehyde *N*-oxide and *p*-dimethylaminoaniline.[399] The nitrones (**678**) and (**680**) were rearranged to give the amides (**682**) and (**683**), respectively, when treated with acetic anhydride or phosphorus halides.[399]

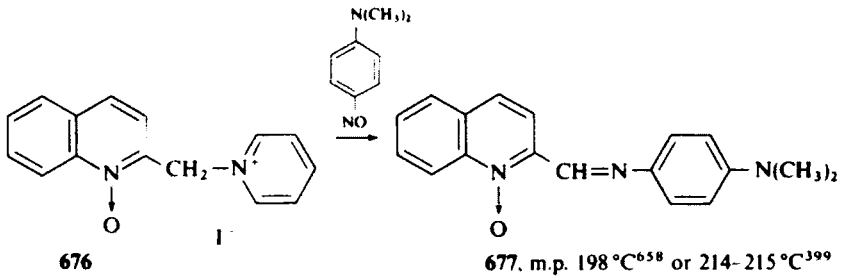
TABLE 27. Alkenylquinoline *N*-Oxides Prepared by Condensation of 2-Methyl- and 4-Methylquinoline *N*-Oxides with Aldehydes

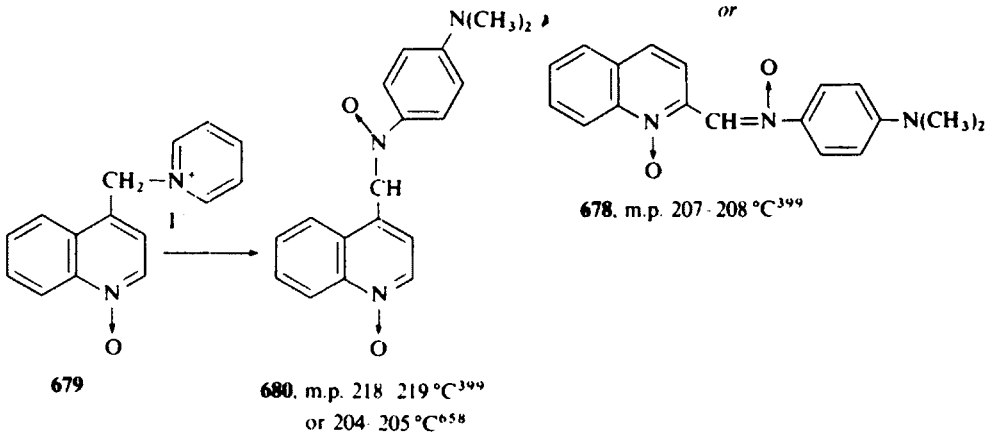


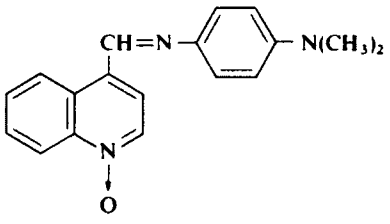
Substituent(s) in *N*-oxide	Aldehyde	Substituent(s) in product: Ar	2 or 4	Other substituents	Condensation conditions	Yield (%)	References	M.p. (°C)
2-Methyl	C_6H_5CHO	C_6H_5	2	—	$KOCH_3$, CH_3OH, boil	92.5	406, 35	123–124
2-Methyl	m-$CH_3C_6H_4CHO$	m-$CH_3C_6H_4$	2	—	$KOCH_3$, CH_3OH, boil	67	368	125
2-Methyl	p-$CH_3C_6H_4CHO$	p-$CH_3C_6H_4$	2	—	$KOCH_3$, CH_3OH, boil	86	406	151
2-Methyl	p-$C_2H_5C_6H_4CHO$	p-$C_2H_5C_6H_4$	2	—	$KOCH_3$, CH_3OH, boil	65	368	116
2-Methyl	p-$(CH_3)_2CHC_6H_4CHO$	p-$(CH_3)_2CHC_6H_4$	2	—	$KOCH_3$, CH_3OH, boil	81	406	75
2-Methyl	p-$(t$-$C_4H_9)C_6H_4CHO$	p-$(t$-$C_4H_9)C_6H_4$	2	—	$KOCH_3$, CH_3OH, boil	77	406	137
2-Methyl	m-ClC_6H_4CHO	m-ClC_6H_4	2	—	$KOCH_3$, CH_3OH, boil	81	368	165
2-Methyl	m-BrC_6H_4CHO	m-BrC_6H_4	2	—	$KOCH_3$, CH_3OH, boil	75	368	163
2-Methyl	p-FC_6H_4CHO	p-FC_6H_4	2	—	$KOCH_3$, CH_3OH, boil	71	368	105
2-Methyl	p-ClC_6H_4CHO	p-ClC_6H_4	2	—	$NaOCH_3$, CH_3OH, boil	64	677	192–193
2-Methyl	2,4-$Cl_2C_6H_3CHO$	2,3-$Cl_2C_6H_3$	2	—	$NaOCH_3$, CH_3OH, boil	83	677	180
2-Methyl	3,4-$Cl_2C_6H_3CHO$	3,4-$Cl_2C_6H_3$	2	—	$NaOCH_3$, CH_3OH, boil	70	677	204
2-Methyl	o-$O_2NC_6H_4CHO$	o-$O_2NC_6H_4$	2	—	$KOCH_3$, CH_3OH, boil	45	368	160
2-Methyl	m-$O_2NC_6H_4CHO$	m-$O_2NC_6H_4$	2	—	$KOCH_2$, CH_3OH, boil	56	368	189
2-Methyl	p-$O_2NC_6H_4CHO$	p-$O_2NC_6H_4$	2	—	$KOCH_3$, CH_3OH, boil	60	368	257
2-Methyl	o-$CH_3OC_6H_4CHO$	o-$CH_3OC_6H_4$	2	—	$KOCH_3$, CH_3OH, boil	80	368	148
2-Methyl	p-$CH_3OC_6H_4CHO$	p-$CH_3OC_6H_4$	2	—	$KOCH_3$, CH_3OH, boil	95	368, 677	140[368]
2-Methyl	2,3-$(CH_3O)_2C_6H_3CHO$	2,3-$(CH_3O)_2C_6H_3$	2	—	$KOCH_3$, CH_3OH, boil	70	368	140
2-Methyl	p-$(CH_3)_2NC_6H_4CHO$	p-$(CH_3)_2NC_6H_4$	2	—	$KOCH_3$, CH_3OH, boil	70	35, 677	224–225[35]
2-Methyl	p-$(CH_3)_2NC_6H_4CHO$	p-$(CH_3)_2NC_6H_4$	2	—	Piperidine, acetic acid, toluene	60	680	213–214
2-Methyl	p-$(C_2H_5)_2NC_6H_4CHO$	p-$(C_2H_5)_2NC_6H_4$	2	—	Piperidine, acetic acid, toluene	42	680	178.7–179.6
2-Methyl	9-Anthracenyl-CHO	9-Anthracenyl	2	—	$KOCH_3$, CH_3OH, boil	37	368	150

2-Methyl	Pyrenyl-CHO	Pyrenyl	2	—	$KOCH_3$, CH_3OH, boil	40	368	181
2-Methyl	1-Naphthyl-CHO	1-Naphthyl	2	—	$KOCH_3$, CH_3OH, boil	72	368	107
2-Methyl	2-Furyl-CHO	2-Furyl	2	—	$KOCH_3$, CH_3OH, boil	77	368	140
2-Methyl	2-Thienyl-CHO	2-Thienyl	2	—	$KOCH_3$, CH_3OH, boil	71	368	154
2-Methyl	2-Pyridyl-CHO	2-Pyridyl	2	—	$KOCH_3$, CH_3OH, boil	75	368	126
2-Methyl	2-Quinolyl-CHO	2-Quinolyl	2	—	$KOCH_3$, CH_3OH, boil	81	368	192
4-Methyl	C_6H_5CHO	C_6H_5	4	—	$KOCH_3$, CH_3OH, boil	—	35, 110	175–176;[35] 178–179[110]
4-Methyl	p-$(CH_3)_2NC_6H_4CHO$	p-$(CH_3)_2NC_6H_4$	4	—	$KOCH_3$, CH_3OH, boil	70	35, 110	199–200[35]; 208–209[110]
4-Methyl	4-Quinolyl-CHO	4-Quinolyl	4	—	$NaOCH_3$, CH_3OH, boil	—	90	242
2-Methyl-4-nitro	C_6H_5CHO	C_6H_5	2	4-NO_2	Piperidine, acetic acid, toluene	58	433, 506	178
2-Methyl-4-nitro	p-$CH_3OC_6H_4CHO$	p-$CH_3OC_6H_4$	2	4-NO_2	Piperidine, acetic acid, toluene	55	433, 506	173
2-Methyl-4-nitro	2-HO-3-$CH_3OC_6H_3CHO$	2-HO-3-$CH_3OC_6H_3$	2	4-NO_2	Piperidine, acetic acid, toluene	53	433, 506	218
2-Methyl-4-nitro	p-$(CH_3)_2NC_6H_4HCO$	p-$(CH_3)_2NC_6H_4$	2	4-NO_2	Piperidine, acetic acid, toluene	73	433, 506	182

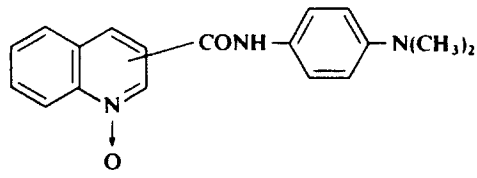

CH3
C6H5NO
or
C6H5NO2
Base
CH=CH
673, m.p. 247 °C
N(CH3)2
NO
Base
CH=N
N(CH3)2
HCl
H2O
CHO
674, m.p. 205 °C
675, m.p. 117 °C;
phenylhydrazone, m.p. 206–207 °C;
oxime, m.p. 239–240 °C;
semicarbazone, m.p. 245–246 °C


N(CH3)2
NO
CH2–N+
I
676
CH=N
N(CH3)2
677, m.p. 198 °C[658] or 214–215 °C[399]


N(CH3)2
or
CH2–N+
I
CH
CH=N
N(CH3)2
678, m.p. 207–208 °C[399]
679
680, m.p. 218–219 °C[399]
or 204–205 °C[658]

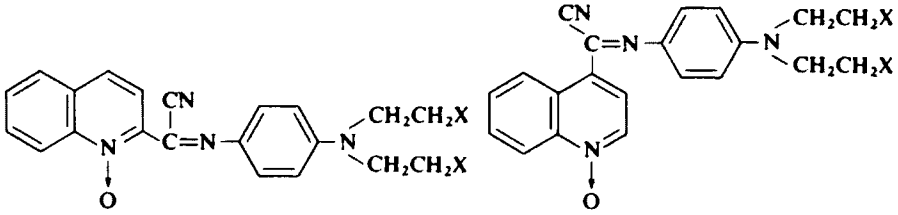


681



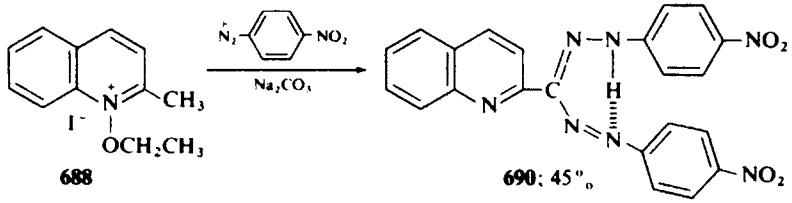
682, 2-substituted, m.p. 222–223 °C
683, 4-substituted, m.p. 252–253 °C; 53%

When the pyridinium salts (676) and (679) were treated with *p*-dialkylaminonitrosobenzenes in the presence of sodium cyanide the anils (684), (685) and (686), (687) were obtained.[683]



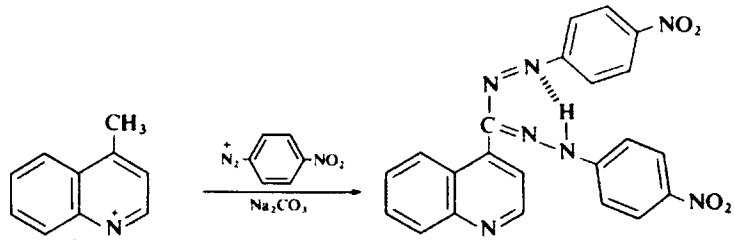
684, X = Cl, m.p. 154–156 °C; 48%
685, X = OH, m.p. 193–195 °C; 80%
686, X = Cl, m.p. 200–202 °C; 36%
687, X = OH, m.p. 180 °C; 53%

The ethiodides of quinaldine *N*-oxide and lepidine *N*-oxide (688) and (689) were treated with *p*-nitrobenzenediazonium chloride to give the formazans (690) and (691).[450]



688

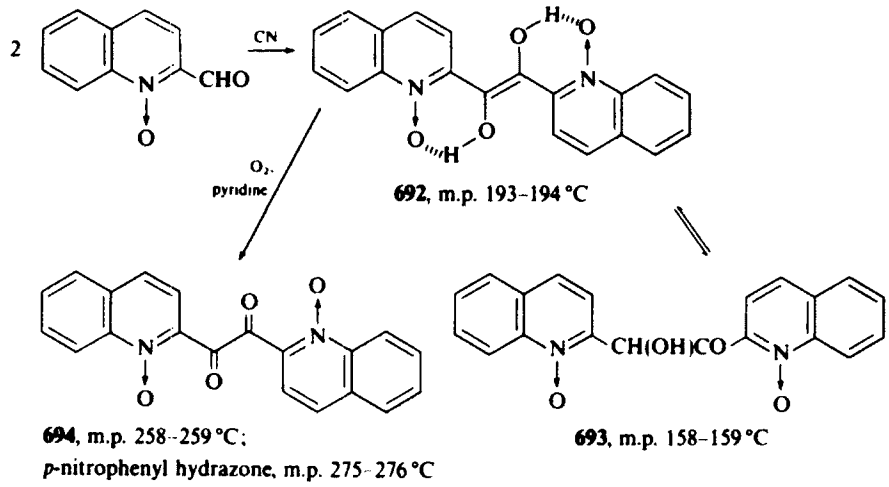
690; 45%



689

691; 80%

Quinoline-2-carboxaldehyde *N*-oxide undergoes a benzoin condensation when treated with potassium cyanide in aqueous pyridine,[427] giving a mixture of the tautomers (692) and (693). Oxidation of the enediol (692) in pyridine solution, using oxygen, gave the diketone (694).

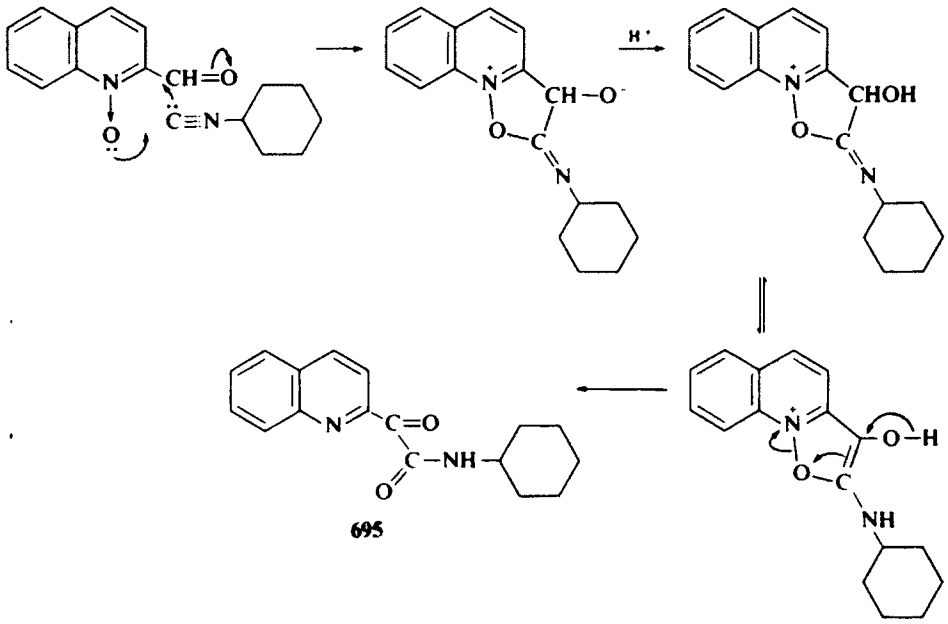


692, m.p. 193–194 °C

694, m.p. 258–259 °C;
p-nitrophenyl hydrazone, m.p. 275–276 °C

693, m.p. 158–159 °C

Quinoline-2-carboxaldehyde *N*-oxide also condenses with cyclohexylisocyanide to give a quantitative yield of the ketoamide (**695**).[684] The mechanism is shown in Scheme 21.

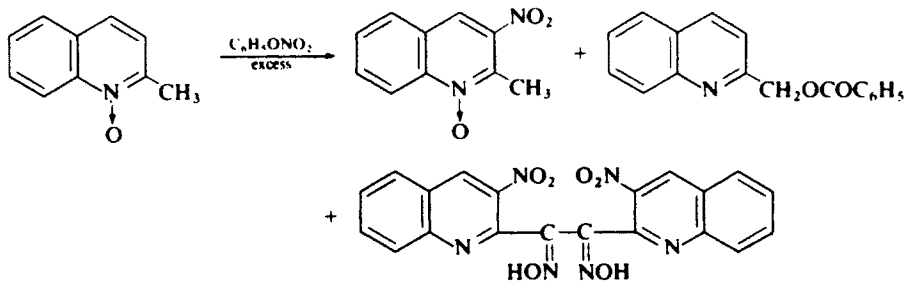


695

SCHEME 21

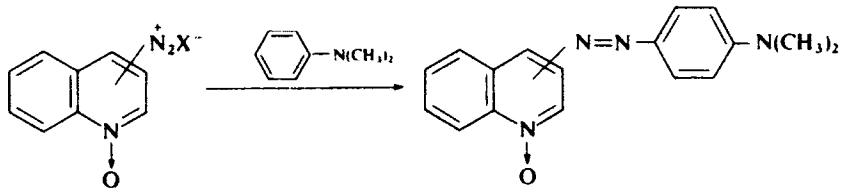
An unusual product from the reaction between quinaldine *N*-oxide and benzoyl nitrate was the dioxime (**696**).[685]

d. MISCELLANEOUS TRANSFORMATIONS OF SUBSTITUENTS Replacement of diazonium groups in quinoline *N*-oxides has been dealt with in Section D. All the possible quinoline



696

diazonium salt *N*-oxides (**697**) have been prepared and coupled with dimethylaniline to give the azo compounds (**698**).[34]



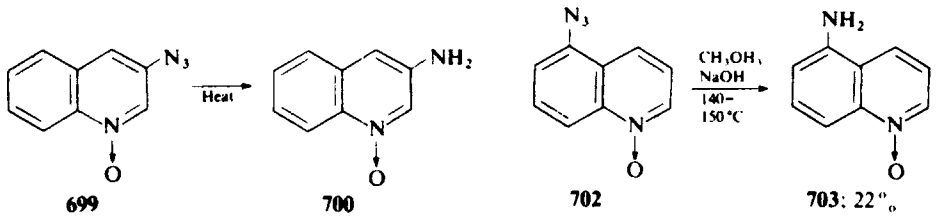
697 698

Position of substituent	Yield (%)	M.p. (°C)
2	45	191
3	69	193–194
4	41	199–200
5	72	197–198
6	73	224
7	71	217–218
8	55	171

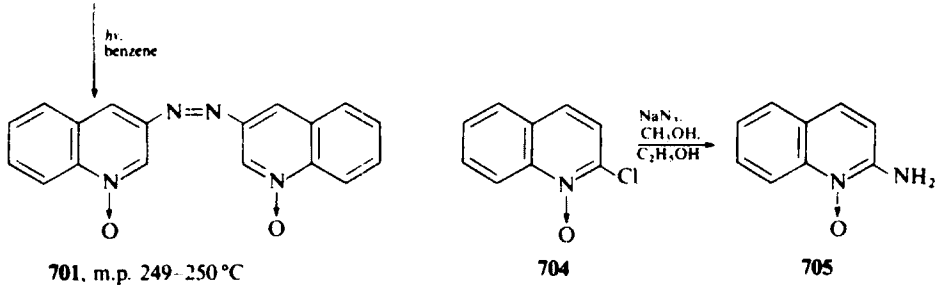
Quinoline *N*-oxides bearing an azide group at positions 2, 3, 4 and 5 have been prepared and their decomposition studied. Kamiya reported that when 3-azidoquinoline *N*-oxide (**699**) was heated in boiling xylene, or with methanol and sodium hydroxide at 130 °C, 3-aminoquinoline *N*-oxide (**700**) was formed.[11] Similarly, 5-azidoquinoline *N*-oxide (**702**) gave 5-aminoquinoline *N*-oxide (**703**), and when 2-chloroquinoline *N*-oxide (**704**) was heated with sodium azide in methanol and ethanol 2-aminoquinoline *N*-oxide (**705**) was formed.[11] Photolysis of 3-azidoquinoline *N*-oxide (**699**) gave the azo compound (**701**).

Decomposition of 4-azidoquinoline *N*-oxide (**706**) was also studied by Kamiya.[412] In benzene or toluene thermal decomposition gave the azocompound (**707**); photolysis in acetone gave a 78% yield of the azocompound (**707**), presumably from triplet azide, formed in high yield by the triplet-sensitizing ketone. On thermolysis in hydrogen-donating solvents 4-aminoquinoline *N*-oxide (**708**) was obtained. From acetoacetate anion and 4-azidoquinoline *N*-oxide the triazole (**709**) was obtained; malonate anion gave the triazole (**710**).[412] Kamiya also investigated the reaction between 4-azido-quinoline *N*-oxide (**706**) and methylating agents.[686]

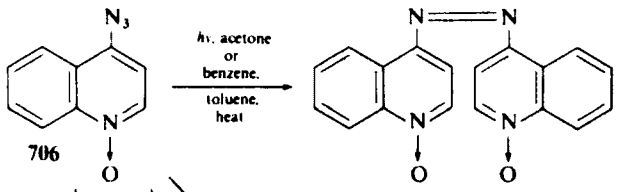
Abramovitch and Cue made a careful study of the decomposition of 2-azidoquinoline *N*-oxide (**711**).[491] Thermolysis in toluene gave 2-aminoquinoline *N*-oxide (**713**) and the



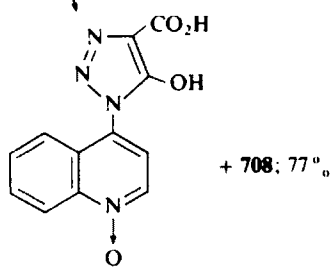
699 **700** **702** **703**: 22 %



701, m.p. 249–250 °C **704** **705**



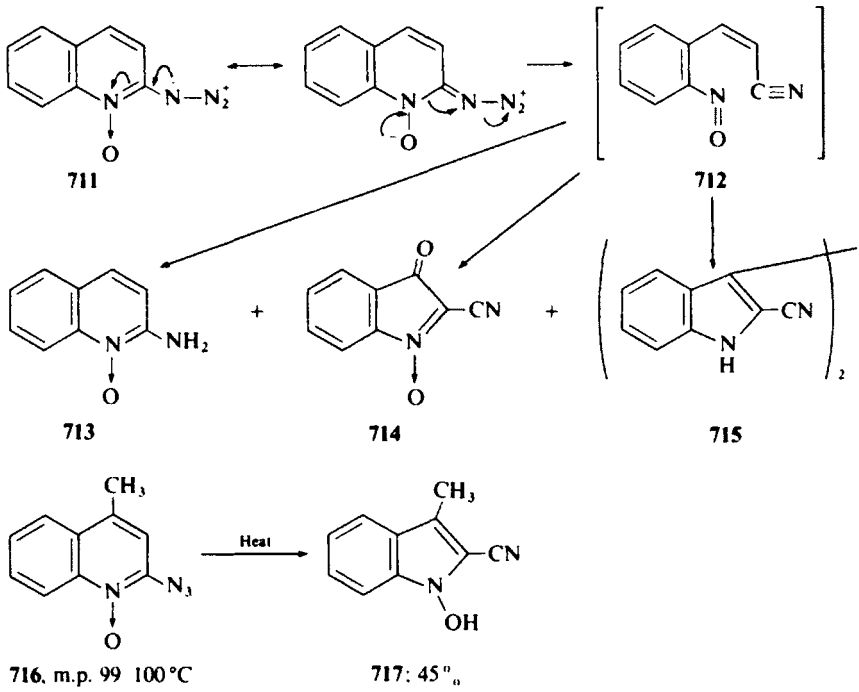
706 **707**, m.p. 235–236 °C (dec.) **708**: 58 % **709**, m.p. 205 °C (dec.)



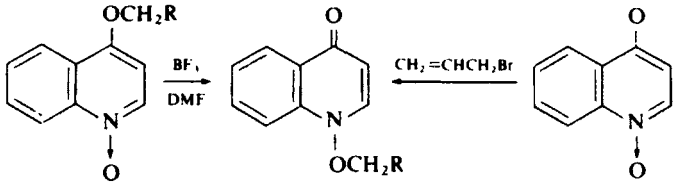
+ **708**: 77 %

710, m.p. 151–152 °C

ring-contracted products (**714**) and (**715**). It was improbable that a free nitrene was formed at this low thermolysis temperature, and a mechanism involving the ring-opened intermediate (**712**) was suggested. When 2-azidolepidine *N*-oxide (**716**) was used, the nucleophilic attack of oxygen which gave compound (**714**) was prevented, and *N*-hydroxy-2-cyano-3-methylindole (**717**) was formed.

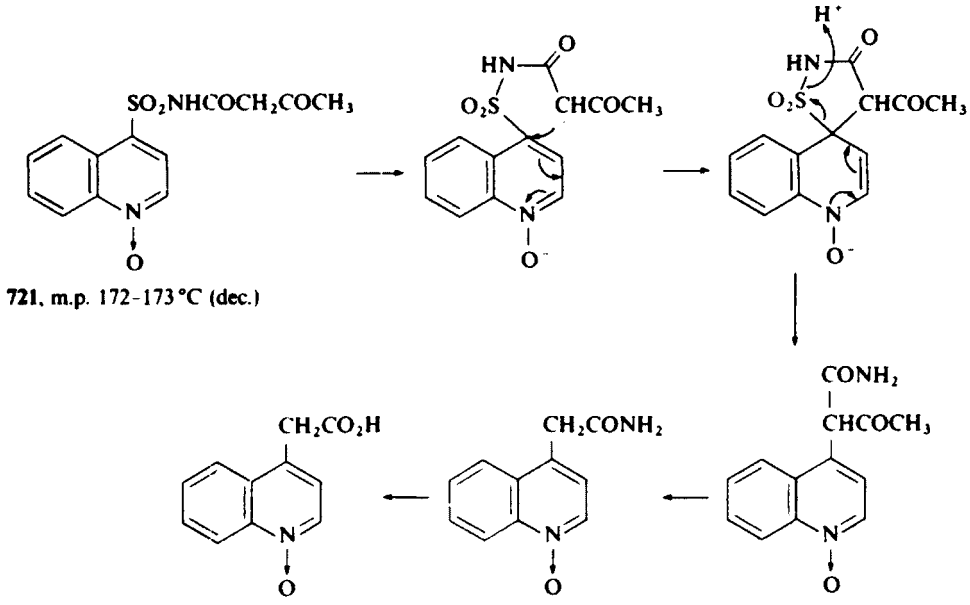


Rearrangement occurred when 4-benzyloxyquinoline *N*-oxide (**718**) or 4-allyloxyquinoline *N*-oxide (**719**) were heated with boron trifluoride in dimethylformamide.[687] Treatment of the anion from 4-hydroxyquinoline *N*-oxide with allyl bromide gave the 1-allyloxyquinolone (**720**).



718, R = C_6H_5
719, R = CH=CH_2
720, R = CH=CH_2

An interesting rearrangement was reported to occur when the sulphonamide (**721**) (prepared from 4-sulphamoylquinoline *N*-oxide and diketene) was treated with sodium hydroxide and the quinolylacetic acid *N*-oxide (**722**) was formed.[436] The mechanism is shown in Scheme 22.

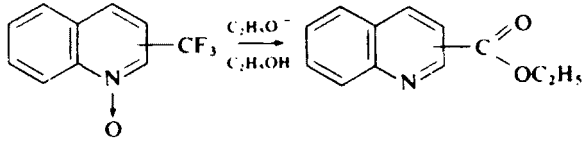


721, m.p. 172–173 °C (dec.)

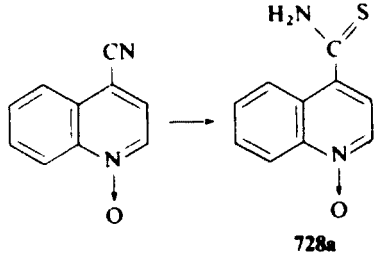
722, m.p. 113 °C (dec.)

SCHEME 22

A reversal of the normal reactivity pattern was reported when the trifluoromethylquinoline *N*-oxides (**723–725**) were boiled with sodium ethoxide in ethanol, the 3-substituted derivative (**724**) being converted into the ester (**727**) while the others were not affected.[688] At higher temperatures all three gave esters (**726–728**).



		78 °C	125–135 °C
723, 2-substituted	**726**, 2-substituted		32%
724, 3-substituted	**727**, 3-substituted	83%	62%
725, 4-substituted	**728**, 4-substituted		58%



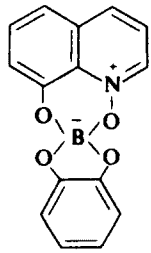
728a

The use of alcohols for deoxygenation has been previously mentioned (p. 430). Many cyanoquinoline *N*-oxides have been hydrolysed to give the corresponding amides (usually by alkaline hydrogen peroxide);[160,52] amides[181] and esters[166] can be hydrolysed to carboxylic acids. A thioamide (**728a**) has been obtained from the cyanide by treatment with hydrogen sulphide and a base.[689]

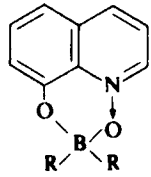
H. Quinoline N-oxides as Ligands

A very large number of inorganic complexes using *N*-oxides of quinoline and its derivatives have been prepared, and are listed in Table 28.

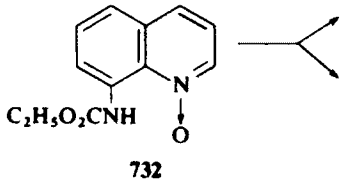
Additionally, 8-hydroxyquinoline *N*-oxide and the 5,7-dichloro or 5,7-dibromo derivatives have been reported as useful for the determination of iron,[744-746] cerium(IV),[747,748] thorium(IV),[747] uranium(VI),[749,750] and ruthenium(III).[751] Stability constants for complexes between 8-hydroxyquinoline *N*-oxide and many metals have been reported;[752,796] also between 5,7-dichloro-8-hydroxyquinoline *N*-oxide or 5,7-dinitroquinoline *N*-oxide and iron(III), aluminium(III), ytterbium(III) and lanthanum(III).[753] Extraction of manganese(II), iron(III) and cobalt(III) was less efficient with 8-hydroxyquinoline *N*-oxide than with 8-hydroxyquinoline.[754] Spiroborates of type (**729**) have been reported from catechol and 8-hydroxyquinoline *N*-oxide;[755] boron chelates (**730**) and (**731**) were formed from 8-hydroxyquinoline *N*-oxide, and the carbamate (**732**) formed two types of boron derivative (**733**) and (**734**).[756] The mass spectra of such boron chelates have been reported.[757]



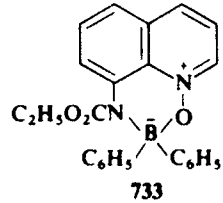
729



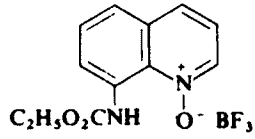
730, R = C_6H_5
731, R = F



732



733



734

TABLE 28. Metal Complexes with Quinoline *N*-Oxides as Ligands (L = *N*-Oxide Ligand)

Metal	*N*-Oxide substituent(s)	Complex	Physical properties reported	References
Copper	None	$LCuCl_2$	Magnetic	690, 691, 784
			Uv/visible	692, 693
	None	L_2CuCl_2	Magnetic	694
	None	$L_2Cu_2Cl_2$		695
	None	$LCuBr_2$	Magnetic	690, 691, 784
			Uv/visible	692, 693
	None	L_2CuBr_2	Magnetic	691, 694
	None	$LCu(C_2H_5OH)Cl_2$		696
	None	$LCu(i\text{-}C_5H_{11}OH)Cl_2$		695
	None	$LCu(CH_3COCH_3)Cl_2$		695
	None	$L_2Cu(NO_3)_2$	Magnetic, spectroscopic	692, 694
	None	$[L_4Cu][ClO_4]_2$	Magnetic, spectroscopic	692, 694
	None	$LCu(CH_3COO)_2$	Magnetic	691, 694
	None	$LCu(CH_3COO)_2 \cdot nH_2O$	Uv/visible, ir, magnetic	697, 698
	None	$LCu(C_6H_5COO)_2$	Magnetic susceptibility, absorption spectra	699, 700
	None	$LCu(o\text{-}HOC_6H_4COO)_2$	Magnetic	701
	None	$L_6Cu_2(p\text{-}HOC_6H_4COO)_2$	Epr	785
	2-Methyl	$LCuCl_2$ (DMF)	Magnetic, ir	702
	2-Methyl	$LCuCl_2$(DMSO)	Magnetic, ir	702
	2-Methyl	L_2CuBr_2	Magnetic, uv, ir	702, 693
	2-Methyl	$LCu(C_6H_5COO)_2$	Magnetic, absorption spectra	699
	4-Methyl	$LCuCl_2$	Magnetic, uv/visible	690, 693, 784
	4-Methyl	L_2CuCl_2	Magnetic	703
	4-Methyl	$LCuBr_2$	Magnetic, uv/visible	690, 693, 784
	4-Methyl	L_2CuBr_2	Magnetic	703
	4-Methyl	$LCu(CH_3COO)_2 \cdot nH_2O$	Uv/visible, magnetic, ir	697, 698
	4-Methyl	$LCu(C_6H_5)COO)_2$	Magnetic, absorption spectra	699
	6-Methyl	$LCuCl_2$	Magnetic, uv, ir	693
	6-Methyl	L_2CuCl_2	Magnetic	703
	6-Methyl	$LCuBr_2$	Magnetic, uv, ir	693
	6-Methyl	L_2CuBr_2	Magnetic	703

	4-Chloro	L_2CuCl_2	Magnetic, uv, ir	703, 693
	4-Chloro	$L_2(CuCl_2)_3$	Magnetic, uv, ir	703, 693
	4-Chloro	$LCuBr_2$	Magnetic, uv, ir	693
	4-Chloro	L_2CuBr_2	Low-temp. magnetic, uv, ir	703
	4-Chloro	$LCu(CH_3COO)_2.nH_2O$	Magnetic, uv/visible	697
	4-Chloro	$L_2Cu_2(CH_3COO)_4$	Magnetic, ir	698
	4-Nitro	$LCuCl_2$	Magnetic	703, 702, 704, 705, 693, 691
	4-Nitro	L_2CuCl_2	Magnetic	702
	4-Nitro	$LCuBr_2$	Magnetic	702, 705, 706, 693
	4-Chloro-6-methyl	L_2CuCl_2	Magnetic, uv/visible, ir	693
	4-Chloro-6-methyl	$L_2(CuCl_2)_3$	Magnetic, uv/visible, ir	693
	4-Chloro-6-methyl	$LCuBr_2$	Magnetic, uv/visible, ir	693
	4-Chloro-6-methyl	L_2CuBr_2	Magnetic, uv/visible, ir	693
	3-Nitro-6-methyl	L_2CuCl_2	Magnetic, uv/visible, ir	693, 703
	3-Nitro-6-methyl	$L_2(CuCl_2)_4$	Magnetic, uv/visible, ir	693
	3-Nitro-6-methyl	$LCuBr_2$	Magnetic, uv/visible, ir	693, 703
	3-Nitro-6-methyl	L_2CuBr_2	Magnetic, uv/visible, ir	693
	4-Nitro-6-methyl	$LCuCl_2$	Magnetic, uv/visible, ir	693
	4-Nitro-6-methyl	L_2CuCl_2	Magnetic, uv/visible, ir	693, 703
	4-Nitro-6-methyl	L_2CuBr_2	Magnetic, uv/visible, ir	693
	8-Hydroxy	L_2Cu	Uv/visible	707
Gold	None	$LAu(C_6F_5)_2P(C_6H_5)_3ClO_4$	Ir	708
Zinc	None	$L_6Zn(ClO_4)_2$	Magnetic, ir	709
	4-Methyl	$L_6Zn(ClO_4)_2$	Magnetic, ir	709
	4-Chloro	$L_6Zn(ClO_4)_2$	Magnetic, ir	709
	4-Nitro	$L_6Zn(ClO_4)_2$	Magnetic, ir	709
	4-Methoxy	$L_6Zn(ClO_4)_2$	Magnetic, ir	709
Rare earths	None	Various	Magnetic	710
LN = lanthanide	None	$L_3LnCl_3.H_2O$	—	711
	None	$L_4LnCl_3.H_2O$	—	711
	None	$L_7Ln[Cr(SCN)_6]$	—	786
	8-Hydroxy	L_2LnI	DTA, ir	712, 787
		$L_2Ln(NO_3)$	DTA, ir	712, 787
	2-Carboxy	$[(LH)_3Ln][Cr(NCS)_6]$	DTA, ir	712, 787, 788

TABLE 28 (*cont.*)

Metal	*N*-Oxide substituent(s)	Complex	Physical properties reported	References
Titanium	None	$L_5TiO(ClO_4)_2$	Uv/visible, ir	789
	None	L_2TiF_4	^{19}F-nmr, ir	713, 714, 715
	4-Methyl	L_2TiF_4	^{19}F-nmr, ir	714, 715
	6-Methyl	L_2TiF_4	^{19}F-nmr, ir	714, 715
	4-Chloro	L_2TiF_4	^{19}F-nmr, ir	714, 715
	6-Chloro	L_2TiF_4	^{19}F-nmr, ir	714, 715
	6-Bromo	L_2TiF_4	^{19}F-nmr, ir	714, 715
	4-Methoxy	L_2TiF_4	^{19}F-nmr, ir	714, 715
	6-Methoxy	L_2TiF_4	^{19}F-nmr, ir	714, 715
	8-Hydroxy	L_2TiO	Uv/visible	716
	4-Cyano	L_2TiF_4	^{19}F-nmr, ir	714, 715
Zirconium	None	$L_6ZrO(ClO_4)_2$	Uv/visible, ir	712, 789
	None	$ZrOCl_2.2L$	Conductance	790
Thorium	None	$L_6Th(ClO_4)_4$	Uv/visible, ir	712, 789
Tin	None	$L_2(CH_3)_2Sn(NCS)_2$	Ir	717
	None	$L(CH_3)_3Sn(NCS)$	Ir	717
	None	$L(C_6H_5)_3Sn(NCS)$	Ir	718
	None	$L(C_6H_5)_3SnCl$	Ir	783
	None	$L_2(C_6H_5)_2Sn(NCS)_2$	Ir	718
	None	$L(C_6H_5)_2Sn(NCS)_2$	Ir	718
	2-Methyl	$L(C_6H_5)_3SnCl$	—	783
Vanadium	None	L_2VOCl_2	Uv/visible, ir magnetic	719, 720, 790
	None	L_2VOBr_2	Uv/visible, ir magnetic	719
	None	$L_2VO(ClO_4)_2$	Uv/visible, ir magnetic	719
	None	$L_2VO(C_2O_4)$	Uv/visible, ir magnetic	719
	None	$L_2VO(SO_4)$	Uv/visible, ir magnetic	719
	None	$L_2VO(NCS)_2$	Uv/visible, ir magnetic	719
	None	$LVO(acac)_2$	Calorimetry	721, 722
	4-Methyl	$LVO(acac)_2$	Calorimetry	721, 722
	6-Methyl	$LVO(acac)_2$	Calorimetry	721
	4-Chloro	$LVO(acac)_2$	Calorimetry	721, 722

	6-Chloro	$LVO(acac)_2$	Calorimetry	721
	4-Nitro	$LVO(acac)_2$	Calorimetry	721, 722
	4-Methoxy	$LVO(acac)_2$	Calorimetry	721, 722
	6-Methoxy	$LVO(acac)_2$	Calorimetry	721
	8-Hydroxy	L_2VO	Magnetic	723
	2-Carboxy	L_2VO	—	791
Antimony	8-Hydroxy	$LSb(OCH_2CCl_3)Cl_4$	Ir	724, 725
Chromium	None	L_6CrO_5	Ir	726
	None	$L_6Cr(ClO_4)_3$	Magnetic, ir	709
	4-Methyl	$L_6Cr(ClO_4)_3$	Magnetic, ir	709
	4-Chloro	$L_6Cr(ClO_4)_3$	Magnetic, ir	709
	4-Nitro	$L_6Cr(ClO_4)_3$	Magnetic, ir	709
	4-Methoxy	$L_6Cr(ClO_4)_3$	Magnetic, ir	709
Molybdenum	None	$LMoO_2Cl_2$	Ir	727
	None	$LMoO_2(NO_3)_2$	Ir	727
	None	L_2MoOCl_2	Ir	727
		L_2MoOCl_2	Ir, molar conductance	793, 794
	None	$L_2MoO(NO_3)_2$	Ir	727
	None	L_3MoOCl_2	Ir	727
	None	$L_3MoO(NO_3)_2$	Ir	727
	8-Hydroxy	L_2MoOCl_2	Ir magnetic	728
	5,7-Dibromo-8-hydroxy	L_2MoOCl_2	Ir, magnetic	728
Uranium	None	$L_2UO_2Cl_2$	Uv/visible, ir	729–731, 790
	None	$L_2UO_2Br_2$	UV/visible, ir	729–731, 790
	None	$L_2UO_2(NO_3)_2$	Uv/visible, ir	729–731, 790
	None	$L_3UO_2(NCS)_2$	Uv/visible, ir	729–731, 790
Manganese	None	$LMnCl_2$ (solvent)	—	732
	None	L_2MnCl_2	—	732
	None	$L_3Mn(NCSe)_2$	Ir, uv/visible	733
	None	$L_2Mn(NCS)_2$	Ir, uv/visible	733
	None	$L_6Mn(ClO_4)_2$	Magnetic, uv/visible, ir	733
	4-Methyl	$L_6Mn(ClO_4)_2$	Magnetic, uv/visible, ir	709, 734
	4-Chloro	$L_6Mn(ClO_4)_2$	Magnetic, uv/visible, ir	709, 734
	4-Nitro	$L_6Mn(ClO_4)_2$	Magnetic, uv/visible, ir	709, 734
	4-Methoxy	$L_6Mn(ClO_4)_2$	Magnetic, uv/visible, ir	709, 734
Iron	None	$L_6Fe(ClO_4)_3$	Magnetic, ir	709
	None	$[L_4FeCl_2]FeCl_4$	Ir	735
	None	$[L_4Fe(NCS)_3]FeCl_4$	Ir	735

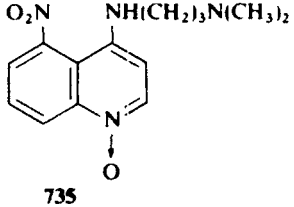
TABLE 28 (*cont.*)

Metal	*N*-Oxide substituent(s)	Complex	Physical properties reported	References
Iron	4-Methyl	$L_6Fe(ClO_4)_3$	Magnetic, ir	709
	4-Chloro	$L_6Fe(ClO_4)_3$	Magnetic, ir	709
	4-Nitro	$L_6Fe(ClO_4)_3$	Magnetic, ir	709
	4-Methoxy	$L_6Fe(ClO_4)_3$	Magnetic, ir	709
	8-Hydroxy	Various		736
Cobalt	None	$LCoCl_2.H_2O$	—	737
	None	L_2CoCl_2	—	737
	None	$L_2Co(NCS)_2$	Uv/visible, ir	733
	None	$L_2Co(NCSe)_2$	Uv/visible, ir	733
	None	$L_6Co(ClO_4)_2.H_2O$	Magnetic	692
	None	$L_6CoX_2.5H_2O$	Magnetic, ir, uv/visible	738
	None	$LCo(acac)_2$	Nmr, ir	727
	2-Methyl	$L_2Co(NO_2)_2$	Magnetic, ir, uv/visible	739
	4-Methyl	$L_6CoX_2.5H_2O$	Magnetic, uv/visible, ir	738
	4-Methyl	$L_2Co(NO_2)_2$	Ir	792
	4-Chloro	$L_6CoX_2.5H_2O$	Magnetic, uv/visible, ir	738
	4-Nitro	$L_6CoX_2.5H_2O$	Magnetic, uv/visible, ir	738
	4-Methoxy	$L_6CoX_2.5H_2O$	Magnetic, uv/visible, ir	738
Nickel	None	$LNiCl_2$	Spectrophotometry	740
	None	L_2NiCl_2	Spectrophotometry	740
	None	$LNiCl.H_2O$	Magnetic	741
	None	$L_2Ni(NCS)_2$	UV/visible, ir	733
	None	$L_2Ni(NCSe)_2$	Uv/visible, ir	733
	None	$L_3Ni(NO_3)_2nH_2O$	Magnetic	741
	None	$L_6Ni(ClO_4)_2.H_2O$	Magnetic	692
	None	$L_6NiX_2.nH_2O$	Uv/visible, ir, magnetic	738
	None	$L_2Ni(acac)_2$	Nmr, spin density, ir	339, 272
	2-Methyl	$L_2Ni(NO_3)_2.4H_2O$	Magnetic	339
	4-Methyl	$L_6NiX_2.H_2O$	Uv/visible, magnetic, ir	738
	4-Methyl	$L_2Ni(ONO)_2$	—	738
	6-Methyl	L_6NiX_2	Uv/visible, magnetic, ir	742

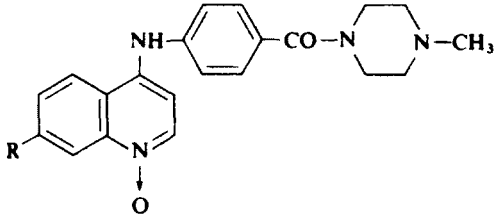
	4-Chloro	$L_6NiX_2.3H_2O$	Uv/visible, magnetic, ir	738
	6-Chloro	L_6NiX_2	Uv/visible, magnetic, ir	742
	6-Bromo	L_6NiX_2	Uv/visible, magnetic, ir	742
	4-Nitro	$L_6NiX_2.6H_2O$	Uv/visible, magnetic, ir	738
	6-Nitro	L_6NiX_2	Uv/visible, magnetic, ir	742
	4-Methoxy	$L_6NiX_2.3H_2O$	Uv/visible, magnetic, ir	738
	6-Methoxy	L_6NiX_2	Uv/visible, magnetic, ir	742
Platinum, palladium, osmium and iridium	8-Hydroxy	Various	Spectra	743

I. Quinoline N-oxides with Medical or Industrial Uses

Some 4-substituted quinoline *N*-oxides are potent carcinogens and mutagens; these are dealt with in Section J. The 4-aminoquinoline *N*-oxide (**735**) was reported to inhibit tumour growth (Crocker's sarcoma);[758] the amines (**736**) and (**737**) caused a decrease in arterial blood pressure.[172] Some quinoline *N*-oxides were tested for protective effect against X-rays.[759] Oxidation of 2-phenylquinoline-4-carboxylic acid gave the *N*-oxide; some esters and salts were prepared in an attempt to make a less toxic agent for treatment of rheumatism and gout.[166] A number of quinoline-2-thiol *N*-oxides and their sodium or zinc salts were reported to combat dandruff.[760,495]

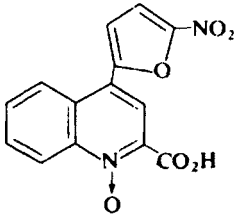


735

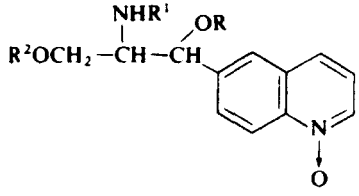


736, R = Cl
737, R = CF_3

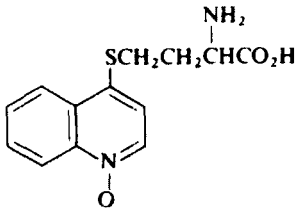
Most of the reported applications involve antibacterial or antifungal activity. In the former class were methylquinoline *N*-oxides and their 4-nitro and 3-chloro-4-nitro derivatives,[761] styrylquinoline *N*-oxides,[506,433] (nitrofuryl)vinylquinoline *N*-oxides,[37,87,88] nitrovinylquinoline *N*-oxides,[112,678,679] the quinaldic acid *N*-oxide (**738**),[762,763] the 6-substituted compounds of type (**739**),[114] the thioether (**740**),[516] 1-hydroxy-2-quinolone[55] and 4-nitro[764,112] or 4-aminoquinoline *N*-oxides.[764] The effect of 2-*n*-heptyl-4-hydroxyquinoline *N*-oxide as a chemotactic repellent for *Bacillus subtilis*



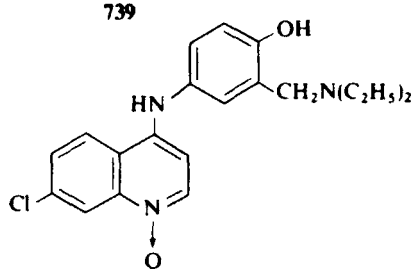
738, Quinaldofur



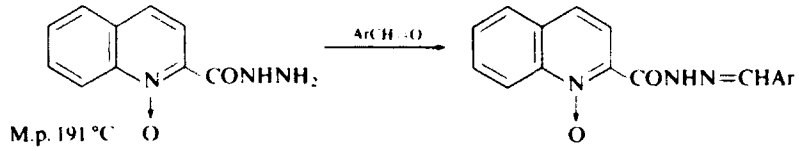
739



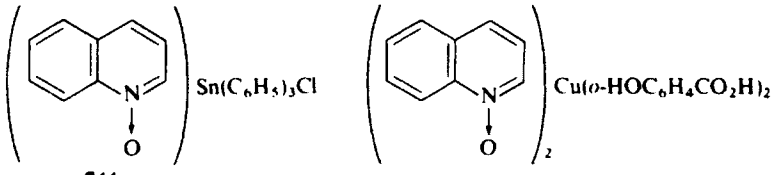
740



743



741. Ar = *p*-HOC_6H_4. m.p. >250 °C; 70%
742. Ar = *p*-$(CH_3)_2NC_6H_4$. m.p. 228 °C; 60%



744 **745**

has been studied.[765] The hydrazides (**741**) and (**742**) showed inhibitory effects on *Mycobacterium tuberculosis*.[52]

Compound (**738**) has been shown to be effective against udder irritation.[762,763] A number of 7-chloro-4-alkylaminoquinoline *N*-oxides have been reported as active against malarial parasites.[507,57,478,766] An outstandingly effective example was said to be compound (**743**).[57]

Antifungal activity has been reported for compounds (**739**),[114] for 6-methyl-4-nitroquinoline *N*-oxide[112] and other nitroquinoline *N*-oxides,[455,84,335,767,768,769,798] styrylquinolines,[433,506] 4-chloroquinoline *N*-oxide (active in the soil to control spore formation of *Erysiphe cinchoracearum*),[770] β-(5-nitrofuryl)vinylquinoline *N*-oxides,[37] the tin complex (**744**)[783,875] and the copper complex (**745**).[771] Addition of 4-nitroquinoline *N*-oxide to gasoline as an antifungal agent has been reported;[772] quinoline *N*-oxide itself has been added to gasoline to prevent carburettor icing,[773] used as a bird and rodent repellent[774] and with diethylzinc in toluene solution to give stereoregular polymers from alkylene oxides.[775] A more complex mixture for the production of stereoregular polypropylene contained δ-titanium chloride ($3TiCl_3.AlCl_3$), an organoaluminium such as $C_2H_5AlCl_2$ and an amine oxide such as quinoline *N*-oxide.[776] Patents have been claimed for photographic material containing a desensitizing material such as 4-nitroquinoline *N*-oxide[777] and for improvement in speed of an emulsion in which a variety of compounds are activated by an organohalide or sulphur compound by addition of an *N*-oxide (including quinoline *N*-oxide).[778] *N*-Oxides of quinoline have also been used as photoactivators, the light producing free radicals from the *N*-oxide which caused a dye-forming or bleaching colour change.[779] Whereas 2- and 4-methylquinoline *N*-oxides have been reported as plant growth stimulants[780] and 7-chloroquinoline *N*-oxide as a herbicide,[781] quinoline *N*-oxide applied to cotton seeds did not affect growth or the total auxin level in 1–14-day-old seedlings, but decreased the ratio between free and bound auxins.[782,1396,1397] Other industrial uses include brightening baths[799] and tyre vulcanization (2- and 4-nitroquinoline *N*-oxides).[800] Polyvinylquinoline *N*-oxides have been prepared by oxidation of polyvinylquinolines.[801]

J. Biological Effects of 4-Nitroquinoline N-oxide, 4-Hydroxyaminoquinoline N-oxide and Related Compounds

A very large number of papers have been published in medical and biological journals on the potent carcinogenic effects of 4-nitroquinoline *N*-oxide and 4-hydroxyaminoquinoline *N*-oxide. A detailed review is outside the scope of this chapter, but a

bibliography up to 1979 is included. There are two major reviews of the topic. The first is a monograph, *Recent Results in Cancer Research*, **34** (1971), and the second a review in *Advances in Cancer Research*, **23**, 131–169 (1976). The subsections given below follow the plan of the first of these reviews; all references in a sub-section are arranged chronologically.

a. Tumour production *in vivo*, references 876–1000.
b. Tumour production *in vitro*, references 1001–1072.
c. Cytological effects, references 1073–1085.
   (i) Chromosome aberrations (cytology), references 1086–1092.
   (ii) Chromosomes in animal cells, references 1093–1101.
d. Metabolism, references 1102–1037.
e. Interaction with DNA, references 1138–1187.
f. Biophysics, charge-transfer complexes, etc., references 1188–1198.
g. Frame shift mutations, references 1199–1205.
h. Base pair mutations, references 1206–1215.
i. Sister chromatid exchange, references 1216–1220.
j. DNA repair, references 1221–1264.
k. RNA effects, references 1265–1268.
l. Interaction with protein, references 1269–1285.
m. Immunological experiments, references 1286–1292.
n. Anticancer effects, references 1293–1299.
o. Microbiology.
   (i) Effect on fungi, references 1300–1319.
   (ii) Effects on bacteria, references 1320–1331.
   (iii) Effects on yeasts, references 1332–1353.
   (iv) Effects on protozoa, references 1354–1362.
p. Screening tests, references 1363–1372.
q. Oxidation inhibition and inhibition of photoreduction by 2-*n*-heptyl-4-hydroxyquinoline *N*-oxide, references 1373–1379.
r. Carcinogenic and anti-cancer effects of 2-[2-(5-nitro-2-furyl)vinyl]quinoline *N*-oxide, references 1380–1387.
s. Miscellaneous. Effects on respiration and glycolysis, references 1388–1390; effect on DPN dep. enzymes, references 1391–1392; haematological effects of 4-nitro-6-carboxyquinoline *N*-oxide, reference 1393; cytocidical effects of 4-nitroquinoline *N*-oxide, reference 1394; kynurenic acid metabolism, reference 1395.

IV. References

1. J. Meisenheimer, *Ber.*, **59**, 1848 (1926).
2. E. Ochiai, *Aromatic Amine Oxides*, Elsevier, Amsterdam, 1967.
3. A. R. Katritzky and J. M. Lagowski, *Chemistry of the Heterocyclic N-Oxides*, Academic Press, London and New York, 1971.
4. E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).
5. M. Bobranski, *Ber.*, **69**, 1113 (1936).
6. M. Bobranski, *Ber.*, **71**, 578 (1938).
7. G. R. Clemo and H. McIlwain, *J. Chem. Soc.*, **1938**, 479.
8. E. Ochiai, M. Katada and E. Hayashi, *Yakugaku Zasshi*, **67**, 33 (1947); *Chem. Abstr.*, **45**, 9541 (1951).
9. Y. Kobayashi, I. Kumadaki and S. Taguchi, *Chem. Pharm. Bull.*, **17**, 2335 (1969).
10. C. A. Benassi, F. M. Veronese, A. De Antoni and P. Pajetta, *Gazz. Chim. Ital.*, **97**, 3 (1967); *Chem. Abstr.*, **69**, 107031 (1968).
11. S. Kamiya, *Yakugaku Zasshi*, **81**, 1743 (1961); *Chem. Abstr.*, **57**, 16556 (1962).

12. J. Foucart, J. Nasielski and E. Van Der Donckt, *Bull. Soc. Chim. Belg.*, **75**, 17 (1966); *Chem. Abstr.*, **64**, 17376 (1966).
13. S. Saeki, H. Honda, Y. Kaku, K. Funakoshi and M. Hamana, *Heterocycles*, **7**, 801 (1977).
14. M. Yamazaki, N. Honjo, K. Noda, Y. Chono and M. Hamana, *Yakugaku Zasshi*, **86**, 749 (1966); *Chem. Abstr.*, **65**, 20095 (1966).
15. R. C. Whitman, *U.S. Pat.* 3,047,579; *Chem. Abstr.*, **58**, 7916 (1962).
16. C. A. Tolstikov, U. M. Emileev, V. P. Yur'ev, F. B. Gershanov and S. R. Rafikov, *Tetrahedron Lett.*, **1971**, 2807.
17. S. Tamura, *Yakugaku Zasshi*, **81**, 855 (1961); *Chem. Abstr.*, **55**, 24745 (1961).
18. D. H. Hey, K. S. Y. Liang and M. J. Perkins, *J. Chem. Soc. C*, **1967**, 2679.
19. E. Ochiai, C. Kaneko, I. Shimada, Y. Murata, T. Kosuge, S. Miyashita and C. Kawasaki, *Chem. Pharm. Bull.*, **8**, 126 (1960).
20. E. Ochiai, H. Tanedo and S. Uyeda, *Chem. Pharm. Bull.*, **5**, 188 (1957).
21. E. Ochiai and H. Tanida, *Chem. Pharm. Bull.*, **5**, 621 (1957).
22. E. Hayashi and N. Shimada, *Yakugaku Zasshi*, **97**, 123 (1977); *Chem. Abstr.*, **87**, 23002 (1977).
23. H. Ito, *Chem. Pharm. Bull.* **12**, 345 (1964).
24. T. Nakashima and I. Suzuki, *Chem. Pharm. Bull.*, **17**, 2293 (1969).
25. M. Bellas and H. Suschitzky, *J. Chem. Soc.*, **1963**, 4007.
26. K. Ramaiah and V. R. Srinavasan, *Proc. Indian Acad. Sci.*, **55A**, 360 (1962); *Chem. Abstr.*, **59**, 567 (1963).
27. A. Risaliti, *Ric. Sci.*, **24**, 2351 (1954); *Chem. Abstr.*, **49**, 15902 (1955).
28. A. M. Khaletskii, V. G. Pesin and C. Tsin, *Zh. Obshch. Khim.*, **28**, 2348 (1958); *Chem. Abstr.*, **53**, 3261 (1959).
29. I. Murase and Y. Demura, *Mem. Fac. Sci. Kyushu Univ. Ser. C*, **4**, 175 (1961); *Chem. Abstr.*, **58**, 3390 (1963).
30. H. Ito, *Chem. Pharm. Bull.*, **12**, 350 (1964).
31. H. Gilman, J. L. Towle and S. M. Spatz, *J. Amer. Chem. Soc.*, **68**, 2017 (1946).
32. R. T. Coutts, K. W. Hindmarsh and G. E. Myers, *Can. J. Chem.*, **48**, 2393 (1970).
33. R. W. Gouley, G. W. Moersch and H. S. Mosher, *J. Amer. Chem. Soc.*, **69**, 303 (1947).
34. E. V. Brown, R. M. Novack and A. A. Hamdan, *J. Org. Chem.*, **26**, 2831 (1961).
35. L. Dentimalli, *Gazz. Chim. Ital.*, **93**, 1093 (1963); *Chem. Abstr.*, **60**, 4108 (1964).
36. C. F. Boehringer und Soehne GmbH, *Belg. Pat.* 616,437; *Chem. Abstr.*, **59**, 12770 (1963).
37. R. R. G. Haber and E. Schoenberger, *S. Afr. Pat.* 66 03320; *Chem. Abstr.*, **71**, 91337 (1969).
38. M. Hamana and H. Noda, *Chem. Pharm. Bull.*, **13**, 912 (1965).
39. J. D. Baty, G. Jones and C. Moore, *J. Org. Chem.*, **34**, 3295 (1969).
40. E. Ochiai, S. Suzuki, Y. Utsunomiya, T. Ohmoto, K. Negatomo and M. Itoh, *Yakugaku Zasshi*, **80**, 339 (1960); *Chem. Abstr.*, **54**, 18525 (1960).
41. H. Kataoka, quoted in *Aromatic Amine Oxides*, ed. E. Ochiai, Elsevier, Amsterdam, 1967.
42. G. Kobayashi, Y. Kuwayama and S. Okamura, *Yakugaku Zasshi*, **83**, 234 (1963); *Chem. Abstr.*, **59**, 5144 (1963).
43. D. E. Ames, C. S. Franklin and T. F. Grey, *J. Chem. Soc.*, **1956**, 3079.
44. A. R. Katritzky, *J. Chem. Soc.*, **1957**, 4385.
45. M. Hamana and S. Kumadaki, *Chem. Pharm. Bull.*, **22**, 1506 (1974).
46. M. Hamana, S. Nomura and T. Kawakita, *Yakugaku Zasshi*, **91**, 134 (1971); *Chem. Abstr.*, **74**, 87787 (1971).
47. E. Ochiai, T. Okamoto and Y. Kobayashi, *Yakugaku Zasshi*, **68**, 109 (1948); *Chem. Abstr.*, **47**, 7513 (1953).
48. E. Ochiai and M. Ishikawa, *Chem. Pharm. Bull.*, **6**, 208 (1958).
49. E. Ochiai, M. Ishikawa and Y. Oka, *Chem. Pharm. Bull.*, **7**, 744 (1959).
50. A. Risaliti and L. Pentimalli, *Ann. Chim. (Rome)*, **46**, 1050 (1956); *Chem. Abstr.*, **51**, 8742 (1957).
51. T. Itai and S. Kamiya, *Chem. Pharm. Bull.*, **9**, 87 (1961).
52. Y. Hamada, *Yakugaku Zasshi*, **79**, 908 (1959); *Chem. Abstr.*, **54**, 539 (1960).
53. H. U. Daeniker and J. Druey, *Helv. Chim. Acta*, **41**, 2148 (1956).
54. J. W. Cornforth and A. T. James, *Biochem. J.*, **63**, 124 (1956).
55. W. A. Lott and E. Shaw, *J. Amer. Chem. Soc.*, **71**, 70 (1949).
56. J. Ellis, E. Gellert and J. Robson, *Aust. J. Chem.*, **26**, 907 (1973).

57. E. F. Elslager, E. H. Gold, F. H. Tendick, L. M. Werbel and D. F. Worth, *J. Heterocycl. Chem.*, **1**, 6 (1964).
58. E. F. Elslager and F. H. Tendick, *Brit. Pat.* 974,348; *Chem. Abstr.*, **62**, 7735 (1965).
59. G. Heller, W. Dietrich and G. Reichardt, *J. Prakt. Chem.*, **118**, 138 (1928).
60. M. Hasegawa, *Yakugaku Zasshi*, **73**, 1326 (1953); *Chem. Abstr.*, **49**, 329 (1955).
61. A. Ohta, *Chem. Pharm. Bull.*, **11**, 1586 (1963).
62. M. Colonna and A. Risaliti, *Gazz. Chim. Ital.*, **83**, 58 (1953); *Chem. Abstr.*, **48**, 8784 (1954).
63. W. E. Hahn and J. Epsztajn, *Rocz. Chem.*, **37**, 403 (1963); *Chem. Abstr.*, **59**, 11412 (1963).
64. H. Gilman and S. M. Spatz, *J. Amer. Chem. Soc.*, **66**, 621 (1944).
65. Y. Tanaka, *Bull. Chem. Soc. Jap.*, **29**, 44 (1956).
66. J. Meisenheimer, *Ber.*, **66B**, 985 (1933).
67. G. Buchmann, *Chem. Tech. (Berlin)*, **9**, 388 (1957); *Chem. Abstr.*, **53**, 2229 (1959).
68. E. Ochiai and S. Zai-Ren, *Yakugaku Zasshi*, **65**, 73 (1945); *Chem. Abstr.*, **45**, 8526 (1951).
69. V. N. Konyukhov and M. K. Murshstein, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, **18**, 1267 (1975); *Chem. Abstr.*, **84**, 30833 (1976).
70. J. Filippi, *Bull. Soc. Chim. Fr.*, **1968**, 259.
71. M. K. Murshstein and V. N. Konyukhov, *Khim. Prod. Koksovaniya Uglei Vostoka SSSR*, **1969**, 342; *Chem. Abstr.*, **74**, 3490 (1971).
72. P. Schroeder and M. Luckner, *Arch. Pharm. (Weinheim)*, **301**, 39 (1968); *Chem. Abstr.*, **68**, 7577 (1968).
73. G. A. Tolstikov, U. M. Dzhemilev and V. P. Yur'ev, *Zh. Org. Khim.*, **8**, 1186 (1972); *Chem. Abstr.*, **77**, 101425 (1972).
74. G. A. Tolstikov, U. M. Dzhemilev, V. P. Yur'ev and M. G. Gaisina, *Khim. Geterosikl. Soedin.*, 7, 1005 (1971); *Chem. Abstr.*, **75**, 151598 (1971).
75. Allied Chemical Corp., *Brit. Pat.* 1,059,702; *Chem. Abstr.*, **67**, 3002 (1967).
76. S. Baba, H. Suzuki and Y. Oyamada, *Yakugaku Zasshi*, **89**, 1317 (1969); *Chem. Abstr.*, **72**, 12520 (1970).
77. G. Buchmann and R. Mund, *East Ger. Pat.* 16,921; *Chem. Abstr.*, **55**, 1665 (1961).
78. R. O. Ragsdale and C. E. Michelson, *Inorg. Chem.*, **9**, 2718 (1970).
79. G. Buchmann, *Z. Chem.*, **1**, 84 (1961); *Chem. Abstr.*, **57**, 16555 (1962).
80. G. Heller and A. Sourlis, *Ber.*, **41**, 2692 (1908).
81. J. Meisenheimer and E. Stotz, *Ber.*, **58**, 2334 (1925).
82. E. Ochiai, M. Takahashi and R. Tanabe, *Chem. Pharm. Bull.*, **15**, 1385 (1967).
83. G. Buchmann and R. Schmuck, *East Ger. Pat.* 23,255; *Chem. Abstr.*, **58**, 3404 (1963).
84. S. Sakai, K. Minoda and S. Akagi, *Jap. Pat.* 61 3872; *Chem. Abstr.*, **58**, 10181 (1964).
85. W. C. Austin, L. H. C. Hunts, M. D. Potter and E. P. Taylor, *J. Pharm. Pharmacol.*, **11**, 80 (1959); *Chem. Abstr.*, **54**, 4613 (1960).
86. W. Ozegowski, M. Wunderwald and D. Krebs, *J. Prakt. Chem.*, **9**, 54 (1959); *Chem. Abstr.*, **54**, 7709 (1960).
87. K. Miura, *Belg. Pat.* 638,220; *Chem. Abstr.*, **62**, 9106 (1965).
88. K. Miura, T. Ohashi, S. Matsuka and Y. Igarashi, *Yakugaku Zasshi*, **83**, 771 (1963); *Chem. Abstr.*, **59**, 13911 (1963).
89. H. Takamatsu, S. Minami, A. Fujita, J. Aritomi, K. Fujimoto and M. Shimizu, *Jap. Pat.* 64 26,407; *Chem. Abstr.*, **62**, 10421 (1965).
90. M. Colonna, *Gazz. Chim. Ital.*, **90**, 1179 (1960); *Chem. Abstr.*, **56**, 5930 (1962).
91. N. K. Ushenko and T. E. Gorizdra, *Ukr. Khim. Zh.*, **15**, 296 (1949); *Chem. Abstr.*, **48**, 3366 (1954).
92. M. Hamana and K. Shimizu, *Yakugaku Zasshi*, **86**, 59 (1966); *Chem. Abstr.*, **64**, 11171 (1966).
93. M. Colonna and A. Risaliti, *Bull. Sci. Fac. Chim. Ind. Bologna*, **9**, 82 (1951); *Chem. Abstr.*, **46**, 7102 (1952).
94. M. Hamana, S. Takeo and H. Noda, *Chem. Pharm. Bull.*, **25**, 1256 (1977).
95. A. Risaliti, *Ric. Sci.*, **26**, 2512 (1956); *Chem. Abstr.*, **52**, 10080 (1958).
96. S. Natsume and T. Itai, *Chem. Pharm. Bull.*, **14**, 557 (1966).
97. T. Nakano, *Yakugaku Zasshi*, **82**, 498 (1962); *Chem. Abstr.*, **58**, 3391 (1963).
98. F. H. Case and J. M. Lesser, *J. Heterocycl. Chem.*, **3**, 170 (1966).
99. R. T. Coutts, W. N. Pitkethly and D. G. Wibberley, *J. Pharm. Sci.*, **54**, 792 (1965); *Chem. Abstr.*, **63**, 5598 (1965).
100. A. C. W. Curran and D. G. Hill, *Brit. Pat.* 1,463,585; *Chem. Abstr.*, **87**, 68186 (1977).

101. Y. Kobayashi, I. Kumadaki, Y. Hirose and Y. Hanzawa, *J. Org. Chem.*, **39**, 1836 (1974).
102. C. E. Kaslow and B. Buchner, *J. Org. Chem.*, **23**, 271 (1958).
103. E. Ochiai, M. Ishikawa and S. Zai-Ren, *Yakukagu Zasshi*, **65**, 72 (1945); *Chem. Abstr.*, **45**, 8526 (1951).
104. M. Katada, *Yakugaku Zasshi*, **68**, 123 (1948); *Chem. Abstr.*, **47**, 8073 (1953).
105. M. Szafran, *Rocz. Chem.*, **42**, 1469 (1968); *Chem. Abstr.*, **70**, 36912 (1969).
106. D. E. Ames and J. L. Archibald, *J. Chem. Soc.*, **1962**, 1475.
107. M. Takahashi, *Itsuu Kenkyusho Nempo*, **1963**, 25; *Chem. Abstr.*, **60**, 1694 (1964).
108. E. Ochiai and M. Takahashi, *Ann. Rep. Itsuu Lab.*, **1968**, 1; *Chem. Abstr.*, **71**, 101753 (1969).
109. M. Ishikawa, T. Kagawa, C. Kaneko, T. Miyasaka and T. Tsuchiya, *Shika Zairyo Kenkyusho Hokoku*, **2**, 181 (1961); *Chem. Abstr.*, **58**, 4609 (1963).
110. M. Hamana and H. Noda, *Yakugaku Zasshi*, **83**, 342 (1963); *Chem. Abstr.*, **59**, 9975 (1963).
111. T. Yoshikawa, *Yakugaku Zasshi*, **81**, 1601 (1961); *Chem. Abstr.*, **56**, 11567 (1962).
112. E. Profft, G. Buchmann and N. Wackrow, *Arzneim.-Forsch.*, **10**, 1029 (1960); *Chem. Abstr.*, **55**, 10442 (1961).
113. E. Profft, G. Buchmann and N. Wackrow, *Wiss. Z. Tech. Nochsch. Chem. Leuna-Merserburg*, **2**, 93 (1959–60); *Chem. Abstr.*, **55**, 1616 (1961).
114. J. E. Hoover and B. Blank, *J. Med. Chem.*, **6**, 628 (1963).
115. O. Buchardt, J. Becher and C. Lohse, *Acta Chem. Scand.*, **20**, 2467 (1966).
116. M. Tokuyama, *Yakugaku Zasshi*, **74**, 699 (1954); *Chem. Abstr.*, **48**, 10748 (1954).
117. R. Roe, Jr., J. S. Paul and P. O'B. Montgomery, Jr., *J. Heterocycl. Chem.*, **9**, 1097 (1972).
118. J. H. Markgraf, R. J. Katt, W. L. Scott and R. N. Shefrin, *J. Org. Chem.*, **34**, 4131 (1969).
119. W. E. Parham and K. B. Sloan, *Tetrahedron Lett.*, **1971**, 1947.
120. G. A. Klimov, M. N. Tilichenko and L. A. Timosheeva, *Khim. Geterosikl. Soedin*, **7**, 1218 (1971); *Chem. Abstr.*, **76**, 153638 (1972).
121. E. Hayashi and A. Miyashita, *Yakugaku Zasshi*, **97**, 211 (1977); *Chem. Abstr.*, **87**, 23008 (1977).
122. H. Gilman, R. V. Christian and S. M. Spatz, *J. Amer. Chem. Soc.*, **68**, 979 (1946).
123. G. A. Klimov, V. N. Ovsyannikova and M. N. Tilichenko, *Khim. Geterosikl.* Soedin, **8**, 1547 (1972); *Chem. Abstr.*, **78**, 58266 (1973).
124. M. Araki, M. Saneyoshi, H. Harada and Y. Kawazoe, *Chem. Pharm. Bull.*, **16**, 1742 (1968).
125. T. Kauffmann and J. Schulz, *Chem. Ber.*, **99**, 1837 (1966).
126. J. G. Murray and C. R. Hauser, *J. Org. Chem.*, **19**, 2008 (1954).
127. K. Mitsuhasi and S. Shiotani, *Yakukagu Zasshi*, **82**, 773 (1962); *Chem. Abstr.*, **58**, 2436 (1963).
128. G. Buchmann and B. Braeuer, *J. Prakt. Chem.*, **16**, 225 (1962).
129. J. K. Landquist, *J. Chem. Soc.*, **1956**, 1885.
130. M. Ishikawa, *Proc. Imp. Acad. (Tokyo)*, **20**, 599 (1944); *Chem. Abstr.*, **49**, 326 (1955).
131. H. Von Euler and H. Hasselquist, *Ark. Kemi*, **12**, 553 (1958).
132. H. Von Euler, H. Hasselquist and O. Heidenberger, *Ark. Kemi*, **13**, 237 (1959).
133. H. Von Euler, H. Hasselquist and D. Nomura, *Ark. Kemi*, **15**, 283 (1960).
134. E. Ochiai and C. Kaneko, *Pharm. Bull. (Tokyo)*, **5**, 56 (1957).
135. E. Ochiai and K. Satake, *Yakugaku Zasshi*, **71**, 1078 (1951); *Chem. Abstr.*, **46**, 5045 (1952).
136. G. Buchmann and R. Niess, *J. Prakt. Chem.*, **16**, 207 (1962).
137. E. Hayashi and R. Goto, *Yakugaku Zasshi*, **85**, 645 (1965); *Chem. Abstr.*, **63**, 9913 (1965).
138. T. Okamoto, *Yakugaku Zasshi*, **70**, 376 (1950); *Chem. Abstr.*, **45**, 2476 (1951).
139. E. Ochiai and Y. Tamai, *Itsuu Kenkyusho Nempo*, No. 13, 13 (1963); *Chem. Abstr.*, **60**, 488 (1964).
140. E. Ochiai, M. Takahashi, Y. Tamai, and H. Kataoka, *Chem. Pharm. Bull.*, **11**, 137 (1963).
141. E. Ochiai and Y. Tamai, *Itsuu Kenkyusho Nempo*, No. 13, 5 (1963); *Chem. Abstr.*, **60**, 488 (1964).
142. E. N. Shaw, *U.S. Pat.* 2,540,218; *Chem. Abstr.*, **45**, 6224 (1951).
143. G. T. Newbold and F. S. Spring, *J. Chem. Soc.*, **1948**, 1864.
144. R. A. Baxter, G. Dunn, J. J. Gallagher, G. T. Newbold, W. Sharp, W. Sweeny and F. S. Spring, *J. Roy. Tech. Coll. (Glasgow)*, **5**, 26 (1950); *Chem. Abstr.*, **44**, 8355 (1950).
145. T. Okamoto, *Yakugaku Zasshi*, **71**, 297 (1951); *Chem. Abstr.*, **46**, 4542 (1952).
146. A. M. Van Arendonk, *U.S. Pat.* 2,416,658; *Chem. Abstr.*, **41**, 3491 (1947); Eli Lilly & Co., *Brit. Pat.* 599,768; *Chem. Abstr.*, **42**, 7345 (1948).

147. E. Ochiai, M. Hamana, Y. Kobayashi and C. Kaneko, *Chem. Pharm. Bull.*, **8**, 487 (1960).
148. T. Takahashi, J. Okada and Y. Hamada, *Yakugaku Zasshi*, **77**, 1243 (1957); *Chem. Abstr.*, **52**, 6342 (1958).
149. M. N. Shchukina and N. V. Savitskaya, *Zh. Obshch. Khim.*, **22**, 1224 (1952); *Chem. Abstr.*, **47**, 7505 (1953).
150. I. Murase, *Nippon Kagaku Zasshi*, **75**, 1180 (1954); *Chem. Abs.*, **49**, 10786 (1955).
151. V. Petrow and B. Sturgeon, *J. Chem. Soc.*, **1954**, 570.
152. R. L. Evans and F. Linsker, *U.S. Pat.* 2,518,130; *Chem. Abstr.*, **45**, 1169 (1951).
153. G. R. Pettit and M. V. Kalnins, *J. Org. Chem.*, **25**, 1365 (1960).
154. K. G. Cunningham, G. T. Newbold, F. S. Spring and J. Stark, *J. Chem. Soc.*, **1949**, 2091.
155. Y. Kobayashi, *Chem. Pharm. Bull.*, **6**, 273 (1958).
156. E. Ochiai, G. Kobayashi and J. Hasegawa, *Yakugaku Zasshi*, **67**, 101 (1947); *Chem. Abstr.*, **45**, 9553 (1951).
157. V. M. Dziomko, I. A. Krasavin and T. N. Egorova, *Metody Poluch. Khim. Reakt. Prep.*, No. 13, 119 (1965); *Chem. Abstr.*, **65**, 7139 (1966).
158. G. Buchmann and W. Grimm, *J. Prakt. Chem.*, **17**, 135 (1962); *Chem. Abstr.*, **58**, 4518 (1963).
159. M. Hamana and M. Yamazaki, *Chem. Pharm. Bull.* **10**, 51 (1962).
160. T. Takahashi and Y. Hamada, *Yakugaku Zasshi*, **75**, 1434 (1955); *Chem. Abstr.*, **50**, 10096 (1956).
161. M. S. Habib and C. W. Rees, *J. Chem. Soc.*, **1960**, 3371.
162. M. Szafran and T. Dziembowska, *Rocz. Chem.*, **44**, 1805 (1970); *Chem. Abs.*, **74**, 87792 (1971).
163. Y. Suzuki, *Yakugaku Zasshi*, **81**, 917 (1961); *Chem. Abs.*, **55**, 27305 (1961).
164. M. Hamana and H. Noda, *Chem. Pharm. Bull.*, **14**, 762 (1966).
165. P. Mamalis and V. Petrow, *J. Chem. Soc.*, **1950**, 703.
166. L. Monti and G. Franchi, *Gazz. Chim. Ital.*, **81**, 544 (1951); *Chem. Abstr.*, **46**, 6129 (1952).
167. T. Takahashi and Y. Hamada, *Yakugaku Zasshi*, **77**, 1244 (1957); *Chem. Abstr.*, **52**, 6342 (1958).
168. T. Okamoto and H. Takahashi, *Chem. Pharm. Bull.*, **19**, 1809 (1971).
169. T. Okamoto and H. Takahashi, *Chem. Pharm. Bull.*, **16**, 1700 (1968).
170. H. Tanida, *Yakugaku Zasshi*, **79**, 1063 (1959); *Chem. Abstr.*, **54**, 4587 (1960).
171. E. Ochiai, C. Kaneko and J. Inomata, *Yakugaku Zasshi*, **78**, 584 (1958); *Chem. Abstr.*, **52**, 18419 (1958).
172. C. E. Coverdale and L. L. Skaletzky, *Ger. Offen.* 2,428,194; *Chem. Abstr.*, **82**, 171059 (1975).
173. P. Friedlander and H. Ostermaier, *Ber.*, **14**, 1916 (1881).
174. S. Gabriel and W. Gerhard, *Ber.*, **54**, 1067 (1921).
175. K. L. McCluskey, *J. Amer. Chem. Soc.*, **44**, 1573 (1922).
176. R. T. Coutts and D. G. Wibberley, *J. Chem. Soc.*, **1963**, 4610.
177. R. T. Coutts and D. G. Wibberley, *J. Chem. Soc.*, **1962**, 2518.
178. H. Lund and L. G. Feoktistov, *Acta Chem. Scand.*, **23**, 3482 (1969).
179. G. Heller and P. Wunderlich, *Ber.*, **47**, 1617 (1914).
180. J. M. Tyler, *J. Chem. Soc.*, **1955**, 203.
181. E. C. Taylor and N. W. Kalenda, *J. Org. Chem.*, **18**, 1755 (1953).
182. R. T. Coutts, *J. Chem. Soc. C*, **1969**, 713.
183. P. N. Preston and G. Tennant, *Chem. Rev.*, **72**, 627 (1972).
184. K. Brand and O. Loehr, *J. Prakt. Chem.*, **109**, 359 (1925).
185. J. D. Loudon and G. Tennant, *J. Chem. Soc.*, **1960**, 3466.
186. J. D. Loudon and I. Wellings, *J. Chem. Soc.*, **1960**, 3462.
187. I. P. Sword, *J. Chem. Soc. C*, **1970**, 1916.
188. Y. Ahmad and S. A. Shamsi, *Pak. J. Sci. Ind. Res.*, **11**, 354 (1968); *Chem. Abstr.*, **71**, 61163 (1969).
189. Y. Ahmad and S. A. Shamsi, *Bull. Chem. Soc. Jap.*, **39**, 195 (1966).
190. J. D. Loudon and I. Wellings, *J. Chem. Soc.*, **1960**, 3470.
191. J. D. Loudon and G. Tennant, *J. Chem. Soc.*, **1962**, 3092.
192. T. W. M. Spence and G. Tennant, *J. Chem. Soc. Chem. Commun.*, **1970**, 1100.
193. T. W. M. Spence and G. Tennant, *J. Chem. Soc. C*, **1971**, 3712.
194. M. Colonna, *Boll. Sci. Fac. Chim. Ind. Bologna*, **86**, (1941); *Chem. Abstr.*, **37**, 3097 (1943).
195. S. Von Niementowski, *Ber.*, **40**, 4285 (1907).

196. S. Gabriel and W. Gerhard, *Ber.*, **54**, 1613 (1921).
197. I. P. Sword, *J. Chem. Soc. C*, **1971**, 820.
198. H. Lund and J. Hakl, unpublished work; quoted by H. Lund *Adv. Heterocycl. Chem.*, **12**, 238 (1970).
199. K. H. Bauer, *Ber.*, **71B**, 2226 (1938).
200. F. Arndt, L. Ergener and O. Kutlu, *Chem. Ber.*, **86**, 957 (1953).
201. R. T. Coutts, G. Mukherjee, R. A. Abramovitch and M. A. Brewster, *J. Chem. Soc. C*, **1969**, 2207.
202. H. Matschiner, P. Gallien, H. Schilling and K. Trautner, *East Ger. Pat.* 126,221; *Chem. Abstr.*, **88**, 62305 (1978).
203. S. Gabriel and R. Wolter, *Ber.*, **56**, 2445 (1923).
204. E. C. Taylor and J. Bartulin, *Tetrahedron Lett.*, **1967**, 2337.
205. M. Wilk, H. Schwab and J. Rochlitz, *Ann.*, **698**, 149 (1966).
206. L. Capuano and V. Diehl, *Chem. Ber.*, **109**, 723 (1976).
207. L. Capuano and W. Ebner, *Chem. Ber.*, **104**, 2221 (1971).
208. B. Ziolkowsky and F. Dörr, *Ber. Bunsenges. Phys. Chem.*, **69**, 448 (1965); *Chem. Abstr.*, **63**, 7770 (1965).
209. O. Buchardt, J. Becher and C. Lohse, *Acta Chem. Scand.*, **19**, 1120 (1965).
210. D. Dal Monte Casoni, A. Mangini and F. Montanari, *Gazz. Chim. Ital.*, **88**, 1035 (1958); *Chem. Abstr.*, **53**, 18946 (1959).
211. T. Okano, M. Goto, H. Matsumoto and A. Takadate, *Chem. Pharm. Bull.*, **20**, 2551 (1972).
212. H. Miyazaki, T. Kubota and M. Yamakawa, *Bull. Chem. Soc. Jap.*, **45**, 780 (1972).
213. T. Kubota, M. Yamakawa and Y. Mizuno, *Bull. Chem. Soc. Jap.*, **45**, 3282 (1972).
214. G. Favaro, *Mol. Photochem.*, **2**, 323 (1970).
215. T. Kubota, *Nippon Kagaku Zasshi*, **79**, 930 (1958); *Chem. Abstr.*, **53**, 15760 (1959).
216. H. Hirayama and T. Kubota, *Yakugaku Zasshi*, **72**, 1025 (1952); *Chem. Abstr.*, **47**, 3314 (1953).
217. A. Mangini and F. Montanari, *Proc. 4th Int. Meet. Mol. Spectrosc., Bologna (1959)*, **2**, 582 (1962); *Chem. Abstr.*, **59**, 5946 (1963).
218. A. Mangini and F. Montanari, *Boll. Sci. Fac. Chim. Ind. Bologna*, **17**, 19 (1959); *Chem. Abstr.*, **53**, 21152 (1959).
219. M. Colonna and A. Risaliti, *Ann. Chim. (Rome)*, **48**, 1395 (1958); *Chem. Abstr.*, **53**, 14683 (1959).
220. K. Ezumi, T. Kubota and T. Shida, *Chem. Lett.*, **1977**, 181.
221. M. Colonna and A. Risaliti, *Atti Acad. Naz. Lincei Rend. Classe Sci. Fis. Mat. Nat.*, **14**, 1809 (1953); *Chem. Abstr.*, **48**, 8045 (1954).
222. T. Kubota and H. Miyazaki, *Chem. Pharm. Bull.*, **9**, 948 (1961).
223. Y. Kawazoe and M. Tachibana, *Chem. Pharm. Bull.*, **15**, 1 (1967).
224. M. Yamakawa, T. Kubota, K. Ezumi and Y. Mizuno, *Spectrochim. Acta*, **30A**, 2013 (1974).
225. T. Kubota, *Yakugaku Zasshi*, **74**, 831 (1954); *Chem. Abstr.*, **48**, 11924 (1954).
226. T. Kubota, *Yakugaku Zasshi*, **75**, 1540 (1955); *Chem. Abstr.*, **50**, 10723 (1956).
227. T. Okano, Y. Sato and S. Takenaka, *Yakugaku Zasshi*, **89**, 994 (1969); *Chem. Abstr.*, **71**, 90497 (1969).
228. T. Okano, T. Miura, M. Yoshida and K. Uekama, *Yakugaku Zasshi*, **89**, 1379 (1969); *Chem. Abstr.*, **72**, 11856 (1970).
229. T. Kubota, H. Akazawa and M. Yamakawa, *Chem. Lett.*, **1972**, 1147.
230. T. Okano, S. Takenaka and Y. Sato, *Chem. Pharm. Bull.*, **16**, 556 (1968).
231. T. Okano, S. Takenaka and Y. Sato, *Gann*, **60**, 307 (1969); *Chem. Abstr.*, **71**, 77347 (1969).
232. M. Tada, M. Tada and T. Takahashi, *Symp. Fundam. Cancer Res.*, **23**, 214 (1970); *Chem. Abstr.*, **75**, 3091 (1971).
233. T. Okano, A. Isobe and H. Matsumoto, *Gann*, **63**, 427 (1972); *Chem. Abstr.*, **78**, 54287 (1973).
234. T. Okano and K. Uekama, *Chem. Pharm. Bull.*, **15**, 1251 (1967).
235. T. Kosuge, H. Zenda, M. Yokota, H. Sawanishi and Y. Suzuki, *Chem. Pharm. Bull.*, **17**, 2181 (1969).
236. T. Okano and Y. Sato, *Gann*, **63**, 713 (1972); *Chem. Abstr.*, **78**, 67671 (1973).
237. T. Okano, H. Matsumoto, A. Takadate and T. Horie, *Gann*, **65**, 187 (1974); *Chem. Abstr.*, **81**, 115669 (1974).

238. T. Okano, J. Maenosono, T. Kano and J. Onoda, *Gann*, **64**, 227 (1973); *Chem. Abstr.*, **79**, 74695 (1973).
239. T. Okano and K. Tsuji, *Yakugaku Zasshi*, **88**, 1103 (1968); *Chem. Abstr.*, **70**, 25748 (1969).
240. T. Okano and K. Tsuji, *Yakugaku Zasshi*, **89**, 297 (1969); *Chem. Abstr.*, **71**, 26273 (1969).
241. T. Okano and K. Uekama, *Chem. Pharm. Bull.*, **15**, 1812 (1967).
242. E. Ochiai and E. Hayashi, *Yakugaku Zasshi*, **67**, 154 (1947); *Chem. Abstr.*, **45**, 9540 (1951).
243. T. Kubota, *Yakugaku Zasshi*, **75**, 1546 (1955); *Chem. Abstr.*, **50**, 5374 (1956).
244. H. Hirayama and T. Kubota, *Yakugaku Zasshi*, **73**, 140 (1953); *Chem. Abstr.*, **47**, 4196 (1953).
245. Y. Yamane, K. Sakai, H. Fukino, M. Ohtawa, M. Iigo and I. Morita, *Yakugaku Zasshi*, **94**, 1603 (1974); *Chem. Abstr.*, **82**, 133612 (1975).
246. T. Okabayashi and A. Yoshimoti, *Chem. Pharm. Bull.*, **12**, 262 (1964).
247. A. A. Kane and I. F. Tupitsyn, *Tr. Gos. Inst. Prikl. Khim.*, **1970**, 114; *Chem. Abstr.*, **76**, 92297 (1972).
248. H. Shindo, *Chem. Pharm. Bull*., **8**, 845 (1960).
249. S. Ghersetti, S. Giorgianni, M. Minari and G. Spunta, *Spectrosc. Lett.*, **6**, 167 (1973).
250. S. Ghersetti, S. Giorgianni, M. Minari and G. Spunta, *Spectrochim. Acta*, **31A**, 445 (1975).
251. E. Moriconi and F. A. Spano, *J. Amer. Chem. Soc.*, **86**, 38 (1964).
252. G. R. Clemo and A. F. Daglish, *J. Chem. Soc.*, **1950**, 1481.
253. G. Costa, P. Blasina and G. Sartori, *Univ. Studi. Trieste Fac. Sci. Ist. Chim.*, No. 9, 11 pp. (1955); *Chem. Abstr.*, **50**, 11823 (1956).
254. A. A. Kane and I. F. Tupitsyn, *Tr. Gos. Inst. Prikl. Khim.*, **1970**, 139; *Chem. Abstr.*, **76**, 92397 (1972).
255. M. Szafran, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **13**, 245 (1965); *Chem. Abstr.*, **63**, 14669 (1965).
256. M. Szafran, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **13**, 333 (1965); *Chem. Abstr.*, **63**, 16191 (1965).
257. T. Dziembowska and M. Szafran, *Rocz. Chem.*, **48**, 1687 (1974); *Chem. Abstr.*, **82**, 111160 (1975).
258. T. Dziembowska and M. Szafran, *Rocz. Chem.*, **48**, 611 (1974); *Chem. Abstr.*, **81**, 62691 (1974).
259. M. Szafran, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **12**, 383 (1964); *Chem. Abstr.*, **62**, 3904 (1965).
260. M. Szafran, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **14**, 335 (1966); *Chem. Abstr.*, **65**, 15206 (1966).
261. M. Szafran and Z. Dega-Szafran, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **15**, 159 (1967); *Chem. Abstr.*, **68**, 73634 (1968).
262. M. Szafran and Z. Dega-Szafran, *Rocz. Chem.*, **44**, 793 (1970); *Chem. Abstr.*, **74**, 3240 (1971).
263. M. Szafran, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **14**, 335 (1966); *Chem. Abstr.*, **65**, 15207 (1966).
264. M. Szafran, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **14**, 621 (1966); *Chem. Abstr.*, **66**, 99877 (1967).
265. M. Szafran, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **11**, 111 (1963); *Chem. Abstr.*, **59**, 11216 (1963).
266. M. Szafran, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **11**, 497 (1963); *Chem. Abstr.*, **60**, 7573 (1964).
267. J. H. Nelson, L. C. Nathan and R. O. Ragsdale, *J. Amer. Chem. Soc.*, **90**, 5754 (1968).
268. K. Tori, M. Ogata and H. Kano, *Chem. Pharm. Bull.*, **11**, 681 (1963).
269. Y. Kawazoe, M. Araki, S. Sawaki and M. Ohnishi, *Chem. Pharm. Bull.*, **18**, 381 (1970).
270. P. Hamm and W. Von Philipsborn, *Helv. Chim. Acta*, **54**, 2363 (1971).
271. R. A. Fletton, G. F. H. Green and J. E. Page, *Chem. Ind. (London)*, **1972**, 167.
272. R. W. Kluiber and W. D. Horrocks, Jr., *J. Amer. Chem. Soc.*, **88**, 1399 (1966).
273. J. M. A. Al-Rawi, J. P. Bloxsidge, C. O'Brien, D. E. Caddy, J. A. Elvidge, J. R. Jones and A. E. Evans, *J. Chem. Soc. Perkin Trans. 2*, **1974**, 1635.
274. Y. Kawazoe and M. Ohnishi, *Chem. Pharm. Bull.*, **15**, 826 (1967).
275. N. N. Zatsepina, I. F. Tupitsyn and L. S. Efros, *Zh. Obshch. Khim.*, **33**, 2705 (1963); *Chem. Abstr.*, **60**, 5292 (1964).

276. N. N. Zatsepina, I. F. Tupitsyn and L. S. Efros, *Dokl. Akad. Nauk SSSR*, **154**, 148 (1964); *Chem. Abstr.*, **60**, 9113 (1964).
277. N. N. Zatsepina, I. F. Tupitsyn and L. S. Efros, *Zh. Obshch. Khim.*, **34**, 4065 (1964); *Chem. Abstr.*, **62**, 8961 (1965).
278. B. Brzezinski, T. Dziembowska and M. Szafran, *Rocz. Chem.*, **47**, 445 (1973); *Chem. Abstr.*, **79**, 65306 (1973).
279. N. S. Vul'fson, V. G. Zaikin, A. A. Bakaev, A. A. Akhrem, L. I. Ukhova and N. F. Marchenko, *Khim. Geterosikl. Soedin.*, **1973**, 74; *Chem. Abstr.*, **80**, 26687 (1974).
280. Z. Dega-Szafran, E. Grech and M. Szafran, *J. Chem. Soc. Perkin Trans. 2*, **1972**, 1839.
281. M. Szafran and M. Rozwadowska, *Rocz. Chem.*, **44**, 1465 (1970); *Chem. Abstr.*, **74**, 8174 (1971).
282. Z. Dega-Szafran, M. Z. Naskret-Barciszewska and M. Szafran, *Rocz. Chem.*, **47**, 749 (1973); *Chem. Abstr.*, **79**, 91391 (1973).
283. T. Okano, A. Takadate and T. Kano, *Gann*, **60**, 557 (1969); *Chem. Abstr.*, **72**, 50924 (1970).
284. P. Van Der Weijer, C. Mohan and D. M. W. Van Der Ham, *Org. Magn. Reson.*, **10**, 165 (1977).
285. L. Stafaniak, *Spectrochim. Acta*, **32A**, 345 (1976).
286. K. Tori, M. Ohtsuru, K. Aono, Y. Kawazoe and M. Ohnishi, *J. Amer. Chem. Soc.*, **89**, 2765 (1967).
287. Y. Kawazoe, M. Ohnishi and N. Kataoka, *Chem. Pharm. Bull.*, **13**, 396 (1965).
288. R. O. Ragsdale, R. S. Stephens and S. D. Lessley, *Inorg. Chem.*, **10**, 1610 (1971).
289. L. Lunazzi, A. Mangini, G. Placucci and F. Taddei, *J. Chem. Soc. B*, **1970**, 440.
290. T. Kubota, K. Nishikida, H. Miyazaki, K. Iwatani and Y. Oishi, *J. Amer. Chem. Soc.*, **90**, 5080 (1968).
291. N. Kataoka, S. Shibata, A. Imamura, Y. Kawazoe, G. Chihara and C. Nagata, *Chem. Pharm. Bull.*, **15**, 220 (1967).
292. C. Nagata, N. Kataoka, A. Imamura, Y. Kawazoe and G. Chihara, *Gann*, **57**, 323 (1966); *Chem. Abstr.*, **65**, 15886 (1966).
293. N. Kataoka, A. Imamura, Y. Kawazoe, G. Chihara and C. Nagata, *Bull. Chem. Soc. Jap.*, **40**, 62 (1967).
294. N. Kataoka, A. Imamura, Y. Kawazoe, G. Chihara and C. Nagata, *Chem. Pharm. Bull.*, **14**, 897 (1966).
295. N. Kataoka, A. Imamura, Y. Kawazoe, G. Chihara and C. Nagata, *Chem. Pharm. Bull.*, **14**, 1171 (1966).
296. T. Okano, A. Takadate and K. Uekama, *Gann*, **61**, 541 (1970); *Chem. Abstr.*, **74**, 94406 (1971).
297. T. Okano and K. Uekama, *Chem. Pharm. Bull.*, **16**, 1411 (1968).
298. T. A. Bryce and J. R. Maxwell, *J. Chem. Soc. Chem. Commun.*, **1965**, 206.
299. A. M. Duffield and O. Buchardt, *Acta Chem. Scand.*, **26**, 2423 (1972).
300. O. Buchardt, A. M. Duffield and R. H. Shapiro, *Tetrahedron*, **24**, 3139 (1968).
301. A. Kubo, S. I. Sakai, S. Yamada, I. Yokoe and C. Kaneko, *Chem. Pharm. Bull.*, **16**, 1533 (1968).
302. R. T. Coutts, *Can. J. Pharm. Sci.*, **3**, 37 (1968); *Chem. Abstr.*, **70**, 37635 (1969).
303. C. W. Koch, R. M. Milberg, R. J. Katt, J. H. Markgraf and P. M. Wege, *J. Heterocycl. Chem.*, **11**, 475 (1974).
304. A. Kubo, S. Sakai, S. Yamada, I. Yokoe, C. Kaneko, A. Tatematsu, H. Yoshizumi, E. Hayashi and H. Nakata, *Chem. Pharm. Bull.*, **15**, 1079 (1967).
305. R. Abramovitch and E. M. Smith, *J. Heterocycl. Chem.*, **12**, 969 (1975).
306. T. R. Bosin and R. P. Maickel, *Res. Commun. Chem. Pathol. Pharmacol.*, **3**, 493 (1972); *Chem. Abstr.*, **77**, 70975 (1972).
307. V. G. Zaikin, A. A. Bakaev, N. S. Wulfson, A. A. Akhrem, L. I. Ukhova and N. F. Marchenko, *Org. Mass Spectrom.*, **12**, 173 (1977).
308. A. T. McPhail and G. A. Sim, *J. Chem. Soc. Chem. Commun.*, **1966**, 21.
309. Z. S. Kosturkevich, *Zh. Strukt. Khim.*, **5**, 323 (1964); *Chem. Abstr.*, **61**, 2562 (1964).
310. Z. S. Kosturkiewicz, *Zesz. Nauk. Uniw. Poznaniu Mat. Fiz. Chem.*, **1967**, 29; *Chem. Abstr.*, **69**, 100753 (1968).
311. R. Desiderato and J. C. Terry, *Tetrahedron Lett.*, **1970**, 3203.

312. A. M. Manotti Lanfredi, A. Tiripicchio and C. Tiripicchio, *Cryst. Struct. Commun.*, **4**, 153 (1975); *Chem. Abstr.*, **83**, 19582 (1975).
313. Z. V. Pushkareva, L. V. Varyukhina and Z. Yu. Kokoshko, *Doklady Akad. Nauk SSSR*, **108**, 1098 (1956); *Chem. Abstr.*, **51**, 21 (1957).
314. J. P. Maier, J. F. Muller, T. Kubota and M. Yamakawa, *Helv. Chim. Acta*, **58**, 1641 (1975).
315. V. K. Kondratov and E. G. Novikov, *Zh. Anal. Khim.*, **22**, 587 (1967); *Chem. Abstr.*, **67**, 60728 (1967).
316. V. K. Kondratov and E. G. Novikov, *Zh. Fiz. Khim.*, **45**, 2224 (1971); *Chem. Abstr.*, **75**, 151248 (1971).
317. C. W. Muth, R. S. Darlak, W. H. English and A. T. Hamner, *Anal. Chem.*, **34**, 1163 (1962).
318. T. Okabayashi and M. Ide, *J. Chromatogr.*, **9**, 523 (1962).
319. L. Reio, *J. Chromatogr.*, **88**, 119 (1974); *Chem. Abstr.*, **80**, 59017 (1974).
320. M. Bieganowska, *Chromatographia*, **9**, 168 (1976).
321. D. Jerchel and W. Jacobs, *Angew. Chem.*, **66**, 298 (1954).
322. K. Kanamuru, I. Suzuki and T. Sengoku, *Showa Yakka Daigaku Kiyo*, **1966**, 1; *Chem. Abstr.*, **69**, 24344 (1968).
323. M. Bieganowska and T. Wawrzynowicz, *Chem. Anal. (Warsaw)*, **21**, 211 (1976); *Chem. Abstr.*, **85**, 52168 (1976).
324. N. A. Coats and A. R. Katritzky, *J. Org. Chem.*, **24**, 1836 (1959).
325. G. Jones, unpublished results.
326. T. Wu, J. S. Lin and H. S. Olcott, *J. Agric. Food Chem.*, **24**, 1255 (1976).
327. T. Kubota, *Yakukagu Zasshi*, **79**, 388 (1959); *Chem. Abstr.*, **53**, 13765 (1959).
328. T. Kubota, *Nippon Kagaku Zasshi*, **80**, 578 (1959); *Chem. Abstr.*, **53**, 13765 (1959).
329. G. Tsoucaris, *J. Chim. Phys.*, **58**, 613 (1961); *Chem. Abstr.*, **55**, 23032 (1961).
330. M. N. Adamov and I. F. Tupitsyn, *Liet. Fiz. Rinkinys. Liet. TSR Mokslu Akad., Liet. TSR Aukst. Mokyklu*, **3**, 277 (1963); *Chem. Abstr.*, **60**, 15165 (1964).
331. M. Yamakawa, T. Kubota and H. Akazawa, *Theor. Chim. Acta*, **15**, 244 (1969).
332. M. Tachibana, S. Sawaki and Y. Kawazoe, *Chem. Pharm. Bull.*, **15**, 1112 (1967).
333. J. S. Paul, P. O. Montgomery, Jr., and J. B. Lovis, *Cancer Res.*, **31**, 413 (1971); *Chem. Abstr.*, **75**, 3092 (1971).
334. K. Fukui, A. Imamura and C. Nagata, *Gann*, **51**, 119 (1960); *Chem. Abstr.*, **55**, 757 (1961).
335. K. Fukui, A. Imamura and C. Nagata, *Bull. Chem. Soc. Jap.*, **33**, 122 (1960).
336. T. Kurihara, H. Ichimura, T. Igaki and A. Ohta, *Chem. Pharm. Bull.*, **19**, 37 (1971).
337. C. Nagata, A. Imamura, K. Fukui and H. Saito, *Gann*, **54**, 401 (1963); *Chem. Abstr.*, **61**, 12431 (1964).
338. Y. Miyaji, H. Ichikawa and M. Ogata, *Chem. Pharm. Bull.*, **23**, 1256 (1975).
339. M. J. Scarlett, A. T. Casey and R. A. Craig, *Aust. J. Chem.*, **24**, 31 (1971).
340. G. Anthoine, J. Nasielski, E. Vander Donckt and N. Vanlautem, *Bull. Soc. Chim. Belg.*, **76**, 230 (1967).
341. L. V. Varyukhina and Z. V. Pushkareva, *Zh. Obshch. Khim.*, **26**, 1740 (1956); *Chem. Abstr.*, **51**, 1960 (1957).
342. G. Horn, *Monatsber. Deut. Akad. Wiss. Berlin*, **3**, 386 (1961); *Chem. Abstr.*, **57**, 3196 (1962).
343. G. Horn, *Acta Chim. Acad. Sci. Hung.*, **27**, 123 (1961); *Chem. Abstr.*, **55**, 23928 (1961).
344. A. Foffani and E. Fornasari, *Atti Accad. Naz. Lincei Cl. Sci. Fis. Mat. Nat. Rend.*, **23**, 62 (1957); *Chem. Abstr.*, **53**, 1960 (1959).
345. A. G. Pozdeeva and E. G. Novikov, *Zh. Prikl. Khim.*, **40**, 213 (1967); *Chem. Abstr.*, **67**, 39574 (1967).
346. E. Fornasari, C. A. Benassi and L. Griggio, *Gazz. Chim. Ital.*, **91**, 1105 (1961); *Chem. Abstr.*, **57**, 1976 (1962).
347. E. G. Novikov and A. G. Pozdeeva, *Zh. Prikl. Khim.*, **40**, 217 (1967); *Chem. Abstr.*, **67**, 39575 (1967).
348. M. Katada, *Yakugaku Zasshi*, **67**, 53 (1947); *Chem. Abstr.*, **45**, 9536 (1951).
349. M. E. C. Biffin, G. Boksteiner, J. Miller and D. B. Paul, *Aust. J. Chem.*, **27**, 789 (1974).
350. L. Horner and H. Roeder, *Chem. Ber.*, **101**, 4179 (1968).
351. E. Ochiai, T. Teshigawara and T. Naito, *Yakugaku Zasshi*, **65B**, 429 (1945); *Chem. Abstr.*, **45**, 8376 (1951).
352. N. Hata, I. Ono and M. Kawasaki, *Chem. Lett.*, **1975**, 25.
353. C. Kaneko, M. Yamamuri, A. Yamamoto and R. Hayashi, *Tetrahedron Lett.*, **1978**, 2799.

354. O. Buchardt, J. Becher, C. Lohse and J. Moeller, *Acta Chem. Scand.*, **20**, 262 (1966).
355. M. Ogata, H. Matsumoto, S. Takahashi and H. Kano, *Chem. Pharm. Bull.*, **18**, 964 (1970).
356. I. Rosenthal and O. Buchardt, *Acta Chem. Scand.*, **26**, 2557 (1972).
357. E. Hayashi, H. Yamanaka and K. Shimizu, *Chem. Pharm. Bull.*, **7**, 146 (1959).
358. M. Hamana and K. Funagoshi, *Yakugaku Zasshi*, **80**, 1027 (1960); *Chem. Abstr.*, **55**, 542 (1961).
359. E. Hayashi, H. Yamanaka and C. Ijima, *Yakugaku Zasshi*, **80**, 839 (1960); *Chem. Abstr.*, **54**, 24730 (1960).
360. K. Takeda and K. Tokuyama, *Yakugaku Zasshi*, **75**, 620 (1955); *Chem. Abstr.*, **50**, 3443 (1956).
361. S. Begum and N. Shakir, *Pak. J. Sci. Ind. Res.*, **17**, 198 (1975); *Chem. Abstr.*, **84**, 121607 (1976).
362. S. Furukawa, *Pharm. Bull. (Tokyo)*, **3**, 230 (1955).
363. M. Hamana, *Yakugaku Zasshi*, **75**, 121 (1955); *Chem. Abstr.*, **50**, 1817 (1956).
364. M. Hamana, *Yakugaku Zasshi*, **75**, 135 (1955); *Chem. Abstr.*, **50**, 1817 (1956).
365. E. Howard, Jr., and W. F. Olszewski, *J. Amer. Chem. Soc.*, **81**, 1483 (1959).
366. M. Hamana, *Yakugaku Zasshi*, **75**, 139 (1955); *Chem. Abstr.*, **50**, 1818 (1956).
367. T. Kametani and H. Nemoto, *Chem. Pharm. Bull.*, **16**, 1696 (1968).
368. G. Buchmann and H. J. Steinbach, *J. Prakt. Chem.*, **28**, 82 (1965).
369. T. Sakai, C. Kaneko and S. Mitsui, *Nippon Kagaku Zasshi*, **86**, 1328 (1965); *Chem. Abstr.*, **65**, 13648 (1966).
370. H. Sawanishi and Y. Kamiya, *Chem. Pharm. Bull.*, **23**, 2949 (1975).
371. M. Hamana, *Yakugaku Zasshi*, **71**, 263 (1951); *Chem. Abstr.*, **46**, 4541 (1952).
372. T. Ukai, Y. Yamamoto, and S. Hirano, *Yakugaku Zasshi*, **73**, 823 (1953); *Chem. Abstr.*, **48**, 9946 (1954).
373. M. Hamana and M. Yamazaki, *Chem. Pharm. Bull.*, **9**, 414 (1961).
374. K. Ramaiah and V. R. Srinavasan, *Indian J. Chem.*, **6**, 635 (1968); *Chem. Abstr.*, **70**, 47254 (1969).
375. M. Hamana, Y. Hoshide and K. Kaneda, *Yakugaku Zasshi*, **76**, 1337 (1956); *Chem. Abstr.*, **51**, 6639 (1957).
376. I. Nakayama, *Yakugaku Zasshi*, **71**, 1088 (1951); *Chem. Abstr.*, **46**, 5046 (1952).
377. T. Ishii, *Yakugaku Zasshi*, **72**, 317 (1952); *Chem. Abstr.*, **47**, 12386 (1953).
378. E. Hayashi, H. Yamanaka and K. Shimizu, *Chem. Pharm. Bull.*, **6**, 323 (1958).
379. Y. Kawazoe and M. Araki, *Chem. Pharm. Bull.*, **16**, 839 (1968).
380. M. Ishikawa and I. Kikkawa, *Yakugaku Zasshi*, **75**, 33 (1955); *Chem. Abstr.*, **50**, 1007 (1956).
381. T. Naito, *Yakugaku Zasshi*, **65**, 5/6A, (1945); *Chem. Abstr.*, **45**, 8528 (1951).
382. E. Hayashi, H. Yamanaka and K. Shimizu, *Chem. Pharm. Bull.*, **7**, 149 (1959).
383. Y. Suzuki, *Yakugaku Zasshi*, **81**, 1151 (1961); *Chem. Abstr.*, **56**, 3447 (1962).
384. M. Hamana, *Yakugaku Zasshi*, **75**, 130 (1955); *Chem. Abstr.*, **50**, 1817 (1956).
385. C. Wagner, H. Pischel and R. Schmidt, *Z. Chem.*, **2**, 86 (1962); *Chem. Abstr.*, **58**, 5776 (1963).
386. M. Hamana, S. Saeki, Y. Hatano and M. Nagakura, *Yakugaku Zasshi*, **83**, 348 (1963); *Chem. Abstr.*, **59**, 9976 (1963).
387. T. Naito, *Yakugaku Zasshi*, **67**, 141 (1947); *Chem. Abstr.*, **45**, 9539 (1951).
388. E. Hayashi, H. Yamanaka and C. Iijimi, *Yakugaku Zasshi*, **80**, 1145 (1960); *Chem. Abstr.*, **55**, 546 (1961).
389. Yu. V. Kurbatov, A. S. Kurbatova, A. S. Otroshchenko, A. S. Sadykov and V. P. Smiyanova, *Tr. Samarkand Gos. Univ.*, No. 206, 220 (1972); *Chem. Abstr.*, **80**, 36900 (1974).
390. A. S. Kurbatova, Yu. V. Kurbatov, O. S. Otroshchenko and A. S. Sadykov, *Khim. Geterosikl. Soedin.*, **1976**, 920; *Chem. Abstr.*, **85**, 159845 (1976).
391. Yu. V. Kurbatov, A. S. Kurbatova, O. S. Otroshchenko and A. S. Sadykov, *Tr. Samarkand Gos. Univ.*, No. 167, 71 (1969); *Chem. Abstr.*, **75**, 139950 (1971).
392. A. S. Kurbatova, Yu. V. Kurbatov, O. S. Otroshchenko and A. S. Sadykov, *Nauch. Tr. Samarkand Univ.*, No. 167, 26 (1969); *Chem. Abstr.*, **74**, 141474 (1971).
393. Yu. V. Kurbatov, A. S. Kurbatova, O. U. Zalyalieva, O. S. Otroshchenko, and A. S. Sadykov, *Nauch. Tr. Samarkand Univ.*, No. 167, 9 (1969); *Chem. Abstr.*, **74**, 142111 (1971).
394. S. Tagami, C. Tabuchi, K. Morimoto and D. Shiho, *Yakugaku Zasshi*, **94**, 929 (1974); *Chem. Abstr.*, **82**, 43264 (1975).

395. A. S. Kurbatova, Yu. V. Kurbatov, M. R. Avezov, O. S. Otroshchenko and A. S. Sadykov, *Tr. Samarkand Gos. Univ.*, No. 167, 38 (1969); *Chem. Abstr.*, **75**, 35643 (1971).
396. A. S. Kurbatova, Yu. V. Kurbatov, M. R. Avezov, O. S. Otroshchenko and A. S. Sadykov, *Nauch. Tr. Samarkand Univ.*, No 167, 38 (1969); *Chem. Abstr.*, **74**, 141478 (1971).
397. M. Hamana, B. Umezawa, and S. Nakashima, *Chem. Pharm. Bull.*, **10**, 969 (1962).
398. M. E. C. Biffin, J. Miller and D. B. Paul, *Tetrahedron Lett.*, **1969**, 1015.
399. M. Hamana, B. Umezawa and S. Nakashima, *Chem. Pharm. Bull.*, **10**, 961 (1962).
400. H. Tanida, *Yakugaku Zasshi*, **78**, 1083 (1958); *Chem. Abstr.*, **53**, 5266 (1959).
401. N. Ikekawa, O. Hoshino and Y. Honma, *Chem. Pharm. Bull.*, **17**, 906 (1969).
402. S. Kozuka, T. Akasaka, S. Furumai and S. Oae, *Chem. Ind. (London)*, **1974**, 452.
403. Y. Kawazoe and M. Tachibana, *Chem. Pharm. Bull.*, **13**, 1103 (1965).
404. S. Miyano and N. Abe, *Chem. Pharm. Bull.*, **15**, 511 (1967).
405. N. O. Saldabol, A. Tsimanis and S. A. Gillers, *Zh. Org. Khim.*, **10**, 1059 (1974); *Chem. Abstr.*, **81**, 49383 (1974).
406. G. Buchmann and H. J. Steinbach, *J. Prakt. Chem.*, **25**, 7 (1964).
407. E. Ochiai and H. Mitarashi, *Ann. Rep. Itsuu Lab.*, **1963**, 19; *Chem. Abstr.*, **60**, 5446 (1964).
408. T. Okano and K. Tsuji, *Yakugaku Zasshi*, **89**, 67 (1969); *Chem. Abstr.*, **70**, 96585 (1969).
409. M. Tachibana, Y. Kawazoe, K. Aoki and W. Nakahara, *Gann*, **56**, 85 (1965); *Chem. Abstr.*, **62**, 16187 (1965).
410. E. Ochiai, A. Ohta and H. Nomura, *Pharm. Bull. (Tokyo)*, **5**, 310 (1957); *Chem. Abstr.*, **52**, 14605 (1958).
411. E. Ochiai and T. Naito, *Yakugaku Zasshi*, **64**, 206 (1944); *Chem. Abstr.*, **45**, 5154 (1951).
412. S. Kamiya, *Chem. Pharm. Bull.*, **10**, 471 (1962).
413. H. J. Richter and N. E. Rustad, *J. Org. Chem.*, **29**, 3381 (1964).
414. Y. Kawazoe, M. Araki and W. Nakahara, *Chem. Pharm. Bull.*, **17**, 544 (1969).
415. I. Morita, M. Iigo, H. Fukino, K. Sakai and Y. Yamane, *Yakugaku Zasshi*, **95**, 954 (1975); *Chem. Abstr.*, **83**, 205534 (1975).
416. M. Hozumi, S. Inuzaka and T. Sugimara, *Cancer Res.*, **27**, 1378 (1967); *Chem. Abstr.*, **67**, 8470 (1967).
417. T. Matsushima, I. Kobuna, F. Fukuoka and T. Sugimura, *Gann*, **59**, 247 (1968); *Chem. Abstr.*, **69**, 42451 (1968).
418. H. Hoshino, F. Fukuoka, K. Okabe and T. Sugimura, *Gann*, **57**, 71 (1966); *Chem. Abstr.*, **64**, 16465 (1966).
419. Y. Kawazoe, M. Tamura and M. Araki, *Gann*, **61**, 593 (1970); *Chem. Abstr.*, **74**, 74182 (1971).
420. T. Sugimura, K. Obabe and H. Endo, *Gann*, **56**, 489 (1965); *Chem. Abstr.*, **64**, 1190 (1966).
421. L. A. Poirier and J. H. Weisburger, *Biochem. Pharmacol.*, **23**, 661 (1974); *Chem. Abstr.*, **81**, 46185 (1974).
422. N. Toriyama, *Nichidai Igaku Zasshi*, **24**, 423 (1965); *Chem. Abstr.*, **66**, 112465 (1967).
423. T. Kumakura, *Nichidai Igaku Zasshi*, **26**, 76 (1967); *Chem. Abstr.*, **70**, 64656 (1969).
424. T. Okabayashi and A. Yoshimoto, *Chem. Pharm. Bull.*, **10**, 1221 (1962).
425. S. Fukuda and N. Yamamoto, *Cancer Res.*, **32**, 435 (1972); *Chem. Abstr.*, **77**, 1253 (1972).
426. J. Haginawa, Y. Higuchi, T. Kawashima and T. Goto, *Yakugaku Zasshi*, **95**, 204 (1975); *Chem. Abstr.*, **83**, 43159 (1975).
427. C. A. Buehler, L. A. Walker and P. Garcia, *J. Org. Chem.*, **26**, 1410 (1961).
428. Y. Mizuno, T. Endo and T. Nakamura, *J. Org. Chem.*, **40**, 1391 (1975).
429. W. S. Chilton and A. K. Butler, *J. Org. Chem.*, **32**, 1270 (1967).
430. H. Saito, H. Muro, S. Saeki and M. Hamana, *Heterocycles*, **5**, (Special Issue), 331 (1976).
431. H. Saito, H. Muro, H. Noda, S. Saeki and M. Hamana, *Heterocycles*, **9**, 110 (1978).
432. M. Takahashi and R. Tanabe, *Chem. Pharm. Bull.*, **15**, 793 (1967).
433. G. Buchmann and D. Kirstein, *J. Prakt. Chem.*, **18**, 175 (1962).
434. M. Hamana, K. Funakoshi and Y. Kuchino, *Chem. Pharm. Bull.*, **22**, 1806 (1974).
435. M. Saneyoshi and M. Ikehara, *Chem. Pharm. Bull.*, **16**, 1390 (1968).
436. T. Naito and R. Dohmori, *Pharm. Bull. (Tokyo)*, **3**, 38 (1955); *Chem. Abstr.*, **50**, 1647 (1956).
437. T. Itai, *Yakugaku Zasshi*, **69**, 542 (1949); *Chem. Abstr.*, **44**, 4473 (1950).
438. I. El-Khiami and R. M. Johnson, *Talanta*, **14**, 745 (1967).
439. T. Kosuge and M. Yokota, *Yakugaku Zasshi*, **85**, 69 (1965); *Chem. Abstr.*, **62**, 10404 (1965).
440. A. Matsuyama and C. Nagata, *Top. Chem. Carcinog. Proc. 2nd Int. Symp., 1971*, **1972**, 35; *Chem. Abstr.*, **80**, 104674 (1974).

441. T. Kosuge, H. Zenda and H. Sawanishi, *Chem. Pharm. Bull.*, **17**, 2389 (1969).
442. U. Bressel, A. R. Katritzky and J. R. Lea, *J. Chem. Soc. B*, **1971**, 4.
443. N. Uehara and Y. Kawazoe, *Chem. Pharm. Bull.*, **18**, 203 (1970).
444. E. Ochiai and T. Okamoto, *Yakugaku Zasshi*, **67**, 86 (1947); *Chem. Abstr.*, **45**, 9059 (1951).
445. M. Yamazaki, Y. Chono, K. Noda and M. Hamana, *Yakugaku Zasshi*, **85**, 62 (1965); *Chem. Abstr.*, **62**, 10409 (1965).
446. E. Ochiai and T. Yokokawa, *Yakugaku Zasshi*, **75**, 213 (1955); *Chem. Abstr.*, **50**, 1819 (1956).
447. E. Hayashi, *Yakugaku Zasshi*, **71**, 213 (1951); *Chem. Abstr.*, **46**, 4541 (1952).
448. T. Naito, *Yakugaku Zasshi*, **67**, 246 (1947); *Chem. Abstr.*, **45**, 9541 (1951).
449. T. Ukai, Y. Yamamoto, Y. Ito, A Yanagi and M. Yotsuzuka, *Yakugaku Zasshi*, **75**, 490 (1955).
450. T. M. Mishina and L. S. Efros, *Zh. Obshch. Khim.*, **32**, 2217 (1962); *Chem. Abstr.*, **58**, 9023 (1963).
451. G. M. Badger and R. C. Buttery, *J. Chem. Soc.*, **1956**, 614.
452. E. Ochiai and T. Okamoto, *Yakugaku Zasshi*, **70**, 384 (1950); *Chem. Abstr.*, **45**, 2476 (1951).
453. E. Ochiai, M. Ishikawa and Sai Zai-ren, *Yakugaku Zasshi*, **63**, 280 (1943); *Chem. Abstr.*, **45**, 5152 (1951).
454. J. T. Gleghorn, R. B. Moodie, E. A. Qureshi and K. Schofield, *J. Chem. Soc. B*, **1968**, 316.
455. Y. Hamada, H. Sugihara and T. Isobe, *Yakugaku Zasshi*, **82**, 1592 (1962); *Chem. Abstr.*, **59**, 564 (1963).
456. M. Hamana and T. Nagayoshi, *Chem. Pharm. Bull.*, **14**, 319 (1966).
457. M. Hamana and M. Yatabe, *Yakagaku Zasshi*, **94**, 566 (1974); *Chem. Abstr.*, **81**, 120419 (1974).
458. E. Ochiai and C. Kaneko, *Chem. Pharm. Bull.*, **7**, 191 (1959).
459. E. Ochiai and A. Ohta, *Chem. Pharm. Bull.*, **10**, 349 (1962).
460. E. Ochiai and A. Ohta, *Sci. Pap. Inst. Phys. Chem. Res. (Tokyo)*, **56**, 189 (1962); *Chem. Abstr.*, **58**, 2433 (1963).
461. H. Tanida, *Yakugaku Zasshi*, **78**, 1079 (1958); *Chem. Abstr.*, **53**, 5266 (1959).
462. E. Ochiai and C. Kaneko, *Chem. Pharm. Bull.*, **8**, 28 (1960).
463. R. Taylor, *J. Chem. Soc. Perkin Trans. 2*, **1975**, 277.
464. E. Ochiai and C. Kaneko, *Chem. Pharm. Bull.*, **7**, 267 (1959).
465. E. Ochiai and E. Hayashi, *Yakugaku Zasshi*, **67**, 157 (1951); *Chem. Abstr.*, **45**, 9541 (1951).
466. E. Ochiai and M. Ikehara, *Yakugaku Zasshi*, **70**, 265 (1950); *Chem. Abstr.*, **45**, 2945 (1951).
467. E. Ochiai, M. Ikehara, T. Kato and N. Ikekawa, *Yakugaku Zasshi*, **71**, 1385 (1951); *Chem. Abstr.*, **46**, 7101 (1952).
468. M. Ishikawa, *Yakugaku Zasshi*, **65**, 3A, 4 (1945); *Chem. Abstr.*, **45**, 8528 (1951).
469. E. Ochiai and H. Mitarashi, *Chem. Pharm. Bull.*, **12**, 1495 (1964).
470. E. Ochiai and C. Kaneko, *Chem. Pharm. Bull.*, **7**, 195 (1959).
471. T. Okamoto, *Yakugaku Zasshi*, **71**, 727 (1951); *Chem. Abstr.*, **46**, 4542 (1952).
472. E. Ochiai and M. Ikehara, *Jap. Pat.* 54 3326; *Chem. Abstr.*, **50**, 1092 (1956).
473. M. Yamazaki, K. Noda, J. Onoyama and M. Hamana, *Yakugaku Zasshi*, **88**, 656 (1968); *Chem. Abstr.*, **69**, 106500 (1968).
474. T. Naito, *Yakugaku Zasshi*, **68**, 209 (1948); *Chem. Abstr.*, **47**, 8075 (1953).
475. K. H. Pausacker, *Aust. J. Chem.*, **11**, 200 (1958).
476. C. Kaneko, *Chem. Pharm. Bull.*, **7**, 273 (1959).
477. E. Ochiai and H. Ogura, *Yakugaku Zasshi*, **72**, 767 (1952); *Chem. Abstr.*, **48**, 2711 (1954).
478. T. Naito, *Yakugaku Zasshi*, **67**, 144 (1947); *Chem. Abstr.*, **45**, 9540 (1951).
479. M. Ishikawa, *Yakugaku Zasshi*, **65**, 3A, 5 (1945); *Chem. Abstr.*, **45**, 8528 (1951).
480. I. F. Tupitsyn, N. N. Zatsepina and A. V. Kirova, *Reakts. Sposobnost. Org. Soedin.*, **5**, 626 (1968); *Chem. Abstr.*, **70**, 76942 (1969).
481. I. F. Tupitsyn, N. N. Zatsepina, A. V. Kirova and Yu. M. Kapustin, *Reakts. Sposobnost. Org. Soedin.*, **5**, 636 (1968); *Chem. Abstr.*, **70**, 76943 (1969).
482. I. F. Tupitsyn, N. N. Zatsepina, A. V. Kirova and Yu. M. Kapustin, *Reakts. Sposobnost. Org. Soedin.*, **5**, 806 (1968); *Chem. Abstr.*, **70**, 76944 (1969).
483. Y. Kobayashi, I. Kumadaki, H. Shato, C. Yokoe and T. Mimura, *Chem. Pharm. Bull.*, **21**, 2066 (1973).
484. Y. Hamada, I. Takeuchi, I. Ozawa, T. Ogaka, and K. Morishita, *Hukusokan Kagaku Toronkai Koen Yoshishu 8th*, **1975**, 139; *Chem. Abstr.*, **84**, 180002 (1976).

485. Y. Hamada and I. Takeuchi, *J. Org. Chem.*, **42**, 4209 (1977).
486. E. Ochiai and A. Ohta, *Chem. Pharm. Bull.*, **10**, 1260 (1962).
487. E. Ochiai and A. Ohta, *Sci. Pap. Inst. Phys. Chem. Res. (Tokyo)*, **56**, 290 (1962); *Chem. Abstr.*, **59**, 2766 (1963).
488. T. Kato and H. Yamanaka, *J. Org. Chem.*, **30**, 910 (1965).
489. T. Kato, H. Yamanaka, T. Sakamoto and T. Shiraishi, *Chem. Pharm. Bull.*, **22**, 1206 (1974).
490. Y. Kobayashi, I. Kumadaki and H. Sato, *J. Org. Chem.*, **37**, 3588 (1972).
491. R. A. Abramovitch and B. W. Cue, Jr., *Heterocycles*, **1**, 227 (1973).
492. V. M. Clark, D. W. Hutchinson and D. E. Wilson, *Angew. Chem.*, **77**, 259 (1965).
493. L. H. Conover, A. R. English and C. E. Larrabee, Jr., *U.S. Pat.* 2,921,073; *Chem. Abstr.*, **54**, 8860 (1960).
494. C. Pfizer and Co. Inc., *Brit. Pat.* 847,701; *Chem. Abstr.*, **55**, 11446 (1961).
495. T. E. Furia and D. H. Steinberg, *Ger. Offen.*, 2,035,171; *Chem. Abstr.*, **74**, 91155 (1971).
496. E. Ochiai and M. Takahashi, *Jap. Pat.* 6528,097; *Chem. Abstr.*, **64**, 11183 (1966).
497. T. Itai, *Yakugaku Zasshi*, **65**, 9 10A, 8 (1945); *Chem. Abstr.*, **45**, 5688 (1951).
498. G. Buchmann, *East Ger. Pat.* 17,051; *Chem. Abstr.*, **54**, 19722 (1960).
499. T. Okabayashi, *Hakko Kogaku Zasshi*, **35**, 20 (1957); *Chem. Abstr.*, **51**, 18100 (1957).
500. K. N. Dixit, S. D. Jolad and S. Rajagopal, *Monatsh. Chem.*, **94**, 414 (1963).
501. K. Shichiri, K. Funakoshi, S. Saeki and M. Hamana, *Chem. Pharm. Bull.*, **28**, 424 (1980); K. Shichiri, K. Funakoshi, S. Saeki and M. Hamana, *Chem. Pharm. Bull.*, **28**, 493 (1980).
502. G. Wagner and R. Schmidt, *Pharmazie*, **20**, 549 (1965); *Chem. Abstr.*, **64**, 6737 (1966).
503. T. Okamoto, H. Hayatsu and Y. Baba, *Chem. Pharm. Bull.*, **8**, 892 (1960).
504. A. S. Tomcufcik, P. F. Fabio and A. M. Hoffman, *Belg. Pat.* 637,271; *Chem. Abstr.*, **62**, 11830 (1965).
505. A. S. Tomcufcik, P. F. Fabio and A. M. Hoffman, *U.S. Pat.* 3,331,843; *Chem. Abstr.*, **67**, 90839 (1967).
506. G. Buchmann and D. Kirstein, *E. Ger. Pat.* 39,934; *Chem. Abstr.*, **63**, 18052 (1965).
507. L. M. Werbel and E. F. Elslager, *U.S. Pat.* 3,136,769; *Chem. Abstr.*, **61**, 5618 (1964).
508. S. I. Yoshida, *Yakugaku Zasshi*, **66**, 60 (1946); *Chem. Abstr.*, **45**, 6637 (1951).
509. T. Yamamori, H. Noda and M. Hamana, *Tetrahedron*, **31**, 945 (1975).
510. Th. Kauffmann and R. Wirthwein, *Angew. Chem.*, **76**, 993 (1964).
511. R. Peereboom and H. J. Den Hertog, *Rec. Trav. Chim.*, **93**, 281 (1974).
512. T. Itai, *Yakugaku Zasshi*, **65**, 70 (1945); *Chem. Abstr.*, **45**, 8525 (1951).
513. T. Okamoto and M. Itoh, *Chem. Pharm. Bull.*, **11**, 785 (1963).
514. M. Hamana and S. Kumadaki, *Yakagaku Zasshi*, **88**, 665 (1968); *Chem. Abstr.*, **69**, 106502 (1968).
515. T. Okano and T. Kano, *Chem. Pharm. Bull.*, **19**, 1293 (1971).
516. T. Okano, *Jap. Kokai*, 7546,672; Chem. Abstr., **83**, 114925 (1975).
517. T. Nakamura, *Yakugaku Zasshi*, **63**, 182 (1943); *Chem. Abstr.*, **46**, 127 (1952).
518. Y. Hamada, *Yakugaku Zasshi*, **80**, 1573 (1960); *Chem. Abstr.*, **55**, 10450 (1961).
519. J. Himeno, K. Noda and M. Yamazaki, *Chem. Pharm. Bull.*, **18**, 2138 (1970).
520. T. Okamoto and M. Mochizuki, *Chem. Pharm. Bull.*, **17**, 987 (1969).
521. S. Al-Kassab, E. Boyland and K. Williams, *Biochem. J.*, **87**, 4 (1963).
522. E. Ochiai and T. Naito, *Yakugaku Zasshi*, **65**, 5/6A, 3 (1945); *Chem. Abstr.*, **45**, 8528 (1951).
523. C. Kaneko, H. Hasegawa, S. Tanaka, K. Sunayashiki and S. Yamada, *Chem. Lett.*, **1974**, 133.
524. J. H. Blumenthal, *U.S. Pat.* 2,874,162; *Chem. Abstr.*, **53**, 12311 (1959).
525. R. E. Lyle, D. E. Portlock, M. J. Kane and J. A. Bristol, *J. Org. Chem.*, **37**, 3967 (1972).
526. M. Hamana, *Yakugaku Zasshi*, **75**, 127 (1955); *Chem. Abstr.*, **50**, 1817 (1956).
527. G. Buchmann and R. Ernst, *East Ger. Pat.* 20,182 (1960); *Chem. Abstr.*, **56**, 462 (1962).
528. E. Ochiai, G. Kobayashi, M. Hamana and T. Sugasawa, *Yakugaku Zasshi*, **71**, 260 (1951); *Chem. Abstr.*, **46**, 515 (1952).
529. M. Hamana and K. Uzu, *Yakugaku Zasshi*, **74**, 1315 (1954); *Chem. Abstr.*, **49**, 15922 (1955).
530. T. Kametani, A. Kozuka and T. Terui, *Yakugaku Zasshi*, **93**, 406 (1973); *Chem. Abstr.*, **79**, 31817 (1973).
531. O. Cervinka, A. Fabryova and L. Matouchova, *Collect. Czech. Chem. Commun.*, **28**, 535 (1963).

532. T. Okamoto and H. Takayama, *Chem. Pharm. Bull.*, **11**, 514 (1963).
533. T. Okamoto and H. Tani, *Chem. Pharm. Bull.*, **7**, 130 (1959).
534. T. Okamoto and H. Tani, *Chem. Pharm. Bull.*, **7**, 925 (1959).
535. W. E. Feely and E. M. Beavers, *J. Amer. Chem. Soc.*, **81**, 4004 (1959).
536. W. A. Feeley, *U.S. Pat.* 2,991,285; *Chem. Abstr.*, **56**, 7283 (1962).
537. L. Bauer and T. E. Dickerhofe, *J. Org. Chem.*, **31**, 939 (1966).
538. D. Redmore, *U.S. Pat.* 3,810,907; *Chem. Abstr.*, **81**, 37646 (1974).
539. D. Redmore, *U.S. Pat.* 3,888,626; *Chem. Abstr.*, **83**, 97569 (1975).
540. D. Redmore, *U.S. Pat.* 3,888,627; *Chem. Abstr.*, **83**, 97570 (1975).
541. I. A. Krasavin, V. M. Dziomko and Yu. P. Radin, *Metody Poluch. Khim. Reakt. Prep.*, No. 13, 68 (1965); *Chem. Abstr.*, **65**, 5437 (1966).
542. M. Henze, *Ber.*, **69**, 1566 (1936).
543. M. Hamana and K. Funagoshi, *Yakugaku Zasshi*, **80**, 1031 (1960); *Chem. Abstr.*, **55**, 542 (1961).
544. E. Hayashi and N. Shimada, *Yakugaku Zasshi*, **97**, 627 (1977); *Chem. Abstr.*, **87**, 167846 (1977).
545. H. Tanida, *Yakugaku Zasshi*, **78**, 611 (1958); *Chem. Abstr.*, **52**, 18420 (1958).
546. F. Montanari and L. Pentimalli, *Gazz. Chim. Ital.*, **83**, 273 (1953); *Chem. Abstr.*, **47**, 12387 (1953).
547. T. Yoshikawa, K. Yamaguchi and Y. Urabe, *Yakugaku Zasshi*, **89**, 756 (1969); *Chem. Abstr.*, **71**, 81110 (1969).
548. F. Montanari and A. Risalita, *Gazz. Chim. Ital.*, **83**, 278 (1953); *Chem. Abstr.*, **47**, 12388 (1953).
549. E. Ochiai and T. Okamoto, *Yakugaku Zasshi*, **68**, 88 (1948); *Chem. Abstr.*, **47**, 8073 (1953).
550. M. Hamana and I. Kumadaki, *Yakugaku Zasshi*, **86**, 1090 (1966); *Chem. Abstr.*, **66**, 104885 (1967).
551. K. Oda, *Yakugaku Zasshi*, **64**, 6 (1944); *Chem. Abstr.*, **45**, 8523 (1951).
552. E. Ochiai and I. Nakayama, *Yakugaku Zasshi*, **65**, 9/10A, 7 (1945); *Chem. Abstr.*, **45**, 8529 (1951).
553. M. Hamana and T. Matsumoto, *Yakugaku Zasshi*, **91**, 269 (1971); *Chem. Abstr.*, **74**, 99834 (1971).
554. C. Kaneko, *Chem. Pharm. Bull.*, **8**, 286 (1960).
555. I. Nakayama, *Yakugaku Zasshi*, **70**, 355 (1950); *Chem. Abstr.*, **45**, 2945 (1951).
556. I. Nakayama, *Jap. Pat.* 3621 (1950); *Chem. Abstr.*, **47**, 3352 (1953).
557. I. Nakayama, *Yakugaku Zasshi*, **70**, 423 (1950); *Chem. Abstr.*, **45**, 2487 (1951).
558 .I. Nakayama, *Yakugaku Zasshi*, **71**, 1391 (1951); *Chem. Abstr.*, **46**, 7101 (1952).
559. E. Hayashi and N. Shimada, *Yakugaku Zasshi*, **97**, 641 (1977); *Chem. Abstr.*, **88**, 22570 (1978).
560. H. Tanida, *Chem. Pharm. Bull.*, **7**, 887 (1959).
561. S. Oae, S. Tamagaki and S. Kozuka, *Tetrahedron Lett.*, **1966**, 1513.
562. M. Hamana and K. Funakoshi, *Yakugaku Zasshi*, **84**, 28 (1964); *Chem. Abstr.*, **61**, 3068 (1964).
563. M. Murakami and E. Matsumura, *J. Chem. Soc. Jap., Pure Chem. Sect.*, **72**, 509 (1951); *Mem. Inst. Sci. Ind. Res., Osaka Univ.*, **8**, 168 (1951); *Chem. Abstr.*, **46**, 6648 (1952).
564. K. Ogino and S. Oae, *Kogyo Kagaku Zasshi*, **73**, 2300 (1970); *Chem. Abstr.*, **74**, 124566 (1971).
565. E. Ochiai, T. Teshigawara, K. Oda, and T. Naito, *Yakugaku Zasshi*, **65**, 5/6A, 1 (1945); *Chem. Abstr.*, **45**, 8527 (1951).
566. P. Bruni and G. Guerra, *Ann. Chim. (Rome)*, **57**, 688 (1967); *Chem. Abstr.*, **67**, 116779 (1967).
567. M. Hamana and I. Kumadaki, *Chem. Pharm. Bull.*, **18**, 1822 (1970).
568. M. Hamana and M. Yamazaki, *Chem. Pharm. Bull.*, **11**, 411 (1963).
569. J. E. Douglass and H. D. Fortner, *J. Heterocycl. Chem.*, **10**, 115 (1973).
570. M. Hamana and M. Yamazaki, *Chem. Pharm. Bull.*, **11**, 415 (1963).
571. A. Pollak, B. Stanovnik, M. Tisler and J. Venetic-Fortuna, *Monatsh. Chem.*, **106**, 473 (1975).
572. M. Yamazaki, K. Noda and M. Hamana, *Chem. Pharm. Bull.*, **18**, 901 (1970).
573. J. Kacens, A. Cebure, and O. Neilands, *Latv. PSR Zinat. Akad. Vestis Kim. Ser.*, **1973**, 100; *Chem. Abstr.*, **78**, 124420 (1973).

574. M. Yamazaki, K. Noda, N. Honjo and M. Hamana, *Chem. Pharm. Bull.*, **21**, 712 (1973).
575. M. Sone, Y. Tominaga, R. Natsuki, Y. Matsuda and G. Kobayashi, *Chem. Pharm. Bull.*, **22**, 617 (1974).
576. T. Endo, S. Saeki and M. Hamana, *Heterocycles*, **3**, 19 (1975).
577. J. E. Douglass and D. Koottungal, *J. Org. Chem.*, **37**, 2913 (1972).
578. J. E. Douglass and D. A. Hunt, *J. Org. Chem.*, **42**, 3974 (1977).
579. V. N. Gogte, K. M. More and B. D. Tilak, *Indian J. Chem.*, **12**, 1238 (1974).
580. S. Furukuwa, T. Kinoshita and M. Watanabe, *Yakugaku Zasshi*, **93**, 1064 (1973); *Chem. Abstr.*, **79**, 105189 (1973).
581. M. Watanabe, M. Kodera, T. Kinoshita and S. Furukawa, *Chem. Pharm. Bull.*, **23**, 2598 (1975).
582. M. Colonna, P. Bruni and A. M. Guerra, *Gazz. Chim. Ital.*, **96**, 1410 (1966).
583. M. Colonna and P. Bruni, *Boll. Sci. Fac. Chim. Ind. Bologna*, **23**, 401 (1965); *Chem. Abstr.*, **64**, 17536 (1966).
584. M. Hamana and I. Kumadaki, *Chem. Pharm. Bull.*, **15**, 363 (1967); **18**, 1742 (1970).
585. M. Hamana and H. Noda, *Chem. Pharm. Bull.*, **15**, 1380 (1967).
586. M. Hamana and O. Hoshino, *Yakugaku Zasshi*, **84**, 35 (1964); *Chem. Abstr.*, **61**, 3069 (1964).
587. M. Hamana and H. Noda, *Chem. Pharm. Bull.*, **11**, 1331 (1963).
588. M. Hamana and H. Noda, *Chem. Pharm. Bull.*, **15**, 474 (1967).
589. M. Hamana and H. Noda, *Yakugaku Zasshi*, **89**, 641 (1969); *Chem. Abstr.*, **71**, 61165 (1969).
590. S. Saeki, A. Yamashita, Y. Matsukura and M. Hamana, *Chem. Pharm. Bull.*, **22**, 2341 (1974).
591. M. Nakanishi and M. Yatabe, *Japan Kokai*, 75 24,278; *Chem. Abstr.*, **83**, 131479 (1975).
592. H. Noda, T. Yamamori, M. Yohshida and M. Hamana, *Heterocycles*, **4**, 453 (1976).
593. P. Bruni and A. Strocchi, *Ann. Chim. (Rome)*, **56**, 767 (1966); *Chem. Abstr.*, **65**, 13649 (1966).
594. M. Hamana and H. Noda, *Chem. Pharm. Bull.*, **18**, 26 (1970).
595. V. N. Gogte, R. N. Sathe and B. D. Tilak, *Indian J. Chem.*, **11**, 1115 (1973).
596. H. Tanida, *Chem. Pharm. Bull.*, **7**, 944 (1959).
597. M. A. Solekhova, Yu. V. Kurbatov, O. S. Otroshchenko and A. S. Sadykov, *Tezisy Dokl. Simp. Khim. Tekhnol. Geterosikl. Soedin. Goryuch. Iskop. 2nd.* **1973**, 168; *Chem. Abstr.*, **85**, 177227 (1976).
598. M. A. Solekhova, Yu. V. Kurbatov, O. S. Otroshchenko and A. S. Sadykov, *Khim. Geterosikl. Soedin.* **1976**, 229; *Chem. Abstr.*, **84**, 150472 (1976).
599. H. Tanida, *Yakugaku Zasshi*, **78**, 608 (1958); *Chem. Abstr.*, **52**, 18420 (1958); *Jap. Pat.* 61 17,464; *Chem. Abstr.*, **54**, 3420 (1960).
600. M. Hamana and S. Kumadaki, *Chem. Pharm. Bull.*, **23**, 2284 (1975).
601. M. Hamana and S. Kumadaki, *Chem. Pharm. Bull.*, **21**, 800 (1973).
602. M. Hamana and K. Funakoshi, *Yakugaku Zasshi*, **82**, 512 (1962); *Chem. Abstr.*, **58**, 4512 (1963).
603. R. A. Abramovitch, R. B. Rogers, and G. M. Singer, *J. Org. Chem.*, **40**, 41 (1975); R. A. Abramovitch and R. B. Rogers, *Tetrahedron Lett.*, **1971**, 1951.
604. M. Hamana and K. Muraoka, *Heterocycles*, **1**, 241 (1973).
605. M. Hamana, K. Funakoshi, H. Shigyo and Y. Kuchino, *Chem. Pharm. Bull.*, **23**, 346 (1975).
606. R. E. Banks, R. N. Haszeldine and J. M. Robinson, *J. Chem. Soc. Perkin Trans. 1*, **1976**, 1126.
607. Y. Kobayashi, I. Kumadaki and S. Fujino, *Heterocycles*, **7**, 871 (1977).
608. R. A. Abramovitch, G. Grins, R. B. Rogers, J. L. Atwood, M. D. Williams and S. Crider, *J. Org. Chem.*, **37**, 3383 (1972); R. A. Abramovitch and I. Shinkai, *J. Chem. Soc. Chem. Commun.*, **1973**, 569.
609. P. Canonne, G. Lemay and R. A. Abramovitch, *Heterocycles*, **9**, 1217 (1978).
610. R. A. Abramovitch and I. Shinkai, *Acc. Chem. Res.*, **9**, 192 (1976).
611. Y. Kobayashi, I. Kumadaki, H. Mochizuki, S. Fujino and T. Kutsuma, *Hukusokan Kagaku Toronkai Koen Yoshishu 8th*, **1975**, 64; *Chem. Abstr.*, **85**, 5474 (1976).
612. M. Hamana, H. Noda and M. Aoyama, *Heterocycles*, **2**, 167 (1974).
613. T. Onaka, *Ann. Rep. Itsuu Lab.*, **1968**, 29; *Chem. Abstr.*, **72**, 90231 (1970).
614. G. Wittig and G. Steinhoff, *Ann.*, **676**, 21 (1964).
615. M. Colonna, *Boll. Sci. Fac. Chim. Ind., Bologna*, **1940**, 134; *Chem. Abstr.*, **34**, 7290 (1940).
616. T. Kato, H. Yamanaka, T. A. Dachi and H. Hiranuma, *J. Org. Chem.*, **32**, 3788 (1967).

617. T. Kato, H. Yamanaka and M. Hikichi, *Yakugaku Zasshi*, **85**, 331 (1965); *Chem. Abstr.*, **63**, 4250 (1965).
618. M. Colonna and A. Risaliti, *Ann. Chim. (Rome)*, **44**, 1029 (1954); *Chem. Abstr.*, **50**, 342 (1956).
619. G. Kobayashi, *Yakugaku Zasshi*, **70**, 381 (1950); *Chem. Abstr.*, **45**, 2491 (1951).
620. K. Takeda and K. Hamamoto, *Yakugaku Zasshi*, **73**, 1158 (1953); *Chem. Abstr.*, **48**, 12748 (1954).
621. S. Kajihara, *Nippon Kagaku Zasshi*, **85**, 672 (1964); *Chem. Abstr.*, **62**, 14624 (1965); K. Hamamoto and T. Kajihara, *Jap. Pat.* 66 13,985; *Chem. Abstr.*, **65**, 20108 (1966).
622. H. Sawanishi and Y. Kamiya, *Yakugaku Zasshi*, **97**, 753 (1977); *Chem. Abstr.*, **87**, 167848 (1977).
623. H. Itokawa, S. Kameyama, T. Inaba, T. Tazaki, R. Haruta, Y. Kawazoe and M. Maeda, *Chem. Pharm. Bull.*, **26**, 1015 (1978).
624. M. H. Palmer and P. S. McIntyre, *Tetrahedron Lett.*, **1968**, 2147.
625. T. Itai, Y. Natsume and M. Natsume, *Jap. Pat.* 70 01,264; *Chem. Abstr.*, **72**, 90320 (1970).
626. T. Kosuge, K. Adachi, M. Yokota and T. Nakao, *Yakugaku Zasshi*, **85**, 66 (1965).
627. M. Natsume, S. Kumadaki and R. Tanabe, *Ann. Rep. Itsuu Lab.*, **1971**, 25; *Chem. Abstr.*, **77**, 61765 (1972).
628. T. Kosuge, M. Yokota, and H. Sawanishi, *Chem. Pharm. Bull.*, **13**, 1480 (1965).
629. T. Kosuge, M. Yokota and H. Sawanishi, *Yakugaku Zasshi*, **88**, 1487 (1968); *Chem. Abstr.*, **70**, 68092 (1969).
630. T. Kosuge, H. Zenda, H. Sawanishi and Y. Suzuki, *Chem. Pharm. Bull.*, **17**, 2178 (1969).
631. O. Buchardt, K. B. Tomer and V. Madsen, *Tetrahedron Lett.*, **1971**, 1311.
632. C. Kaneko, S. Hayashi and Y. Kobayashi, *Chem. Pharm. Bull.*, **22**, 2147 (1974).
633. O. Buchardt, B. Jensen and I. K. Larsen, *Acta Chem. Scand.*, **21**, 1841 (1967).
634. C. Kaneko and S. Yamada, *Chem. Pharm. Bull.*, **14**, 555 (1966).
635. O. Buchardt, *Tetrahedron Lett.*, **1966**, 6221.
636. R. Kitamura, H. Fujii, K. Hashiba, M. Somei and C. Kaneko, *Tetrahedron Lett.*, **1977**, 2911.
637. O. Buchardt, P. L. Kumler and C. Lohse, *Acta Chem. Scand.*, **23**, 1155 (1969).
638. I. Yokoe, M. Ishikawa, and C. Kaneko, *Rep. Res. Inst. Med. Eng., Tokyo Medico-Dental Univ.*, **6**, 18 (1972); *Chem. Abstr.*, **81**, 105233 (1974).
639. C. Kaneko, S. Yamada and M. Ishikawa, *Tetrahedron Lett.*, **1966**, 2145.
640. C. Kaneko and S. Yamada, *Shika Zairyo Kenkyusho Kokoku*, **2**, 804 (1966); *Chem. Abstr.*, **69**, 96524 (1968).
641. C. Kaneko and S. Yamada, *Chem. Pharm. Bull.*, **15**, 663 (1967).
642. M. Ishikawa, C. Kaneko, S. Yamada, M. Hasebe and K. Sunayashiki, *Japan Kokai*, 74 43,972; *Chem. Abstr.*, **81**, 120450 (1974).
643. N. Hata and I. Ono, *Bull. Chem. Soc. Jap.*, **49**, 1794 (1976).
644. N. Hata and T. Oguro, *Chem. Lett.*, **1978**, 597.
645. O. Buchardt, *Acta Chem. Scand.*, **17**, 1461 (1963).
646. O. Buchardt, P. L. Kumler and C. Lohse, *Acta Chem. Scand.*, **23**, 159 (1969).
647. M. Ishikawa, S. Yamada, H. Hotsa and C. Kaneko, *Chem. Pharm. Bull.*, **14**, 1102 (1966).
648. O. Buchardt, P. L. Kumler and C. Lohse, *Acta Chem. Scand.*, **23**, 2149 (1969).
649. C. Kaneko, I. Yokoe and S. Yamada, *Tetrahedron Lett.*, **1967**, 775.
650. G. G. Spence, E. C. Taylor and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970).
651. C. Kaneko, I. Yokoe and M. Ishikawa, *Tetrahedron Lett.*, **1967**, 5237.
652. M. Ishikawa, S. Yamada and C. Kaneko, *Chem. Pharm. Bull.*, **13**, 747 (1965).
653. O. Buchardt and C. Lohse, *Tetrahedron Lett.*, **1966**, 4355.
654. C. Kaneko, S. Yamada, I. Yokoe and M. Ishikawa, *Tetrahedron Lett.*, **1967**, 1873.
655. A. Ide, Y. Mori, K. Matsumori and H. Watanabe, *Bull. Chem. Soc. Jap.*, **50**, 1959 (1977).
656. T. Kato and T. Niitsuma, *Yakugaku Zasshi*, **94**, 766 (1974); *Chem. Abstr.*, **81**, 91302 (1974).
657. T. Kato, Y. Goto and M. Kondo, *Yakugaku Zasshi*, **84**, 290 (1964); *Chem. Abstr.*, **61**, 3070 (1964).
658. M. Colonna, *Gazz. Chim. Ital.*, **91**, 34 (1961); *Chem. Abstr.*, **56**, 12851 (1962).
659. S. Tamagaki, K. Ogino, S. Kozuka and S. Oae, *Tetrahedron*, **26**, 4675 (1970).
660. C. W. Muth, R. S. Darlak, M. L. Dematte and G. F. Chovanec, *J. Org. Chem.*, **33**, 2762 (1968).

661. S. Tamagaki, S. Kozuka and S. Oae, *Tetrahedron Lett.*, **1968**, 4765.
662. S. Oae, S. Tamagaki, T. Negoro, K. Ogino and S. Kozuka, *Tetrahedron Lett.*, **1968**, 917.
663. S. Furukawa, *Yakugaku Zasshi*, **59**, 492 (1959); *Chem. Abstr.*, **53**, 18029 (1959).
664. S. Oae, T. Kitao and Y. Kitaoka, *J. Amer. Chem. Soc.*, **84**, 3359 (1963).
665. S. Oae, T. Kitao and Y. Kitaoka, *J. Amer. Chem. Soc.*, **84**, 3362 (1963).
666. S. Kozuka, S. Tamagaki, T. Negoro and S. Oae, *Tetrahedron Lett.*, **1968**, 923.
667. C. W. Muth and R. S. Darlak, *J. Org. Chem.*, **30**, 1909 (1965).
668. M. Henze, *Ber.*, **69**, 534 (1936).
669. I. J. Pachter, *J. Amer. Chem. Soc.*, **75**, 3026 (1953).
670. S. Oae and S. Kozuka, *Tetrahedron*, **20**, 2671 (1964).
671. G. Kobayashi, S. Furukawa, Y. Akimoto and T. Hoshi, *Yakugaku Zasshi*, **74**, 791 (1954); *Chem. Abstr.*, **49**, 11659 (1955).
672. S. Furukawa, *Pharm. Bull. (Tokyo)*, **3**, 413 (1955); *Chem. Abstr.*, **50**, 13926 (1956).
673. T. Kato, Y. Goto and Y. Yamamoto, *Yakugaku Zasshi*, **82**, 1649 (1962); *Chem. Abstr.*, **59**, 2765 (1963).
674. K. Ogino, S. Kozuka and S. Oae, *Tetrahedron Lett.*, **1969**, 3559.
675. M. Yamazaki, K. Noda, Y. Chono, N. Honjo and M. Hamana, *Yakugaku Zasshi*, **88**, 661 (1968); *Chem. Abstr.*, **69**, 106501 (1968).
676. F. Gerhart and L. Wilde, *Tetrahedron Lett.*, **1974**, 475.
677. K. Ramaiah and V. R. Srinivasan, *Indian J. Chem.*, **1**, 351 (1963).
678. M. Koremura and M. Nagawa, *Nippon Nogei Kagaku Kaishi*, **36**, 629 (1962); *Chem. Abstr.*, **62**, 4004 (1965).
679. Y. Nakawa, M. Koremura and Z. Hattori, *Jap. Pat.* 63 5685; *Chem. Abstr.*, **59**, 11449 (1963).
680. E. D. Parker and A. Furst, *J. Org. Chem.*, **23**, 201 (1958).
681. M. Colonna and L. Zamparella, *Gazz. Chim. Ital.*, **92**, 301 (1962); *Chem. Abstr.*, **57**, 9815 (1962).
682. M. Colonna, *Gazz. Chim. Ital.*, **90**, 1197 (1960); *Chem. Abstr.*, **56**, 5930 (1962).
683. W. Schulze, *J. Prakt. Chem.*, **19**, 91 (1962).
684. Y. Mizuno and J. Kobayashi, *J. Chem. Soc. Chem. Commun.*, **1975**, 308.
685. F. Ochiai and H. Tanida, *Pharm. Bull. (Tokyo)*, **5**, 313 (1957); *Chem. Abstr.*, **52**, 14606 (1958).
686. S. Kamiya, *Chem. Pharm. Bull. (Tokyo)*, **10**, 669 (1962).
687. H. Tanida, *Yakugaku Zasshi*, **78**, 613 (1958); *Chem. Abstr.*, **52**, 18420 (1958).
688. Y. Kobayashi, I. Kumadaki and S. Taguchi, *Chem. Pharm. Bull.*, **19**, 624 (1971).
689. Y. Suzuki, *Yakugaku Zasshi*, **81**, 1204 (1961); *Chem. Abstr.*, **56**, 3445 (1962).
690. Y. Muto, M. Kato, H. B. Jonassen and L. C. Cusachs, *Bull. Chem. Soc. Jap.*, **42**, 417 (1969).
691. R. W. Jotham, S. F. A. Kettle and J. A. Marks, *J. Chem. Soc. Dalton Trans.*, **1972**, 1133.
692. C. M. Harris, E. Kokot, S. L. Lenzer and T. N. Lockyer, *Chem. Ind. (London)*, **1962**, 651.
693. R. Whyman, D. B. Copley and W. E. Hatfield, *J. Amer. Chem. Soc.*, **89**, 3135 (1967).
694. S. J. Gruber, C. M. Harris, E. Kokot, S. L. Lenzer, T. N. Lockyer and E. Sinn, *Aust. J. Chem.*, **20**, 2403 (1967).
695. T. T. Tuichibaev, *Nauchn. Tr. Tashk. Gos. Univ.*, **379**, 142 (1970); *Chem. Abstr.*, **81**, 111927 (1974); *Chem. Abstr.*, **76**, 118035 (1972).
696. T. T. Tuichibaev, *Nauchn. Tr. Tashk. Gos. Univ.*, **379**, 137 (1970); *Chem. Abstr.*, **81**, 98756 (1974); *Chem. Abstr.*, **76**, 104591 (1972).
697. J. J. MacDougall, L. C. Nathan and J. H. Nelson, *Inorg. Chim. Acta*, **17**, 243 (1976).
698. J. Kratsmar-Smogrovic and M. Zemlicka, *Z. Naturforsch. B*, **28**, 689 (1973); *Chem. Abstr.*, **80**, 103329 (1974).
699. J. Kratsmar-Smogrovic and M. Melnik, *Z. Naturforsch. B*, **24**, 1479 (1969).
700. M. Melnik and J. Kratsmar-Smogrovic, *Chem. Zvesti*, **27**, 594 (1973); *Chem. Abstr.*, **80**, 88826 (1974).
701. J. Kohout and J. Kratsmar-Smogrovic, *Chem. Zvesti*, **22**, 481 (1968); *Chem. Abstr.*, **69**, 101022 (1968).
702. Y. Muto and H. B. Jonassen, *Bull. Chem. Soc. Jap.*, **39**, 58 (1966).
703. W. E. Hatfield, D. B. Copley and R. Whyman, *Inorg. Nucl. Chem. Lett.*, **2**, 375 (1966); *Chem. Abstr.*, **66**, 101191 (1967).
704. E. Sinn, *Inorg. Nucl. Chem. Lett.*, **5**, 193 (1969).

705. H. B. Jonassen, Y. Muto, and M. Kato, *U.S. Dept. Com. Office Tech. Serv. AD*, 403, 801 (1964); *Chem. Abstr.*, **61**, 15530 (1965).
706. J. A. Barnes, W. C. Barnes and W. E. Hatfield, *Inorg. Chim. Acta*, **5**, 276 (1971); *Chem. Abstr.*, **75**, 102937 (1971).
707. Y. Kidani and N. Chiba, *Chem. Pharm. Bull.*, **7**, 84 (1959).
708. R. Uson, A. Laguna and J. L. Sanjoaquin, *J. Organomet. Chem.*, **80**, 147 (1974).
709. L. C. Nathan and R. O. Ragsdale, *Inorg. Chim. Acta*, **3**, 473 (1969).
710. E. S. Pavlenko, V. N. Kumok and V. V. Serebrennikov, *Tr. Tomsk. Gos. Univ.*, **237**, 104 (1973); *Chem. Abstr.*, **80**, 55440 (1974).
711. J. V. Kingston, E. M. Krankovits and R. J. Magee, *J. Inorg. Nucl. Chem.*, **31**, 3181 (1969).
712. T. M. Shevchenko, E. Pavlenko and V. V. Serebrennikov, *Zh. Obshch. Khim.*, **45**, 2263 (1975); *Chem. Abstr.*, **84**, 53320 (1976).
713. D. S. Dyer and R. O. Ragsdale, *Inorg. Chem.*, **8**, 1116 (1969).
714. C. E. Michelson, D. S. Dyer and R. O. Ragsdale, *J. Chem. Soc. A*, **1970**, 2296.
715. C. E. Michelson, D. S. Dyer and R. O. Ragsdale, *J. Inorg. Nucl. Chem.*, **32**, 833 (1970).
716. R. D. Gupta, G. S. Manku, A. N. Bhat and B. D. Jain, *Curr. Sci.*, **38**, 265 (1969); *Chem. Abstr.*, **72**, 59855 (1970).
717. J. H. Holloway, G. P. McQuillan and D. S. Ross, *J. Chem. Soc. A*, **1969**, 2505.
718. J. H. Holloway, G. P. McQuillan and D. S. Ross, *J. Chem. Soc. A*, **1971**, 1935.
719. G. Durgaprasad and C. C. Patel, *Indian J. Chem.*, **11**, 1300 (1973); *Chem. Abstr.*, **80**, 127678 (1974).
720. R. G. Bhattacharyya, *J. Indian Chem. Soc.*, **51**, 652 (1974).
721. C. J. Popp and R. O. Ragsdale, *J. Chem. Soc. A*, **1969**, 1892.
722. R. G. Garvey, *Proc. N. Dak. Acad. Sci.*, **22**, 113 (1968); *Chem. Abstr.*, **72**, 54535 (1970).
723. R. L. Dutta and S. Lahiry, *J. Indian Chem. Soc.*, **41**, 62 (1964); *Chem. Abstr.*, **60**, 14108 (1964).
724. R. C. Paul, D. K. Airon and S. L. Chadha, *Indian J. Chem.*, **14A**, 51 (1976); *Chem. Abstr.*, **84**, 144088 (1976).
725. R. C. Paul, H. Madan and S. L. Chadha, *J. Inorg. Nucl. Chem.*, **36**, 737 (1974).
726. V. N. Kumok, *Tr. Tomsk. Univ.*, **1971**, 79; *Chem. Abstr.*, **77**, 172093 (1972).
727. A. K. Majumdar, R. G. Bhattacharyya and D. C. Bera, *Proc. Chem. Symp.*, **2**, 121 (1972); *Chem. Abstr.*, **82**, 9610 (1975).
728. B. Chatterjee, *J. Indian Chem. Soc.*, **50**, 755 (1973).
729. A. K. Majumdar and R. G. Bhattacharyya, *Proc. 2nd Chem. Symp., 1970*, **1** 293 (1971); *Chem. Abstr.*, **76**, 135157 1(972).
730. A. K. Majumdar and R. G. Bhattacharyya, *Sci. Cult.*, **35**, 271 (1969); *Chem. Abstr.*, **72**, 38402 (1970).
731. A. K. Majumdar and R. G. Bhattacharyya, *J. Indian Chem. Soc.*, **50**, 701 (1973).
732. T. T. Tuichibaev, *Nauchn. Tr. Tashk. Gos. Univ.*, **379**, 148 (1970); *Chem. Abstr.*, **81**, 98754 (1974); *Chem. Abstr.*, **76**, 118034 (1972).
733. G. B. Aitken and G. P. McQuillan, *J. Chem. Soc. Dalton Trans.*, **1973**, 2637.
734. L. C. Nathan, J. Cullen and R. O. Ragsdale, *Inorg. Nucl. Chem. Lett.*, **12**, 137 (1976).
735. C. P. Prabhakaran and C. C. Patel, *Indian J. Chem.*, **10**, 438 (1972); *Chem. Abstr.*, **77**, 121599 (1972).
736. M. N. Al-Zagoum, *Diss. Abstr. Int. B*, **30**, 533 (1969); *Chem. Abstr.*, **72**, 96172 (1970).
737. A. K. Majumdar and R. G. Bhattacharyya, *J. Indian Chem. Soc.*, **50**, 646 (1973).
738. J. H. Nelson, L. C. Nathan and R. O. Ragsdale, *Inorg. Chem.*, **7**, 1840 (1968).
739. L. El-Sayed and R. O. Ragsdale, *Inorg. Chem.*, **6**, 1644 (1967).
740. K. R. Rakhimov, A. G. Muftakhov and T. T. Tuichibaev, *Uzb. Khim. Zh.*, **16**, 10 (1972); *Chem. Abstr.*, **76**, 159117 (1972).
741. J. H. Nelson and R. O. Ragsdale, *Inorg. Chim. Acta*, **2**, 439 (1968).
742. J. H. Nelson and R. O. Ragsdale, *Inorg. Chim. Acta*, **2**, 230 (1968).
743. D. R. Gupta, G. S. Manku, A. N. Bhat and B. D. Jain, *Talanta*, **17**, 772 (1970).
744. A. N. Bhat, R. D. Gupta and B. D. Jain, *J. Indian Chem. Soc.*, **44**, 187 (1967); *Chem. Abstr.*, **67**, 39836 (1967).
745. A. N. Bhat, D. R. Gupta and B. D. Jain, *Indian J. Appl. Chem.*, **32**, 52 (1969); *Chem. Abstr.*, **74**, 134486 (1971).

746. A. N. Bhat and B. D. Jain, *J. Sci. Ind. Res. (India)*, **19B**, 295 (1960); *Chem. Abstr.*, **55**, 6136 (1961).
747. P. G. Bhatia, R. D. Gupta, A. N. Bhat and B. D. Jain, *Anal. Chim. Acta*, **62**, 481 (1972).
748. A. N. Bhat and B. D. Jain, *J. Indian Chem. Soc.*, **38**, 327 (1961).
749. A. N. Bhat, R. D. Gupta, and B. D. Jain, *Indian J. Appl. Chem.*, **30**, 110 (1967); *Chem. Abstr.*, **69**, 15919 (1968).
750. A. N. Bhat and B. D. Jain, *J. Sci. Ind. Res. (India)*, **19B**, 16 (1960); *Chem. Abstr.*, **54**, 18162 (1960).
751. R. D. Gupta, G. S. Manku, A. N. Bhat and B. D. Jain, *Anal. Chim. Acta*, **50**, 109 (1970).
752. R. D. Gupta, G. S. Manku, A. N. Bhat and B. D. Jain, *Aust. J. Chem.*, **23**, 1387 (1970).
753. R. D. Gupta, G. S. Manku, A. N. Bhat and B. D. Jain, *J. Less-Common Metals*, **18**, 139 (1969); *Chem. Abstr.*, **71**, 7068 (1969).
754. J. Mikulski, *Kernenergie*, **6**, 71 (1963); *Chem. Abstr.*, **62**, 9 (1965).
755. A. T. Balaban, I. Bally, R. J. Bishop, C. N. Rentea and L. E. Sutton, *J. Chem. Soc.*, **1964**, 2383.
756. E. Hohaus and F. Umland, *Chem. Ber.*, **102**, 4025 (1969).
757. E. Hohaus and W. Riepe, *Z. Naturforsch. B*, **28**, 440 (1973).
758. B. Stefanska, J. A. Zirra, J. Peryt, K. Kaminski and A. Ledochowski, *Rocz. Chem.*, **47**, 2339 (1973); *Chem. Abstr.*, **81**, 45237 (1974).
759. T. J. Haley, A. M. Flesher and L. Mavis, *Arch. Int. Pharmacodyn.*, **138**, 133 (1962); *Chem. Abstr.*, **57**, 15461 (1962).
760. T. E. Furia and D. H. Steinberg, *U.S. Pat.* 3,961,054; *Chem. Abstr.*, **85**, 166638 (1976).
761. G. Buchmann, *Wiss. Z. Tech. Hochsch. Chem. Leuna-Merseburg*, **4**, 219 (1962); *Chem. Abstr.*, **59**, 4492 (1963).
762. G. Ziv and A. Saran, *Zentralbl. Veterinaermed., Reihe B*, **23**, 310 (1976); *Chem. Abstr.*, **85**, 116690 (1976).
763. G. Ziv, A. Saran, and E. Schoenberger, *Zentralbl. Verterinaermed., Reihe B*, **23**, 301 (1976); *Chem. Abstr.*, **85**, 117294 (1976).
764. I. Arai and I. Nakayama, *Yakugaku Zasshi*, **72**, 167 (1952); *Chem. Abstr.*, **46**, 8187 (1952).
765. G. W. Ordal and D. J. Goldman, *J. Mol. Biol.*, **100**, 103 (1976).
766. Parke, Davis & Co., *Fr. Pat.* 1,437,359; *Chem. Abstr.*, **66**, 2486 (1967).
767. H. Freytag, F. Lober and P. E. Frohberger, *Ger. Pat.* 1,013,113; *Chem. Abstr.*, **54**, 16732 (1960).
768. G. Buchmann, *Wiss. Z. Tech. Hochsch. Chem. Leuna-Merseburg*, **4**, 213 (1962); *Chem. Abstr.*, **59**, 4492 (1963).
769. G. Buchmann, *Pharmazie*, **17**, 283 (1962).
770. J. Demecko, J. Kratsmar-Smogrovic, J. Kovac and M. Zemlicka, *Czech. Pat.* 161,368; *Chem. Abstr.*, **85**, 15351 (1976).
771. B. Lucanska, M. Blahova, O. Hulkova and J. Kratsmar-Smogrovic, *Acta Fac. Pharm. Univ. Comeniana*, **24**, 29 (1973); *Chem. Abstr.*, **80**, 11079 (1974).
772. S. N. Litvinenko and Ya. N. Ivashchenko, *Fiziol. Aktiv. Veshchestva*, **5**, 99 (1973); *Chem. Abstr.*, **81**, 72919 (1974).
772. E. N. Case and R. Koncos, *U.S. Pat.* 3,219,424; *Chem. Abstr.*, **64**, 4840 (1966).
774. L. D. Goodhue and K. E. Cantrel, *U.S. Pat.* 3,044,930; *Chem. Abstr.*, **57**, 15079 (1962).
775. G. Hayakawa and Y. Watanabe, *Jap Pat.* 70 22,345; *Chem. Abstr.*, **73**, 88384 (1970).
776. K. Iwasaki, K. Yamaguchi, J. Inomata, Y. Otsuka and K. Kasahara, *Jap. Pat.* 69 20,098; *Chem. Abstr.*, **72**, 3928 (1970).
777. G. P. Duffin, *U.S. Pat.* 3,050,395; *Chem. Abstr.*, **58**, 164 (1963).
778. E. Wainer and J. E. Shirey, *U.S. Pat.* 3,481,739; *Chem. Abstr.*, **72**, 37727 (1970).
779. K. Itano, M. Nakano, A. Kato and S. Hosino, *U.S. Pat.* 3,582,342; *Chem. Abstr.*, **75**, 69542 (1971).
780. E. G. Novikov, Ya. N. Ivashchenko, M. N. Zrazhevskii, O. A. Kochina, V. M. Lebezhenina and T. S. Konryakova, *Russ. Pat.* 162,003; *Chem. Abstr.*, **61**, 8830 (1964).
781. D. Cartwright, D. J. Collins, T. Lewis and J. W. Slater, *Ger. Offen.* 2,322,143; *Chem. Abstr.*, **80**, 104879 (1974).
782. E. L. Rempel, O. S. Otroshchenko and A. S. Sadykov, *Nauch. Tr. Tashkent Gos. Univ.*, No. 419, 228 (1972); *Chem. Abstr.*, **80**, 129118 (1974).
783. C. H. Boehringer Sohn, *Fr. Pat.* 1,389,821; *Chem. Abstr.*, **63**, 1816 (1965).

784. Y. Muto, M. Kato, H. B. Jonassen and K. Kakiuchi, *Bull. Chem. Soc. Jap.*, **41**, 1495 (1968).
785. G. A. Popovich, A. V. Ablov, G. A. Klosse and I. I. Zheru, *Zh. Strukt. Khim.*, **12**, 817 (1971); *Chem. Abstr.*, **76**, 20785 (1972).
786. V. V. Serebrennikov, E. S. Pavlenko, V. N. Kumok and N. I. Belousova, *Zh. Obshch. Khim.*, **39**, 306 (1969); *Chem. Abstr.*, **71**, 9249 (1969).
787. T. M. Shevchenko, E. S. Pavlenko and V. V. Serebrennikov, *Sb. Nauch. Tr. Kuzbasskii Politekh. Inst. 1972*, **1973**, 38; *Chem. Abstr.*, **81**, 32689 (1974).
788. K. N. Gan, S. D. Poplavskaya and E. S. Pavlenko, *Sb. Nauch. Tr. Kuzbasskii Politekh. Inst.*, **1974**, 37; *Chem. Abstr.*, **83**, 171978 (1975).
789. V. Krishnan and C. C. Patel, *Can. J. Chem.*, **44**, 972 (1966).
790. A. K. Majumdar and R. G. Bhattacharyya, *J. Inorg. Nucl. Chem.*, **35**, 4296 (1973).
791. R. L. Dutta, S. Ghosh and S. Lahiry, *Sci. Cult. (Calcutta)*, **30**, 551 (1964); *Chem. Abstr.*, **62**, 12734 (1965).
792. R. H. Buch, L. El-Sayed and R. O. Ragsdale, *Inorg. Synth.*, **13**, 202 (1971); *Chem. Abstr.*, **75**, 104587 (1971).
793. R. G. Bhattacharyya and D. C. Bera, *J. Indian Chem. Soc.*, **52**, 282 (1975).
794. R. G. Bhattacharyya and D. C. Bera, *J. Indian Chem. Soc.*, **52**, 1212 (1975).
795. T. Koyama, T. Nanba, T. Hirota, S. Ohmori and M. Yamato, *Chem. Pharm. Bull.*, **25**, 964 (1977).
796. R. D. Gupta, G. S. Manku, A. N. Bhat and B. D. Jain, *Z. Anorg. Allg. Chem.*, **379**, 312 (1970); *Chem. Abstr.*, **75**, 41137 (1971).
797. T. Okamoto and H. Takayama, *Yakugaku Zasshi*, **82**, 1076 (1962); *Chem. Abstr.*, **58**, 4609 (1963).
798. W. Frey and K. Milles, *Ger. Offen.* 2,112,832; *Chem. Abstr.*, **78**, 4142 (1973).
799. J. D. Rushmere, *U.S. Pat.* 3,296,105; *Chem. Abstr.*, **66**, 51712 (1967).
800. G. Kraus and K. W. Rollmann, *U.S. Pat.* 3,314,926; *Chem. Abstr.*, **67**, 12373 (1967).
801. C. Bonsall and P. Holt, *Makromol. Chem.*, **175**, 749 (1974).
802. T. Kato and H. Yamanaka, *Chem. Pharm. Bull.*, **12**, 18 (1964).
803. T. Okabayashi, *Yakugaku Zasshi*, **73**, 946 (1953); *Chem. Abstr.*, **48**, 11419 (1954).
804. T. Okamoto and T. Takahashi, *Jap. Pat.* 70 03,380; *Chem. Abstr.*, **72**, 111308 (1970).
805. G. B. Bachman and D. E. Cooper, *J. Org. Chem.*, **9**, 302 (1944).
806. G. Buchmann and W. Grimm, *J. Prakt. Chem.*, **17**, 135 (1962).
807. F. Leonard and A. Wajngurt, *J. Org. Chem.*, **21**, 1077 (1956).
808. E. Ochiai and C. Kaneko, *Chem. Pharm. Bull.*, **8**, 284 (1960).
809. H. Tanida, *Chem. Pharm. Bull.*, **7**, 540 (1959).
810. Y. Kobayashi, I. Kumadaki and H. Sato, *Chem. Pharm. Bull.*, **18**, 861 (1970).
811. T. Dziembowska and M. Szafran, *Rocz. Chem.*, **48**, 2293 (1974); *Chem. Abstr.*, **83**, 58621 (1975).
812. G. G. Aloisi and G. Favaro, *J. Chem. Soc. Perkin Trans. 2*, **1976**, 456.
813. J. Streith, H. K. Darrah and M. Weil, *Tetrahedron Lett.*, **1966**, 5555.
814. M. Makosza, I. Kmiotek-Skarzynska and M. Jawdosiuk, *Synthesis*, **1977**, 56.
815. E. Ochiai, T. Watanabe and S. Suzuki, *Yakugaku Zasshi*, **76**, 1421 (1956); *Chem. Abstr.*, **51**, 6639 (1957).
816. K. Ogino and S. Oae, *Tetrahedron*, **27**, 6037 (1971).
817. E. Ochiai and M. Ikehara, *Yakugaku Zasshi*, **68**, 139 (1948); *Chem. Abstr.*, **47**, 8074 (1953).
818. J. S. Wieczorek and R. Wojtowski, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.*, **20**, 309 (1972); *Chem. Abstr.*, **77**, 126384 (1972).
819. L. A. Paquette, *Tetrahedron*, **22**, 25 (1966).
820. D. Redmore, *U.S. Pat.* 3,770,750; *Chem. Abstr.*, **80**, 37285 (1974); *U.S. Pat.* 3,786,055; *Chem. Abstr.*, **80**, 96154 (1974).
821. J. Haginiwa and Y. Higuchi, *Yakugaku Zasshi*, **93**, 144 (1973); *Chem. Abstr.*, **78**, 147751 (1973).
822. T. Kudo, A. Nose and M. Hamana, *Yakugaku Zasshi*, **95**, 521 (1975); *Chem. Abstr.*, **83**, 146716 (1975).
823. G. Buchmann and H. Pracht, *J. Prakt. Chem.*, **16**, 55 (1962).
824. G. Horn, *Acta Chim. Acad. Sci. Hung.*, **33**, 287 (1963); *Chem. Abstr.*, **59**, 3546 (1963).
825. A. G. Pozdeeva and E. G. Novikov, *Zh. Prikl. Khim. (Leningrad)*, **42**, 2626 (1969); *Chem. Abstr.*, **72**, 74009 (1970).

826. A. G. Stromberg and T. M. Markacheva, *Zh. Fiz. Khim.*, **28**, 671 (1954); *Chem. Abstr.*, **48**, 11218 (1954).
827. K. Ezumi, T. Kubota, H. Miyazaki and M. Yamakawa, *J. Phys. Chem.*, **80**, 980 (1976).
828. T. Kubota, H. Akazawa and M. Yamakawa, *Chem. Lett.*, **1972**, 1147.
829. T. Okano, A. Niitsuma, A. Takadate and K. Uekama, *Gann*, **60**, 97 (1969); *Chem. Abstr.*, **70**, 111596 (1969).
830. S. Kawashima and M. Tomoeda, *Chem. Pharm. Bull.*, **18**, 620 (1970).
831. M. Kaneko and C. Nagata, *Chem.-Biol. Interactions*, **3**, 459 (1971); *Chem. Abstr.*, **75**, 147725 (1971).
832. M. Ohtsuru, K. Tori and H. Wantanabe, *Chem. Pharm. Bull.*, **15**, 1015 (1967).
833. C. A. Benassi, E. Fornasari, L. Griggio and F. M. Veronese, *Gazz. Chim. Ital.*, **94**, 467 (1964); *Chem. Abstr.*, **61**, 6904 (1964).
834. C. Kaneko, S. Yamada, I. Yokoe and T. Kubota, *Tetrahedron Lett.*, **1970**, 2333.
835. Y. Kawazoe and M. Araki, *Gann*, **58**, 485 (1967); *Chem. Abstr.*, **68**, 114402 (1968).
836. M. N. Al-Zagoum and C. G. Warren, *J. Inorg. Nucl. Chem.*, **31**, 3465 (1969).
837. M. Szafran and T. Dziembowska, *Rocz. Chem.*, **46**, 187 (1972); *Chem. Abstr.*, **77**, 4465 (1972).
838. C. Kaneko, *Yakugaku Zasshi*, **79**, 428 (1959); *Chem. Abstr.*, **53**, 17126 (1959).
839. Z. Dega-Szafran, E. Grech, M. Z. Naskret and M. Szafran, *Rocz. Chem.*, **47**, 1849 (1973); *Chem. Abstr.*, **80**, 20148 (1974).
840. Z. Dega-Szafran, M. Szafran and J. Rychlewski, *J. Chem. Soc. Perkin Trans. 2*, **1978**, 536.
841. M. Szafran, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **14**, 509 (1966); *Chem. Abstr.*, **66**, 41955 (1967).
842. M. Szafran, E. Grech and Z. Dega-Szafran, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.*, **19**, 643 (1971); *Chem. Abstr.*, **76**, 103876 (1972).
843. C. Nagata, K. Fujii and S. S. Epstein, *Nature*, **215**, 972 (1967).
844. T. Kosuge, H. Zenda and H. Sawanishi, *Chem. Pharm. Bull.*, **19**, 1291 (1971).
845. E. Ochiai, M. Katada and T. Naito, *Yakugaku Zasshi*, **64**, 210 (1944); *Chem. Abstr.*, **45**, 5154 (1951).
846. C. Reichard, *Chem. Ber.*, **99**, 1769 (1966).
847. N. N. Zatsepina, A. V. Kirova and I. F. Tupitsyn, *Reakts. Sposobnost Org. Soedin. Tartu Gos. Univ.*, **5**, 70 (1968); *Chem. Abstr.*, **69**, 76469 (1968).
848. A. El-Anani, J. Banger, G. Bianchi, S. Clementi, C. D. Johnson and A. R. Katritzky, *J. Chem. Soc. Perkin Trans. 2*, **1973**, 1065.
849. Y. Kawazoe, M. Ohnishi and Y. Yoshioka, *Chem. Pharm. Bull.*, **15**, 1225 (1967).
850. N. N. Zatsepina, I. F. Tupitsyn, V. P. Dushina, Yu. M. Kapustin and Yu. L. Kaminskii, *Reakts. Sposobnost Org. Soedin.*, **9**, 745 (1972); *Chem. Abstr.*, **78**, 147198 (1973).
851. T. R. Bosin and R. P. Maickel, *Res. Commun. Chem. Pathol. Pharmacol.*, **6**, 813 (1973); *Chem. Abstr.* **80**, 59085 (1974).
852. D. A. Cowan, L. A. Damani and J. W. Gorrod, *Biomed. Mass Spectrom.*, **5**, 551 (1978); *Chem. Abstr.*, **90**, 185866 (1979).
853. I. Yavari and J. D. Roberts, *Org. Magn. Reson.*, **12**, 87 (1979).
854. G. Barbieri, R. Benassi, P. Lazzeretti, L. Schenetti and F. Taddei, *Org. Magn. Reson.*, **7**, 451 (1975).
856. N. S. Vostrikov, U. M. Dzhemilev, S. Bylina, A. M. Moiseenkov, A. V. Semenovskii and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1978**, 2337; *Chem. Abstr.*, **90**, 72019 (1979).
857. H. Gunther and A. Gronenborn, *Heterocycles*, **11**, 337 (1978).
858. C. Kaneko, A. Yamamoto and M. Gomi, *Heterocycles*, **12**, 227 (1979).
859. C. Kaneko, R. Hayashi, H. Fujii and A. Yamamoto, *Chem. Pharm. Bull.*, **26**, 3582 (1978).
860. Ja-an Su, E. Siew, E. V. Brown and S. L. Smith, *Org. Magn. Reson.*, **11**, 565 (1978).
861. H. Saito and M. Hamana, *Heterocycles*, **12**, 475 (1979).
862. M. Hamana and S. Kumadaki, *Chem. Pharm. Bull.*, **26**, 3856 (1978).
863. M. Hamana, F. Sato, Y. Kimura, M. Nishikawa and H. Noda, *Heterocycles*, **11**, 371 (1978).
864. K. Funakoshi, H. Sonoda, Y. Sonoda and M. Hamana, *Chem. Pharm. Bull.*, **26**, 3504 (1978).
865. H. Yamanaka, H. Egawa and T. Sakamoto, *Chem. Pharm. Bull.*, **26**, 2759 (1978).
866. H. Yamanaka, M. Komatsu, S. Ogawa and S. Konno, *Chem. Pharm. Bull.*, **27**, 806 (1979).
867. H. Yamanaka, H. Egawa and T. Sakamoto, *Chem. Pharm. Bull.*, **27**, 1004 (1979).
868. H. Takayama and T. Okamoto, *Chem. Pharm. Bull.*, **26**, 2435 (1978).

869. Sh. V. Abdullaev, M. Eshmuradova and M. Kadyrova, *Mater. Resp. Nauchno-Tekh. Konf. Molodykh Uch. Pererab. Nefti Neftekhim. 3rd*, **1976**, 19; *Chem. Abstr.*, **90**, 38758 (1979).
870. E. Hayashi and N. Shimada, *Yakugaku Zasshi*, **98**, 1503 (1978); *Chem. Abstr.*, **90**, 137639 (1979).
871. A. Albini, G. F. Bettinetti and G. Minoli, *Tetrahedron Lett.*, **1979**, 3761.
872. N. Hata, *Chem. Lett.*, **1978**, 1359.
873. C. Kaneko, A. Yamamoto and M. Hashiba, *Chem. Pharm. Bull.*, **27**, 946 (1979).
874. C. Kaneko, T. Naito, M. Hashiba, H. Fujii and M. Somei, *Chem. Pharm. Bull.*, **27**, 1813 (1979).
875. P. Schicke, K. R. Appel, and L. Schroeder, *Pflanzenschutzberichte*, **38**, 189 (1968); *Chem. Abstr.*, **70**, 27921 (1969).
876. W. Nakahara, F. Fukuoka and T. Sugimura, *Gann*, **48**, 129 (1957).
877. W. Nakahara, F. Fukuoka and S. Sakai, *Gann*, **49**, 33 (1958).
878. Y. Hayashi, *Gann*, **50**, 219 (1959).
879. W. Nakahara and F. Fukuoka, *Naturwissenschaften*, **47**, 44 (1960); *Chem. Abstr.*, **54**, 21445 (1960).
880. W. Nakahara and F. Fukuoka, *Gann*, **51**, 125 (1960).
881. K. Fukui, A. Imamura and C. Nagata, *Gann*, **51**, 119 (1960).
882. S. Takayama, *Gann*, **51**, 139 (1960).
883. A. Lacassagne, N. P. Buu-Hoi and F. Zajdela, *C. R. Soc. Biol.*, **154**, 528 (1960).
884. A. Lacassagne, N. P. Buu-Hoi and F. Zajdela, *C. R. Soc. Biol.*, **155**, 444 (1961).
885. K. Mori and A. Yasuno, *Gann*, **52**, 149 (1961).
886. K. Mori, *Gann*, **52**, 265 (1961).
887. W. Nakahara, *Prog. Exp. Tumor Res.*, **2**, 158 (1961); *Chem. Abstr.*, **63**, 13817 (1965).
888. E. V. Brown, R. M. Novack and A. A. Hamdan, *J. Nat. Cancer Inst.*, **26**, 1461 (1961); *Chem. Abstr.*, **55**, 21342 (1961).
889. S. Takayama and K. Oota, *Gann*, **52**, 321 (1961).
890. S. Majima, T. Takohashi and T. Narisawa, *Exp. Carcinoma Glandular Stomach, Proc. U.S.-Jap. Symp.*, **1961**, 317; *Chem. Abstr.*, **75**, 17680 (1971).
891. S. Takayama, *Gann*, **52**, 165 (1961).
892. S. Takayama, *Gann*, **53**, 167 (1962).
893. K. Mori, *Gann*, **53**, 303 (1962).
894. T. Baba, Y. Misu and S. Takayama, *Gann*, **53**, 381 (1962).
895. K. Mori, *J. Showa Med. Assoc.*, **22**, 51, (1962).
896. T. Chino, *Fukuoka Igaku Zasshi*, **53**, 1053 (1962); *Chem. Abstr.*, **59**, 10590 (1963).
897. C. E. Searle and D. L. Woodhouse, *Acta Unio Int. Contra Cancrum*, **19**, 519 (1963).
898. Y. Shirasu, *Gann*, **54**, 487 (1963).
899. Y. Shirasu and A. Ohta, *Gann*, **54**, 221 (1963).
900. H. Endo and F. Kume, *Naturwissenschaften*, **50**, 525 (1963).
901. S. Irino, I. Miyoshi, T. Sezaki, M. Kunisada and M. Sato, *Proc. Jap. Cancer Assoc., 22nd Gen. Meet, Okayama*, **1963**, 209.
902. H. Endo and F. Kume, *Gann*, **54**, 443 (1963).
903. K. Mori, *Gann*, **54**, 415 (1963).
904. T. Tanaka, T. Kakefuda and R. Kinosita, *Proc. Amer. Assoc. Cancer Res.*, **4**, 67 (1963).
905. K. Mori, *Gann*, **55**, 277 (1964).
906. K. Mori, *Gann*, **55**, 315 (1964).
907. W. Nakahara, *Arzneim.-Forsch.*, **7**, 842 (1964).
908. C. E. Searle and D. L. Woodhouse, *Cancer Res.*, **24**, 245 (1964).
909. I. Kimura and Y. Tsubura, *Proc. Jap. Cancer Assoc., 23rd Gen. Meet., Tokyo*, **1964**, 19.
910. E. Okajima, *Nara Igaku Zasshi*, **15**, 1 (1964); *Chem. Abstr.*, **61**, 13715 (1964).
911. Y. Nishizuka, K. Nakakuki and T. Sakakura, *Gann*, **55**, 495 (1964); *Chem. Abstr.*, **62**, 15203 (1965).
912. H. Fujino, T. Chino, and T. Imai, *J. Nat. Cancer Inst.*, **35**, 907 (1965).
913. T. Chino and T. Kameyama, *Kurume Med. J.*, **12**, 160 (1965).
914. T. Okabayashi, M. Ide, A Yoshimoto and M. Otsubo, *Chem. Pharm. Bull.*, **13**, 610 (1965).
915. H. Endo and F. Kume, *Gann*, **56**, 261 (1965).
916. T. Hisamatsu, K. Mori and K. Okamoto, *Gann*, **56**, 77 (1965).

917. A. Horie, S. Kohchi and M. Kuratsune, *Gann*, **56**, 429 (1965); *Chem. Abstr.*, **64**, 7160 (1966).
918. Y. Shirasu, *Proc. Soc. Exp. Biol. Med.*, **118**, 812 (1965); *Chem. Abstr.*, **63**, 1040 (1965).
919. C. E. Searle, *Cancer Res.*, **25**, 933 (1965); *Chem. Abstr.*, **63**, 10530 (1965).
920. R. Kinoshita and T. Tanaka, *Lung Tumours Anim. Proc. Quadrennial Conf. Cancer, 3rd, Perugia, Italy*, **1965**, 717; *Chem. Abstr.*, **68**, 37537 (1968).
921. T. Kawachi, Y. Hirata and T. Sugimura, *Gann*, **56**, 415 (1965).
922. K. Mori, *Gann*, **56**, 513 (1965).
923. K. Mori and I. Hirafuku, *Gann*, **57**, 1 (1966).
924. K. Mori and M. Kondo, *Gann*, **57**, 543 (1966).
925. K. Mori, M. Kondo and S. Suzuki, *Gann*, **57**, 559 (1966).
926. D. J. Parish and C. E. Searle, *Brit. J. Cancer*, **20**, 200 (1966).
927. D. J. Parish and C. E. Searle, *Brit. J. Cancer*, **20**, 206 (1966).
928. C. E. Searle and A. T. Spencer, *Brit. J. Cancer*, **20**, 877 (1966).
929. A. Lacassagne, N. P. Buu-Hoi, F. Zajdela, J. P. Hoeffinger and P. Jacquignon, *Life Sci.*, **5**, 1945 (1966).
930. T. Hisamatsu, K. Mori and K. Okamoto, *Gann*, **57**, 299 (1966); *Chem. Abstr.*, **65**, 7748 (1966).
931. K. Mori, M. Kondo, E. Koibuchi and A. Hashimoto, *Gann*, **58**, 105 (1967).
932. K. Mori, *Gann*, **58**, 389 (1967).
933. K. Mori and A. Ohta, *Gann*, **58**, 551 (1967).
934. K. Mori, *Proc. Jap. Cancer Assoc., 26th Gen. Meet., Nagoya*, **1967**, 187.
935. Y. Kawazoe, M. Tachibana, K. Aoki and W. Nakahara, *Biochem. Pharmacol*, **16**, 631 (1967).
936. Y. Kawazoe and M. Araki, *Gann*, **58**, 485 (1967).
937. M. Ito, S. Yamada and T. Nagayo, *Proc. Jap. Cancer Assoc., 26th Gen. Meet., Nagoya*, **1967**, 188.
938. R. L. Carter, N. Heathcote and F. J. C. Roe, *Nature*, **215**, 549 (1967); *Chem. Abstr.*, **67**, 80531 (1967).
939. T. Kawachi, Y. Hirata and T. Sugimura, *Gann*, **58**, 397 (1967).
940. J. C. Arcos and M. F. Argus, *Adv. Cancer Res.*, **11**, 305 (1968).
941. H. Hoshino, H. Tanooka and F. Fukuoka, *Gann*, **59**, 43 (1968).
942. K. Mori, *Exp. Carcinoma Glandular Stomach, Proc. U.S.-Jap. Symp.*, **1969**, 233; *Chem. Abstr.*, **75**, 32931 (1971).
943. K. Mori, A. Ohta, T. Murakami, M. Tamura, M. Kondo and H. Ichimura, *Gann*, **60**, 627 (1969).
944. R. Kinosita, *Exp. Carcinoma Glandular Stomach, Proc. U.S.-Jap. Symp.*, **1969**, 263; *Chem. Abstr.*, **75**, 61245 (1971).
945. M. Takahashi and H. Sato, *Exp. Carcinoma Glandular Stomach, Proc. U.S.-Jap. Symp.*, **1969**, 241; *Chem. Abstr.*, **75**, 61284 (1971).
946. M. Takahashi, and S. Sato, *Gann Monogr.*, No. 8, 241 (1969).
947. S. Odashima, *Gann*, **60**, 211 (1969).
948. M. Ito, S. Yamada, H. Suzuki and T. Nagayo, *Gann*, **60**, 223 (1969).
949. Y. Kawazoe, M. Araki and W. Nakahara, *Chem. Pharm. Bull.*, **17**, 544 (1969).
950. M. Araki, Y. Kawazoe and C. Nagata, *Chem. Pharm. Bull.*, **17**, 1344 (1969).
951. M. Hozumi, *Gann*, **60**, 161 (1969).
952. K. Sato, T. Saito and M. Enomoto, *Jap. J. Exp. Med.*, **40**, 475 (1970).
953. N. Kobayashi, H. Katsuki anc Y. Yamane, *Gann*, **61**, 239 (1970).
954. Y. Hayashi, T. Hagegawa and K. Hiro, *Jap. J. Pharmacol.*, **20**, 264 (1970); *Chem. Abstr.*, **73**, 64273 (1970).
955. T. Morita, I. Hirota and I. Mifuchi, *Igaku To Seibutsugaku*, **84**, 209 (1972); *Chem. Abstr.*, **77**, 137269 (1972).
956. S. Majima, T. Takohashi and T. Narisawa, *Exp. Carcinoma Glandular Stomach, Proc. U.S.-Jap. Symp.*, **1961**, 317; *Chem. Abstr.*, **75**, 17680 (1971).
957. M. Takahashi, *Gann*, **61**, 27 (1970).
958. H. Hoshino, Y. Kawazoe and F. Fukuoka, *Gann*, **60**, 523 (1970).
959. Y. Shirasu, T. Mitzutani and S. Yamamoto, *Abstr. Tenth Int. Cancer Congr., Houston, Texas*, **1970**, 20.
960. H. F. Stich, *Top. Chem. Carcinog. Proc. 2nd Int. Symp., 1971*, **1972**, 17; *Chem. Abstr.*, **80**, 91679 (1974).
961. Y. Hayashi and T. Hasegawa, *Gann*, **62**, 329 (1971).

962. M. Enomoto, E. C. Miller and J. A. Miller, *Proc. Soc. Exp. Biol. Med.*, **136**, 1206 (1971).
963. Y. Kawazoe, M. Araki and G. F. Huang, *Top. Chem. Carcinog. Proc. 2nd Int. Symp., 1971*, **1972**, 1; *Chem. Abstr.*, **80**, 91678 (1974).
964. Y. Yamane, K. Sakai and Y. Amemiya, *Gann*, **63**, 153 (1972); *Chem. Abstr.*, **77**, 59796 (1972).
965. Y. Hayashi, H. Furukawa and T. Hasegawa; *Top. Chem. Carcinog. Proc. 2nd Int. Symp., 1971*, **1972**, 53; *Chem. Abstr.*, **80**, 91841 (1974).
966. T. Morita, I. Hirota and I. Mifuchi, *Igaku To Seibutsugaku*, **84**, 209 (1972); *Chem. Abstr.*, **77**, 137269 (1972).
967. T. Satoh and N. Yamamoto, *Cancer Res.*, **32**, 440 (1972).
968. H. Sugiura, *Nagoya Med. J.*, **18**, 157 (1973); *Chem. Abstr.*, **80**, 23369 (1974).
969. E. I. Rempel, V. P. Malikova and I. B. Sorokina, *Nauchn. Tr. Tashk. Gos. Univ.*, **457**, 82 (1973); *Chem. Abstr.*, **83**, 37836 (1975).
970. A. Shurgin and F. F. Becker, *J. Nat. Cancer Inst.*, **53**, 159 (1974); *Chem. Abstr.*, **82**, 26925 (1975).
971. T. Nomura, E. Okamoto, N. Tateishi, S. Kimura, Y. Isa, H. Manabe and Y. Sakamoto, *Cancer Res.*, **34**, 3373 (1974); *Chem. Abstr.*, **82**, 81507 (1975).
972. H. Shinozuka, *Proc. Amer. Assoc. Cancer Res.*, **15**, 5 (1974).
973. M. Tatematsu, *Nagoya Shiritsu Daigaku Igakkai Zasshi*, **25**, 187 (1974); *Chem. Abstr.*, **83**, 142749 (1975).
974. Y. Konishi, J. A. Popp and H. Shinozuka, *J. Nat. Cancer Inst.*, **52**, 917 (1974); *Chem. Abstr.*, **81**, 34283 (1974).
975. M. Higuchi, *Kurume Med. J.*, **22**, 113 (1975); *Chem. Abstr.*, **84**, 116715 (1976).
976. U. Lekholm, K. Wallenius and G. Heyden, *Histochemistry*, **44**, 147 (1975); *Chem. Abstr.*, **83**, 112158 (1975).
977. M. Tatematsu, M. Takahashi, S. Fukushima, M. Hananouchi and T. Shirai, *J. Nat. Cancer Inst.*, **55**, 101 (1975); *Chem. Abstr.*, **83**, 145525 (1975).
978. Y. Tabuchi, T. Mitsuno and T. Sugiyama, *J. Nat. Cancer Inst.*, **55**, 1395 (1975); *Chem. Abstr.*, **84**, 100607 (1976).
979. M. Calvin, *Naturwissenschaften*, **62**, 504 (1975).
980. H. Otsu and G. Ide, *Taiki Osen Kenkyu*, **9**, 702 (1975); *Chem. Abstr.*, **83**, 109594 (1975).
981. J. K. Reddy, M. S. Rao, D. J. Svolvocha and J. D. Prasad, *Lab. Invest.*, **32**, 98 (1975); *Chem. Abstr.*, **82**, 107332 (1975).
982. M. Tada, M. Tada, G. Huang and Y. Kawazoe, *Gann, Proc. Jap. Cancer Assoc., 33rd Annual Meeting, October, 1974*, **1975**, 61.
983. Y. Tabuchi, *Igaku Kankyu*, **45**, 263 (1975); *Chem. Abstr.*, **84**, 116714 (1976).
984. Y. Konishi, A. Denda, H. Kawabata, S. Takahashi, M. Sunagawa and H. Kondo, in *Prevention and Detection of Cancer. Part I. Prevention. Vol. 2. Etiology—Prevention Methods. Proceedings of the Third International Symposium on Detection and Prevention of Cancer, 26 April–1 May, 1976, New York*, ed. H. E. Nieburgs, 2402 pp., Marcel Dekker, New York, 1978.
985. M. S. Rao, *J. Pathol.*, **120**, 109 (1976).
986. M. S. Rao and J. K. Reddy, *Proc. Soc. Exp. Biol. Med.*, **153**, 166 (1976).
987. Y. Konishi, A. Denda, S. Inui, S. Takahashi and H. Kondo, *Gann*, **67**, 919 (1976).
988. D. J. Koropatnick and H. F. Stich, *Int. J. Cancer*, **17**, 765 (1976).
989. Y. Konishi, A. Denda, Y. Miyata and H. Kawabata, *Gann*, **67**, 91 (1976).
990. Y. Konishi, A. Denda, H. Kawabata, M. Sunagawa and H. Kondo, *Proc. Amer. Assoc. Cancer Res.*, **17**, 198 (1976).
991. H. Shinozuka, J. A. Popp and Y. Konishi, *Lab. Invest.*, **34**, 501 (1976).
992. J. W. Eveson and D. G. MacDonald, *Oral Surg.*, **44**, 600 (1977).
993. A. Denda, S. Inui and Y. Konishi, *Chem. Biol. Interact.*, **19**, 225 (1977).
994. Y. Kawazoe, O. Ogawa, K. Takahashi, H. Sawanishi and N. Ito, *Gann*, **69**, 835 (1978).
995. J. Ashby, *Brit. J. Cancer*, **37**, 904 (1978).
996. Y. Konishi, A. Denda, S. Inui, S. Takahashi, N. Ueda and M. Namiki, *Cancer Lett.*, **4**, 229 (1978).
997. K. Takahashi, Y. Kawazoe, M. Tada, M. Tada, N. Ito and M. Okada, *Gann*, **69**, 499 (1978).
998. A. Denda, *Proc. Jap. Cancer Assoc.*, **1978**, 28.
999. W. J. Dunn and S. Wold, *J. Med. Chem.*, **21**, 1001 (1978).
1000. H. Shinozuka and S. L. Katyal, *Fed. Proc.*, **38**, 1403 (1979).

1001. S. Sakai, K. Minoda, G. Saito, S. Akagi, A. Ueno and F. Fukuoka, *Gann*, **46**, 605 (1955); *Chem. Abstr.*, **50**, 11526 (1956).
1002. F. Fukuoka and H. Naora, *Gann*, **48**, 271 (1957); *Chem. Abstr.*, **55**, 11657 (1961).
1003. F. Fukuoka, T. Ono, M. Ohashi and S. Nishimura, *Gann*, **50**, 23 (1959).
1004. P. R. Moore, L. J. Mannering, J. L. Teply and B. E. Kline, *Cancer Res.*, **20**, 5, 628 (1960); *Chem. Abstr.*, **60**, 8506 (1964)
1005. D. Amsterdam and A. C. Zahalsky, *Fed. Proc.*, **22**, 373 (1963).
1006. T. Kuroki, M. Goto and H. Sato, *Cancer Cells Cult. Proc. 9th Int. Conf. Tissue Cult. Cancer Res.*, **1966**, 364; *Chem. Abstr.*, **70**, 66200 (1969).
1007. H. Sato and T. Kuroki, *Proc. Jap. Acad.*, **42**, 1211 (1966); *Chem. Abstr.*, **67**, 1546 (1967).
1008. J. Kamahora and T. Kakunaga, *Biken J.*, **9**, 295 (1966).
1009. J. Kamahora and T. Kakunaga, *Proc. Jap. Acad.*, **42**, 1079 (1966).
1010. T. J. Yoshida, T. Kuroki and H. Masuki, *Proc. Jap. Cancer Assoc., 26th Gen. Meet., Nagoya*, **1967**, 131.
1011. I. H. Pan, *J. Formosan Med. Assoc.*, **66**, 17 (1967).
1012. T. Kuroki, M. Goto and H. Sato, *Tohuku J. Exp. Med.*, **91**, 109 (1967); *Chem. Abstr.*, **66**, 103777 (1967).
1013. J. Kamahora, *Kanazawa Daigaku Gan Kenkyusho Nempo 1*, **1967**, 9A; *Chem. Abstr.*, **70**, 94791 (1969).
1014. T. Kato and T. Takaoka, *Proc. Jap. Cancer Assoc., 26th Gen. Meet., Nagoya*, **1967**, 182.
1015. T. Kakunaga and J. Kamahora, *Proc. Jap. Cancer Assoc., 26th Gen Meet., Nagoya*, **1967**, 181.
1016. J. Kamahora and T. Kakunaga, *Biken J.*, **10**, 219 (1967).
1017. Y. Kurita and H. Sato, *Proc. Jap. Cancer Assoc., 26th Gen. Meet., Nagoya*, **1967**, 181.
1018. Y. Kurita, M. Goto and H. Sato, *Tohoku J. Exp. Med.*, **91**, 109 (1967).
1019. T. Kakunaga and J. Kamahora, *Biken J.*, **11**, 313 (1968).
1020. T. Kuroki and H. Sato, *J. Nat. Cancer Inst.*, **41**, 53, 1968; *Chem. Abstr.*, **69**, 75167 (1968).
1021. T. Sugahara, M. Horikawa and M. Sakurai, *Proc. Jap. Cancer Assoc., 27th Gen. Meet., Tokyo*, **1968**, 96.
1022. M. Namba, H. Masuji and J. Sato, *Proc. Jap. Cancer Assoc., 27th Gen. Meet., Tokyo*, **1968**, 92.
1023. T. Kato and T. Takaoka, *Proc. Jap. Cancer Assoc., 27th Gen. Meet., Tokyo*, **1968**, 95.
1024. J. Kamahora and T. Kakunaga, *Biken J.*, **11**, 139 (1968).
1025. J. Kamahora, T. Kakunaga, J. Furuyama and Y. Murata, *Proc. Jap. Cancer Assoc., 27th Gen Meet., Tokyo*, **1968**, 93.
1026. Y. Kurita and H. Sato, *J. Nat. Cancer Inst.*, **41**, 83 (1968).
1027. Y. Kurita and H. Sato, *Proc. Jap. Cancer Assoc., 27th Gen. Meet., Tokyo*, **1968**, 97.
1028. Y. Kurita, M. Goto and H. Sato, in *Cancer Cells in Culture*, ed. H. Katsuta, pp. 364–381, University of Tokyo Press, Tokyo, 1968.
1029. Y. Kurita, M. Goto and H. Sato, *Symp. Cell. Chem.*, **20**, 111 (1969).
1030. Y. Kurita, J. Ishizawa and H. Sato, *Gann*, **60**, 261 (1969).
1031. K. Kometani, H. Okumura and S. Tamura, *Saibo Seibutsugaku Shimpojumu*, **20**, 127 (1969); *Chem. Abstr.*, **74**, 139025 (1971).
1032. T. Kakunaga and J. Kamahora, *Symp. Cell. Chem.*, **20**, 135 (1969).
1033. C. Izard and D. Valadaud, *C. R. Acad. Sci., D*, **269**, 55 (1969).
1034. T. Kuroki, J. Ishizawa and H. Sato, *Gann*, **60**, 261 (1969).
1035. M. Namba and J. Sato, *Symp. Cell Chem.*, **20**, 149 (1969); *Chem. Abstr.*, **75**, 3095 (1971).
1036. M. Namba, H. Masuji and J. Sato, *Jap. J. Exp. Med.*, **39**, 253 (1969); *Chem. Abstr.*, **73**, 1908 (1970).
1037. T. Kakunaga and J. Kamahora, *Symp. Cell. Chem.*, **20**, 135 (1969); *Chem. Abstr.*, **75**, 3094 (1971).
1038. M. Namba and T. Sato, *Gann*, **61**, 583 (1970); *Chem. Abstr.*, **74**, 74181 (1971).
1039. Y. Kurita, R. Kanamaru and H. Sato, *Gann*, **61**, 373 (1970).
1040. K. Koshiba, M. Namba and T. Oda, *Gann*, **61**, 233 (1970); *Chem. Abstr.*, **73**, 64257 (1970).
1041. M. Ochiai, *Nippon Hinyokika Gakkai Zassi*, **62**, 1 (1971); *Chem. Abstr.*, **76**, 81991 (1972).
1042. T. Kuroki and H. Sato, *Oncology*, **1**, 91 (1971); *Chem. Abstr.*, **78**, 12479 (1973).
1043. S. Sekiya, T. Kuwata and K. Nakamura, *Igaku To Seibutsugaku*, **83**, 41 (1971); *Chem. Abstr.*, **77**, 84222 (1972).

1044. H. Katsuta, *Oncology*, **1**, 103 (1971); *Chem. Abstr.*, **78**, 12480 (1973).
1045. K. Toyoshima, H. Tsuji and Y. Tsubura, *Nara Igaku Zasshi*, **22**, 162 (1971); *Chem. Abstr.*, **77**, 620 (1972).
1046. M. Namba and J. Sato, *Jap. J. Exp. Med.*, **41**, 233 (1971); *Chem. Abstr.*, **75**, 86523 (1971).
1047. T. Yamada, T. Takoka, H. Katsuta, M. Namba and S. Jiro, *Jap. J. Exp. Med.*, **42**, 377 (1972); *Chem. Abstr.*, **77**, 148276 (1972).
1048. S. Nakashima and S. Ono, *Gann*, **63**, 111 (1972).
1049. Y. Tsubura, K. Toyoshima, H. Tsuji and T. Fukuyama, *Lab. Anim. Drug Test, Symp. Int. Comm. Lab. Anim. 5th 1972*, 229 (1973); *Chem. Abstr.*, **81**, 100470 (1974).
1050. H. Katsuta and T. Takaoka, *J. Nat. Cancer Inst.*, **49**, 1563 (1972); *Chem. Abstr.*, **78**, 80651 (1973).
1051. N. C. Popescu and J. A. Dipaolo, *Cytogenetics*, **11**, 500 (1972); *Chem. Abstr.*, **80**, 142715 (1974).
1052. J. A. Dipaolo and N. C. Popescu, *Cancer Res.*, **33**, 3259 (1973); *Chem. Abstr.*, **80**, 104678 (1974).
1053. M. S. Sasaki, *Mutat. Res.*, **20**, 291 (1973); *Chem. Abstr.*, **80**, 44403 (1974).
1054. J. Fujimoto, *J. Nat. Cancer Inst.*, **50**, 79 (1973); *Chem. Abstr.*, **78**, 106801 (1973).
1055. H. F. Stich, R. H. San and Y. Kawazoe, *Mutat. Res.*, **17**, 127 (1973).
1056. T. Kakunaga, *Int. J. Cancer*, **12**, 463 (1973); *Chem. Abstr.*, **80**, 647 (1973).
1057. T. Sugimura, M. Nagao, M. Takeuchi, T. Yahagi, K. Hara and T. Matsushima, *Excerpta Med. Int. Congr. Ser.*, **350**, 15 (1974); *Chem. Abstr.*, **83**, 173247 (1975).
1058. Y. Tsubura, K. Toyoshima, H. Tsuji and T. Fukuyama, *Lab. Anim. Drug Test, Symp. Int. Comm. Lab. Anim. 5th, 1972*, **1973**, 197; *Chem. Abstr.*, **81**, 100470 (1974).
1059. S. Sutou and F. Tokuyama, *Cancer Res.*, **34**, 2615 (1974); *Chem. Abstr.*, **82**, 719 (1975).
1060. K. K. Sanford, S. L. Handleman, C. H. Fox, J. F. Burris, M. L. Hursey, J. T. Mitchell, J. L. Jackson and R. Parsha, *J. Nat. Cancer Inst.*, **53**, 1647 (1974); *Chem. Abstr.*, **82**, 150250 (1975).
1061. K. Hirai, V. Defendi and L. Diamond, *Cancer Res.*, **34**, 3497 (1974); *Chem. Abstr.*, **82**, 69063 (1975).
1062. R. Kanamaru, T. Kuroki, H. Sato and T. Saito, *Sci. Rep. Res. Inst. Tohoku Univ. Ser. C*, **21**, 69 (1974); *Chem. Abstr.*, **83**, 54329 (1975).
1063. B. A. Sela and L. Sachs, *J. Cell. Physiol.*, **83**, 27 (1974); *Chem. Abstr.*, **80**, 106676 (1974).
1064. J. A. DiPaolo and N. C. Popescu, *Brit. J. Cancer*, **30**, 103 (1974).
1065. L. Diamond, R. Knorr and Y. Shimizu, *Cancer Res.*, **34**, 2599 (1974); *Chem. Abstr.*, **82**, 1007 (1975).
1066. T. Andoh, T. Ide, M. Saito and Y. Kawazoe, *Cancer Res.*, **35**, 521 (1975).
1067. H. Katsuta and T. Takaoka, *Gann Monogr. Cancer Res.*, **17**, 59 (1975); *Chem. Abstr.*, **84**, 70152 (1976).
1068. G. Dimayorca, N. Mishra and P. Kimball, *Bibl. Haematol. (Basle)*, **40**, 117 (1975); *Chem. Abstr.*, **83**, 142751 (1975).
1069. S. Odashima, S. Takayama and H. Sato, *Gann Monogr. Cancer Res.*, **17**, 456 (1976).
1070. V. Altanerova, *Neoplasma*, **22**, 599 (1975); *Chem. Abstr.*, **84**, 100628 (1976).
1071. Y. Konishi, A. Denda, S. Inui, S. Takahashi, N. Ueda and M. Namiki, *Cancer Lett.*, **4**, 229 (1978).
1072. T. Kakunaga, *Proc. Nat. Acad. Sci. USA*, **75**, 1334 (1978).
1073. H. Endo, M. Aoki and Y. Aoyama, *Gann*, **50**, 209 (1959).
1074. H. Endo, S. Takayama, T. Kasuga and M. Ohashi, *Gann*, **52**, 173 (1961).
1075. H. Endo, *Symp. Cell. Chem.*, **12**, 183 (1962).
1076. H. Endo and F. Kume, *Naturwissenschaften*, **50**, 596 (1963).
1077. R. C. Reynolds, P. O. Montgomery and D. H. Karney, *Cancer Res.*, **23**, 535 (1963).
1078. R. C. Reynolds and P. O'B. Montogomery, *Proc. Amer. Assoc. Cancer Res. 6*, **53**, 2965 (1965).
1079. S. S. Lazarus, V. G. Vethamany, S. H. Shapiro and D. Amsterdam, *Cancer Res.*, **26**, 2229 (1966).
1080. P. Sentein, *Chromosoma*, **20**, 44 (1966).
1081. I. H. Pan, *T'ai-wan I Hsueh Hui Tsa Chih*, **66**, 17 (1967); *Chem. Abstr.*, **67**, 89490 (1967).
1082. Y. Harada, M. Sunagawa and K. Katagiri, *Gann*, **59**, 513 (1968); *C.A.*, **70**, 45899 (1969).
1083. Y. Hayashi and T. Hasegawa, *Proc. Jap. Cancer Assoc., 27th Gen. Meet., Tokyo*, **1968**, 82.
1084. Y. Hayashi and T. Hasegawa, *Gann*, **61**, 347 (1970).

1085. M. Watanabe and M. Horikawa, *Mutat. Res.*, **28**, 295 (1975); *Chem. Abstr.*, **83**, 38549 (1975).
1086. T. Kuroki, M. Goto, and H. Sato, *Saibo Seibutsugaku Shinpojumu*, **20**, 111 (1969); *Chem. Abstr.*, **75**, 3093 (1971).
1087. H. F. Stich and R. H. C. San, *Mutat. Res.*, **10**, 389 (1970).
1088. S. Fujimoto, *Nara Joshi Daigaku Seibutsu Gakkaishi*, **1973**, 33; *Chem. Abstr.*, **82**, 11657 (1975).
1089. H. F. Stich, W. Stich and R. H. San, *Proc. Soc. Exp. Biol. Med.*, **142**, 1141 (1973).
1090. S. Sutou, *Mutat. Res.*, **18**, 171 (1973).
1091. H. Isaka, *Gann Monogr. Cancer Res.*, **17**, 31 (1975); *Chem. Abstr.*, **84**, 100612 (1976).
1092. S. Sutou and Y. Arai, *Exp. Cell. Res.*, **92**, 15 (1975); *Chem. Abstr.*, **83**, 53940 (1975).
1093. S. D. Ancona, *Riv. Biol.*, **54**, 263 (1961); *Chem. Abstr.*, **57**, 9157 (1962).
1094. K. Moriwaki, Y. Kurita and H. Yoshida, *Annu. Rep. Nat. Inst. Genet.*, **14**, 46 (1963).
1095. T. H. Yoshida, Y. Kurita and K. Moriwaki, *Gann*, **56**, 523 (1965).
1096. T. H. Yoshida, T. Kuroki, H. Masuji and H. Sato, *Gann*, **61**, 131 (1970).
1097. H. Isaka, *Gann*, **61**, 193 (1970).
1098. Y. Hayashi, T. Hagegawa and K. Toyoshima, *Experientia*, **27**, 925 (1971).
1099. N. Yamamoto, O. Morita and T. Satoh, *Johns Hopkins Med. J. Suppl.*, **1**, 248 (1972); *Chem. Abstr.*, **77**, 148281 (1972).
1100. H. Isaka, S. Koura, M. Koura and K. Hattanmaru, *Gann*, **68**, 251 (1977).
1101. K. Sato and N. Hieda, *Int. J. Radiat. Biol.*, **35**, 83 (1979).
1102. M. Hara, *Nippon Univ. J. Med.*, **2**, 295 (1960); *Chem. Abstr.*, **56**, 13486 (1962).
1103. R. Ito, H. Otaka, S. Usui and Y. Hashimoto, *Nippon Univ. J. Med.*, **3**, 79 (1961); *Chem. Abstr.*, **68**, 13013 (1963).
1104. T. Okabayashi and A. Yoshimoto, *Chem. Pharm. Bull.*, **12**, 262 (1964).
1105. T. Fujino, A. Ando and T. Hasegawa, *Nichidai Igaku Zasshi*, **24**, 33 (1965); *Chem. Abstr.*, **67**, 1543 (1967).
1106. T. Sugimura, K. Okabe and H. Endo, *Gann*, **56**, 489 (1965).
1107. M. Terasawa, *Nichidai Igaku Zasshi*, **24**, 731 (1965).
1108. T. Sugimura, K. Okabe and M. Nagao, *Cancer Res.*, **26**, 1717 (1966); *Chem. Abstr.*, **65**, 12678 (1966).
1109. A Kumakura, *Nichidai Igaku Zasshi*, **25**, 1135 (1966).
1110. H. Hoshino, F. Fukuoka, K. Okabe and S. Sugimura, *Gann*, **57**, 71 (1966).
1111. T. Fujino, *Nichidai Igaku Zasshi*, **25**, 18 (1966); *Chem. Abstr.*, **65**, 4453 (1966).
1112. M. Takamiya, *Nichidai Igaku Zasshi*, **26**, 671 (1967).
1113. T. Matsushima, I. Kobuna, F. Fukuoka and T. Sugimura, *Gann*, **59**, 247 (1968).
1114. G. B. Brown, *Prog. Nucleic Acid Res.*, **8**, 209 (1968).
1115. M. Hozumi, *Gann*, **60**, 83 (1969).
1116. Y. Kawazoe, N. Uehara, M. Araki and M. Tamura, *Gann*, **60**, 617 (1969).
1117. S. Yatsu, *Nichidai Igaku Zasshi*, **28**, 1208 (1969); *Chem. Abstr.*, **72**, 119746 (1970).
1118. R. Kato, A. Takahashi, W. Ngamwatana and Y. Omori, *Gann*, **61**, 415 (1970).
1119. M. Araki, T. Matsushima and T. Sugimura, *Experientia*, **26**, 528 (1970).
1120. R. Kato, A. Takahashi and T. Oshima, *Biochem. Pharmacol.*, **19**, 45 (1970).
1121. Y. Kawazoe, M. Tamura and M. Araki, *Gann*, **61**, 593 (1970).
1122. T. Matsushima and T. Sugimura, *Recent Results Cancer Res.*, **34**, 53 (1971); *Chem. Abstr.*, **75**, 29858 (1971).
1123. Y. Yamane, M. Ohtawa and M. Iigo, *Yakugaku Zasshi*, **92**, 631 (1972); *Chem. Abstr.*, **77**, 97394 (1972).
1124. M. Tada and M. Tada, *Biochem. Biophys. Res. Commun.*, **46**, 1025 (1972); *Chem. Abstr.*, **76**, 149757 (1972).
1125. S. Fukuda and N. Yamamoto, *Cancer Res.*, **32**, 435 (1972).
1126. A. Stier, I. Reitz and E. Sackmann, *Naunyn-Schmiedebergs Arch. Pharmacol.*, **274**, 189 (1972); *Chem. Abstr.*, **78**, 29023 (1973).
1127. M. Tada and M. Tada, *Gann*, **65**, 281 (1974).
1128. L. A. Poirier and J. H. Weisberger, *Biochem. Pharmacol.*, **23**, 661 (1974).
1129. Y. Miyaji, H. Ichikawa and M. Ogata, *Chem. Pharm. Bull.*, **23**, 1256 (1975).
1130. M. Tada and M. Tada, *Nature*, **255**, 510 (1975).
1131. J. E. Biaglow, B. E. Jacobson and O. F. Nygaard, *Cancer Res.*, **37**, 3306 (1977).

1132. M. Ohtawa and Y. Yamane. *Proc. Jap. Cancer Assoc. 37th Annu. Meet., Tokyo, 1978*, **1978**, 283.
1133. Y. Yamane, K. Sakai and I. Morita, *Chem. Pharm. Bull.*, **26**, 497 (1978).
1134. K. Suzuki, *Gann*, **69**, 229 (1978).
1135. T. Takasu, *Experientia*, **35**, 668 (1979).
1136. M. L. Ide, *Diss. Abstr. Int.*, **40**, 1689B (1979).
1137. Y. Yamane and M. Ohtawa, *Gann*, **70**, 147 (1979).
1138. I. H. Pan, *J. Formosan Med. Assoc.*, **62**, 107 (1963); *Chem. Abstr.*, **60**, 9648 (1964).
1139. T. Ono, Y. Iwamura and M. Ohashi, *J. Jap. Biochem. Soc.*, **35**, 574 (1963).
1140. H. Endo, M. Ishizawa and T. Kamiya, *Nature*, **198**, 195 (1963).
1141. K. Zenda, M. Saneyoshi and G. Chihara, *Proc. Jap. Cancer Assoc., 24th Gen. Meet., Fukuoka*, **1965**, 155.
1142. K. Fukui, *Kagaku To Seibutsu*, **3**, 394 (1965); *Chem. Abstr.*, **68**, 1442 (1968).
1143. T. Ono, *Tampakushitsu Kakausan Koso*, **9**, 62 (1964); *Chem. Abstr.*, **64**, 2323 (1966).
1144. M. F. Malkins and A. C. Zahalsky, *Science*, **154**, 1665 (1966).
1145. C. Nagata, M. Kodama, Y. Tagashire and A. Imamura, *Biopolymers*, **4**, 409 (1966).
1146. T. Okano and K. Uekama, *Chem. Pharm. Bull.*, **15**, 1812 (1967).
1147. M. Tada, M. Tada and T. Takahashi, *Biochem. Biophys. Res. Commun.*, **29**, 469 (1967); *Chem. Abstr.*, **68**, 47725 (1968).
1148. T. Okano and K. Uekama, *Chem. Pharm. Bull.*, **15**, 1251 (1967).
1149. T. Matshushima, I. Kobuna and T. Sugimura, *Nature*, **216**, 508 (1967).
1150. E. de Mayer and J. A. de Mayer-Guignard, *Arch. Gesamte Virusforsch.*, **22**, 61 (1967); *Chem. Abstr.*, **68**, 47999 (1968).
1151. M. Kodama, Y. Tagashira and C. Nagata, *J. Biochem., (Tokyo)*, **64**, 167 (1968); *Chem. Abstr.*, **69**, 83345 (1968).
1152. M. Enomoto, K. Sato, E. C. Miller and J. A. Miller, *Life Sci.*, **7**, 1025 (1968).
1153. T. Okano and K. Uekama, *Chem. Pharm. Bull.*, **16**, 1411 (1968).
1154. T. Sugimura, H. Otake and T. Matsushima, *Nature*, **218**, 392 (1968).
1155. S. Epstein and I. Saporoshetz, *Experientia*, **24**, 1245 (1968).
1156. H. D. Hoffmann and W. Mueller, *Phys. Chem. Mech. Carcinog. Proc. Int. Symp.*, **1968**, 183; *Chem. Abstr.*, **76**, 22084 (1972).
1157. H. Adachi, M. Inuzuka and M. Tomoeda, *Idengaku Zasshi*, **44**, 31 (1969); *Chem. Abstr.*, **75**, 72895 (1971).
1158. S. Ikegami, N. Nemoto, S. Sato and T. Sugimura, *Chem.-Biol. Interactions*, **1**, 321 (1969/70).
1159. T. Okano, A. Takadate and T. Kano, *Gann*, **60**, 557 (1969).
1160. H. Tanooka, Y. Kawazoe and M. Araki, *Gann*, **60**, 537 (1969).
1161. H. Hirokawa and F. Kadlubar, *J. Virol.*, **3**, 205 (1969); *Chem. Abstr.*, **70**, 75392 (1969).
1162. M. Tada, M. Tada and T. Takahashi, in *Genetic Concepts and Neoplasia (A collection of Papers Presented at the Twenty-third Annual Symposium on Fundamental Cancer Research)*, p. 214, Williams & Wilkins, Baltimore, 1970.
1163. M. Tada, M. Tada and T. Takahashi, *Cancer Res.*, **23**, 214 (1970); *Chem. Abstr.*, **75**, 3091 (1971).
1164. Y. Yamamoto, S. Fukuda and N. Takebe, *Cancer Res.*, **30**, 2532 (1970); *Chem. Abstr.*, **74**, 2179 (1971).
1165. S. Yamamoto, T. Mizutani, C. Kameuchi and Y. Shirasu, *Proc. Soc. Exp. Biol.*, **133**, 303 (1970).
1166. F. Miyazawa, K. Yoshikawa and S. Iwahara, *J. Biochem. (Tokyo)*, **67**, 325 (1970); *Chem. Abstr.*, **73**, 145 (1970).
1167. J. S. Paul and P. O. Montgomery, *Mol. Pharmacol.*, **6**, 315 (1970); *Chem. Abstr.*, **73**, 73027 (1970).
1168. M. Tada and M. Tada, *Chem. Biol. Interactions*, **3**, 225 (1971); *Chem. Abstr.*, **75**, 74019 (1971).
1169. A. D. Laumbach and I. C. Felkner, *Mutat. Res.*, **15**, 233 (1972); *Chem. Abstr.*, **77**, 72435 (1972).
1170. H. Tanooka and A. Takahashi, *Chem. Biol. Interactions*, **5**, 351 (1972); *Chem. Abstr.*, **78**, 24551 (1973).
1171. Y. Kawazoe, G. F. Huang, M. Araki and C. Koga, *Gann*, **63**, 161 (1972).

1172. K. Yoshikawa and S. Iwahara, *Eisei Shikenjo Kokoku*, **91**, 94 (1973); *Chem. Abstr.*, **81**, 146270 (1974).
1173. M. Watanabe and M. Horikawa, *J. Radiat. Res.*, **14**, 258 (1973); *Chem. Abstr.*, **80**, 1175 (1974).
1174. C. C. Irving, *Methods Cancer Res.*, **7**, 189 (1973).
1175. Yu. S. Kondrat'ev and A. G. Skavronskaya, *Ultrafiolet 12 Luch Ego Primen. Biol. Mater. Vses. Soveshch., 10th, 1973*, **1973**, 52; *Chem. Abstr.*, **82**, 26550 (1975).
1176. Y. Kawazoe, M. Araki, G. F. Huong, T. Okamoto, M. Tada and M. Tada, *Chem. Pharm. Bull.*, **23**, 3041 (1975).
1177. M. Tada and M. Tada, *Biochim. Biophys. Acta*, **454**, 558 (1976).
1178. S. Yoshida, M. Tada and M. Tada, *Nucleic Acids Res.*, **3**, 3227 (1976).
1179. M. Horikawa, M. Watanabe and T. Sugahara, *Stud. Biophys.*, **53**, 2 (1976); *Chem. Abstr.*, **84**, 132100 (1976).
1180. O. Yamamoto and I. Gholipour-Khalili, *J. Radiat. Res. (Tokyo)*, **18**, 194 (1977).
1181. M. Kodama, C. Nagata, M. Mochizuki and M. Okada, *Gann*, **69**, 285 (1978).
1182. Y. Yamane and M. Ohtawa, *Gann*, **69**, 477 (1978).
1183. S. A. Winkle and I. Tinoco, *Biochemistry (Washington)*, **17**, 1352 (1978).
1184. O. Gotoh, A. Wada, M. Tada and M. Tada, *Gann*, **69**, 61 (1978).
1185. H. I. Hadler and T. M. Cao, *Chem. Biol. Interactions*, **20**, 219 (1978).
1186. Y. Yamane and M. Ohtawa, *Gann*, **70**, 361 (1979).
1187. R. L. Ornstein and R. Rein, *Chem. Biol. Interactions*, **27**, 291 (1979).
1188. C. Nagata, A. Imamura, K. Fukui and H. Saito, *Gann*, **54**, 401 (1963).
1189. C. Nagata, K. Fujii and S. S. Epstein, *Nature*, **215**, 972 (1967).
1190. T. Okano, S. Takenaka and Y. Sato, *Chem. Pharm. Bull.*, **16**, 556 (1968).
1191. T. Okano, K. Uekama and E. Taguchi, *Gann*, **60**, 295 (1969).
1192. T. Okano, A. Niitsuma, A. Takadate and K. Uekama, *Gann*, **60**, 97 (1969).
1193. T. Okano and K. Tsuji, *Yakugaku Zasshi*, **89**, 297 (1969).
1194. T. Okano, T. Miura, M. Yoshida and K. Uekama, *Yakugaku Zasshi*, **89**, 1379 (1969).
1195. J. Fujimoto, H. Higashi, E. Ito, T. Mori and D. Jinnai, *Med. J. Osaka Univ.*, **20**, 7 (1969); *Chem. Abstr.*, **74**, 40562 (1971).
1196. C. Nagata, *Recent Results Cancer Res.*, **34**, 17 (1971); *Chem. Abstr.*, **75**, 29859 (1971).
1179. T. Okano, A. Isobe and H. Matsumoto, *Gann*, **63**, 427 (1972).
1198. H. Katsuta and T. Takaoka, *Jap. J. Exp. Med.*, **42**, 341 (1972); *Chem. Abstr.*, **77**, 148275 (1972).
1199. M. Ishizawa, *Igaku Kenkyu*, **40**, 227 (1970); *Chem. Abstr.*, **75**, 33496 (1971).
1200. P. E. Hartman, K. Levine, Z. Hartman and H. Berger, *Science*, **172**, 1058 (1971).
1201. R. Fahrig, *Agents Actions*, **3**, 99 (1973).
1202. K. Isono and J. Yourno, *Proc. Nat. Acad. Sci. U.S.A.*, **71**, 1612 (1974).
1203. K. Yamamoto and Y. Ishii, *Mutat. Res.*, **22**, 81 (1974); *Chem. Abstr.*, **80**, 91602 (1974).
1204. N. Yamamoto, M. D. Anderson and J. A. Dipaolo, *Mol. Pharmacol.*, **10**, 640 (1974); *Chem. Abstr.*, **82**, 14662 (1975).
1205. C. D. Mayorca, N. Mishra, and P. Kimbale, *Bibl. Haematol. (Basle)*, **40**, 117 (1975); *Chem. Abstr.*, **83**, 142751 (1975).
1206. M. Ishizawa and H. Endo, *Biochem. Pharmacol.*, **16**, 637 (1967); *Chem. Abstr.*, **66**, 11311 (1967).
1207. M. Ishizawa and H. Endo, *Mutat. Res.*, **9**, 134 (1970); *Chem. Abstr.*, **72**, 52151 (1970).
1208. M. Ishizawa and H. Endo, *Mutat. Res.*, **12**, 1 (1971); *Chem. Abstr.*, **75**, 60229 (1971).
1209. M. Ishizawa and H. Endo, *Gann*, **63**, 511 (1972).
1210. L. Prakash and F. Sherman, *J. Mol. Biol.*, **79**, 65 (1973).
1213. L. Prakash, J. W. Stewart and F. Sherman, *J. Mol. Biol.*, **85**, 51 (1974).
1214. L. Prakash and F. Sherman, *Genetics*, **77**, 245 (1974); *Chem. Abstr.*, **82**, 11627 (1975).
1215. T-M. Ong, B. E. Matter and F. J. de Serres, *Cancer Res.*, **35**, 291 (1975); *Chem. Abstr.*, **82**, 165656 (1975).
1216. H. Kato, *Exp. Cell Res.*, **85**, 239 (1974); *Chem. Abstr.*, **81**, 10157 (1974).
1217. W. D. MacRae, E. A. MacKinnon and H. F. Stich, *Mutat. Res.*, **62**, 495 (1979).
1218. D. P. Yang, F. Graupensperger, L. C. Minecci and B. A. Rubin, *In Vitro*, **15**, 173 (1979).
1219. N. C. Popescu, S. C. Amsbaugh and J. A. Dipaolo, *Mutat. Res.*, **60**, 313 (1979).
1220. Y. Nakanishi and E. L. Schneider, *Mutat. Res.*, **60**, 329 (1979).

1221. M. Tada, M. Tada and T. Takahashi, *Biochem. Biophys. Res. Commun.*, **29**, 469 (1967); *Chem. Abstr.*, **68**, 47725 (1968).
1222. E. de Mayer and J. A. de Mayer-Guignard, *Arch. Gesamte Virusforsch.*, **22**, 61 (1967); *Chem. Abstr.*, **68**, 47999 (1968).
1223. I. C. Felkner and F. Kadlubar, *J. Bacteriol.*, **96**, 1448 (1968); *Chem. Abstr.*, **69**, 104116 (1968).
1224. M. Horikawa, O. Nikaido and T. Sugahara, *Exp. Cell Res.*, **55**, 65 (1969); *Chem. Abstr.*, **71**, 20404 (1969).
1225. M. Horikawa, O. Nikaido, T. Tanaka, H. Nagata and T. Sugahara, *Exp. Cell Res.*, **59**, 147 (1969); *Chem. Abstr.*, **72**, 53077 (1970).
1226. S. Kondo, H. Ichikawa, K. Iwo and T. Kato, *Genetics*, **66**, 187 (1970).
1227. M. Tada, M. Tada and T. Takahashi, *Collect. Pap., 23rd Annu. Symp. Fundam. Cancer Res.*, **1970**, 216.
1228. M. Horikawa, O. Nikaido, T. Tanaka, H. Nagata and T. Sugahara, *Exp. Cell Res.*, **59**, 147 (1970).
1229. H. F. Stich and R. H. San, *Mutat. Res.*, **10**, 389 (1970); *Chem. Abstr.*, **74**, 19419 (1971).
1230. H. F. Stich and R. H. San, *Mutat. Res.*, **13**, 279 (1971); *Chem. Abstr.*, **76**, 68762 (1972).
1231. H. F. Stich, R. H. San and Y. Kawazoe, *Nature*, **229**, 416 (1971); *Chem. Abstr.*, **74**, 96927 (1971).
1232. Y. Ishi and S. Kondo, *Mutat. Res.*, **13**, 193 (1971).
1233. T. Kada, K. Tutikawa and Y. Sadaie, *Mutat. Res.*, **16**, 165 (1972).
1234. M. Horikawa, M. Fukuhara, F. Suzuki, O. Nikaido and T. Sugahara, *Exp. Cell Res.*, **70**, 349 (1972); *Chem. Abstr.*, **76**, 122680 (1972).
1235. E. C. Friedberg, *Mutat. Res.*, **15**, 113 (1972).
1236. M. Nagao and T. Sugimura, *Cancer Res.*, **32**, 2369 (1972); *Chem. Abstr.*, **78**, 120012 (1973).
1237. H. Takebe, J. Furuyama, Y. Miki and S. Kondo, *Mutat. Res.*, **15**, 98 (1972); *Chem. Abstr.*, **77**, 43879 (1972).
1238. T. Andoh and T. Ide, *Cancer Res.*, **32**, 1230 (1972); *Chem. Abstr.*, **77**, 97526 (1972).
1239. T. Ide and T. Andoh, *Cancer Res.*, **32**, 1236 (1972); *Chem. Abstr.*, **77**, 97527 (1972).
1240. T. Satoh and N. Yamamoto, *Cancer Res.*, **32**, 440 (1972).
1241. A. J. Jacobs, R. L. O'Brien and J. W. Parker, *Mutat. Res.*, **16**, 420 (1972); *Chem. Abstr.*, **78**, 25032 (1973).
1242. M. Horikawa, M. Fukuhara, K. Isomura and F. Suzuki, *Saibo Seibutsugaku Shimpojiumu*, **23**, 11 (1972); *Chem. Abstr.*, **80**, 93587 (1974).
1243. A. J. Jacobs, R. L. O'Brien and J. W. Parker, *Int. J. Cancer*, **10**, 118 (1972); *Chem. Abstr.*, **77**, 136059 (1972).
1244. A. G. Skavronskaya, I. V. Andreeva and A. A. Kiryushkina, *Mutat. Res.*, **18**, 259 (1973).
1245. C. L. Kemp and K. M. Malloy, *Mutat. Res.*, **20**, 191 (1973); *Chem. Abstr.*, **80**, 44304 (1974).
1246. R. E. Kuske and H. F. Stich, *Mutat. Res.*, **19**, 265 (1973); *Chem. Abstr.*, **80**, 23206 (1974).
1247. S. Wolff and J. E. Cleaver, *Mutat. Res.*, **20**, 71 (1973); *Chem. Abstr.*, **80**, 23104 (1974).
1248. K. Isomura, O. Nikaido, M. Horikawa and T. Sugahara, *Radiat. Res.*, **53**, 143 (1973); *Chem. Abstr.*, **78**, 82727 (1973).
1249. J. D. Regan and R. B. Setlow, in *Chemical Mutagens*, ed. A. Hollaender, Vol. III, p. 151, 1973, Plenum, New York.
1250. H. Tanooka, *Kyoto Diagaku Genshiro Jikkensho Tanki Kenkyukai Hokoku Kurri-TR-120*, **1973**, 67; *Chem. Abstr.*, **85**, 1813 (1976).
1251. S. Kondo, *Genetics*, **74**, Suppl., 109 (1973).
1252. A. G. Skavronskaya, I. V. Andreeva and A. A. Kiryushkina, *Mutat. Res.*, **23**, 275 (1974).
1253. J. D. Regan and R. B. Setlow, *Cancer Res.*, **34**, 3318 (1974); *Chem. Abstr.*, **82**, 69058 (1975).
1254. D. M. Sweet and B. E. B. Moseley, *Mutat. Res.*, **23**, 311 (1974).
1255. F. M. Makino and S. Okada, *Mutat. Res.*, **23**, 387 (1974); *Chem. Abstr.*, **81**, 72530 (1974).
1256. H. F. Stich and D. Kieser, *Proc. Soc. Exp. Biol. Med.*, **145**, 1339 (1974); *Chem. Abstr.*, **81**, 21861 (1974).
1257. Z. M. Iqbal, M. Majdan and S. S. Epstein, *Cancer Res.*, **36**, 1108 (1976).
1258. Z. M. Iqbal and S. S. Epstein, *Proc. Amer. Assoc. Cancer Res.*, **17**, 192 (1976).
1259. A. C. Chan, S. K. C. Ng and I. G. Walker, *J. Cell. Biol.*, **70**, 685 (1976); *Chem. Abstr.*, **85**, 91422 (1976).
1260. I. G. Walker and R. Sridhar, *Chem. Biol. Interactions*, **12**, 229 (1976); *Chem. Abstr.*, **84**, 130951 (1976).

1261. J. D. Regan, Report 1975 CONF-750745-1, *Nucl. Sci. Abstr.*, **33**, 9442 (1976); *Chem. Abstr.*, **84**, 174912 (1976).
1262. V. M. Maher, D. J. Dorney, R. H. Heflich, J. W. Levinson, A. L. Mendrala and J. J. McCormick, *DNA Repair Mechanisms, Proceedings of the ICN–UCLA 1978 Symposium on Molecular and Cellular Biology Held in Keystone, Co., February, 1978*, eds. P. C. Hanawalt, E. C. Friedberg and C. F. Fox, Vol. 9, p. 813, Academic Press, New York, 1978.
1263. G. D. Zasukhina, T. A. Sinel'shchikova and G. N. L'vova, *Dokl. Akad. Nauk SSSR*, **1978**, 238.
1264. A. J. Brown, T. H. Fickel, J. E. Cleaver, P. H. Lohman, M. H. Wade and R. Waters, *Cancer Res.*, **39**, 2522 (1979).
1265. H. Endo, A. Wada, K. Miura, J. Hidaka and C. Hiruki, *Nature*, **190**, 833 (1961).
1266. J. S. Paul, R. C. Reynolds and P. O'B. Montogomery, *J. Cell Biol.*, **35**, 100A (1967).
1267. J. S. Paul, R. C. Reynolds and P. O'B. Montogomery, *Nature*, **215**, 74 (1967).
1268. J. S. Paul, R. C. Reynolds and P. O'B. Montogomery, *Cancer Res.*, **29**, 558 (1969); *Chem. Abstr.*, **70**, 95132 (1969).
1269. T. Okabayashi, *Yakugaku Zasshi*, **73**, 946 (1953).
1270. H. Endo., *Gann*, **49**, 151 (1958).
1271. W. Nakahara and F. Fukuoka, *Gann*, **50**, 1 (1959).
1272. S. Nishimura, T. Ono and F. Fukuoka, *Gann*, **52**, 83 (1961).
1273. S. Al-Kassab, E. Borland and K. Williams, *Biochem. J.*, **83**, 12 (1962).
1274. T. Okamoto and M. Ito, *Chem. Pharm. Bull.*, **11**, 785 (1963).
1275. H. Naora and H. Naora, *Gann*, **57**, 497 (1966).
1276. T. Matsushima, S. Inuzuka, I. Kobuna and T. Sugimura, *Proc. Jap. Cancer Assoc., 26th Gen. Meet., Nagoya*, **1967**, 189.
1277. M. Hozumi, S. Inuzuka and T. Sugimura, *Cancer Res.*, **27**, 1378 (1967).
1278. M. Hozumi, *Biochem. Pharmacol.*, **17**, 769 (1968).
1279. T. Okano, S. Takenaka and Y. Sato, *Gann*, **60**, 307 (1969).
1280. T. Mita, H. Munakata and W. Nakahara, *Exp. Cell Res.*, **60**, 299 (1970).
1281. T. Andoh, K. Kato, T. Takaoka and H. Katsuta, *Int. J. Cancer*, **7**, 455 (1971); *Chem. Abstr.*, **75**, 61249 (1971).
1282. T. Okano and Y. Sato, *Gann*, **63**, 713 (1972).
1283. T. Andoh and T. Ide, *Saibo Seibutsugaku Shimpojiumu*, **23**, 69 (1972); *Chem. Abstr.*, **81**, 349 (1974).
1284. M. E. Varnes and J. E. Biaglow, *Fed. Proc.*, **37**, 1542 (1978).
1285. M. E. Varnes and J. E. Biaglow, *Cancer Res.*, **39**, 2960 (1979).
1286. S. Nakashima, *J. Biochem. (Tokyo)*, **69**, 605 (1971); *Chem. Abstr.*, **75**, 3365 (1971).
1287. S. Nagashima, K. Sugimura and S. Ono, *J. Biochem. (Tokyo)*, **71**, 849 (1972); *Chem. Abstr.*, **77**, 17763 (1972).
1288. J. M. Phillips, *Int. J. Cancer*, **9**, 39 (1972); *Chem. Abstr.*, **76**, 136628 (1972).
1289. S. Nakashima and S. Ono, *Gann*, **63**, 111 (1972).
1290. H. C. Outzen and R. T. Prehn, *Cancer Res.*, **33**, 408 (1973); *Chem. Abstr.*, **78**, 132537 (1973).
1291. S. Nakashima, S. Ono and H. Hayashi, *Gann*, **65**, 411 (1974).
1292. H. R. Coltne and T. Borsos, *J. Immunol.*, **112**, 1107 (1974); *Chem. Abstr.*, **81**, 34260 (1974).
1293. S. Sakai, K. Minoda, G. Saito, S. Akagi, A. Ueno and F. Fukuoka, *Gann*, **46**, 605 (1955).
1294. F. Fukuoka, T. Sugimura and S. Suzuki, *Gann*, **48**, 263 (1957).
1295. T. Okamoto, Y. Hasegawa, T. Kinoshita, M. Ishiguro and D. Mizuno, *Yakugaku Zasshi*, **85**, 720 (1965).
1296. F. Fukuoka, *Recent Results Cancer Res.*, **34**, 66 (1971); *Chem. Abstr.*, **75**, 18388 (1971).
1297. T. Kakunaga, *Int. J. Cancer*, **12**, 463 (1973); *Chem. Abstr.*, **80**, 647 (1974).
1298. T. Kakunaga, *Nature*, **258**, 248 (1975).
1299. T. Nomura, *Nature*, **260**, 547 (1976).
1300. T. Okabayashi, *J. Fermentation Technol.*, **31**, 373 (1953); *Chem. Abstr.*, **48**, 5276 (1954).
1301. T. Okabayashi, *J. Fermentation Technol.*, **32**, 108 (1954); *Chem. Abstr.*, **48**, 12886 (1954).
1302. T. Okabayashi, *J. Fermentation Technol.*, **33**, 513 (1955); *Chem. Abstr.*, **50**, 7940 (1956).
1303. F. Leonard, F. A. Barkley, E. V. Brown, F. E. Anderson and D. M. Green, *Antibiot. Chemother.*, **6**, 261 (1956); *Chem. Abstr.*, **50**, 14970 (1956).
1304. T. Okabayashi and E. Masuo, *J. Fermentation Technol.*, **34**, 7 (1956); *Chem. Abstr.*, **51**, 2117 (1957).

1305. K. Yamagata, M. Oda and T. Ando, *J. Fermentation Technol*, **34**, 378 (1956); *Chem. Abstr.*, **51**, 12231 (1957).
1306. S. Sakai, K. Minoda, S. Akagi, A. Ueno, G. Saito and A. Sato, *J. Sci. Res. Inst. (Tokyo)*, **51**, 18 (1957); *Chem. Abstr.*, **51**, 16940 (1957).
1307. K. Yamagata and M. Oda, *Hakko Kogaku Zasshi*, **35**, 67 (1957); *Chem. Abstr.*, **51**, 16687 (1957).
1308. T. Okabayashi, *Hakko Kogaku Zasshi*, **35**, 17 (1957); *Chem. Abstr.*, **51**, 18100 (1957).
1309. G. Buchmann, *Pharmazie*, **17**, 283 (1962); *Chem. Abstr.*, **57**, 16760 (1962).
1310. G. Buchmann, *Wiss. Z. Tech. Hochsch. Chem. Leuna-Merseburg*, **4**, 213 (1962); *Chem. Abstr.*, **59**, 4492 (1963).
1311. T. Okabayashi and A. Yoshimoto, *Chem. Pharm. Bull.*, **10**, 1221 (1962).
1312. T. Okabayashi, *Chem. Pharm. Bull.*, **10**, 1127 (1962).
1313. Z. Narita and Y. Tomita, *Itsuu Kenkyusho Nempo*, **13**, 41 (1963); *Chem. Abstr.*, **60**, 4503 (1964).
1314. T. Okabayashi, A. Yoshimoto and M. Ide, *Chem. Pharm. Bull.*, **12**, 257 (1964).
1315. E. P. Shumilenko, *Tr. Sverdl. Sel'skokhoz. Inst.*, **14**, 79 (1965); *Chem. Abstr.*, **66**, 27954 (1967).
1316. E. G. Novikov, A. G. Pozdeeva, N. M. Golyshin and L. G. Fedoseenko, *Khim. Sel'sk. Khoz.*, **5**, 910 (1967); *Chem. Abstr.*, **68**, 104080 (1968).
1317. T. Mita, *Recent Results Cancer Res.*, **34**, 74 (1971); *Chem. Abstr.*, **75**, 31517 (1971).
1318. M. T. Ong, B. E. Matter and F. J. De Serres, *Cancer Res.*, **35**, 291 (1975); *Chem. Abstr.*, **82**, 165656 (1975).
1319. S. Suguma, M. Hara, T. Ooba, J. Tamada and H. Murukami, *Misc. No Kangaku To Crijutsu*, **254**, 25 (1975); *Chem. Abstr.*, **83**, 129975 (1975).
1320. I. Arai and I. Nakayama, *Yakugaku Zasshi*, **72**, 167 (1952).
1321. J. W. Lightbronn, *Giorn. ital. Chemioterap.*, **4**, 22 (1957); *Chem. Abstr.*, **52**, 18651 (1958).
1322. I. H. Pan, *J. Formosan Med. Assoc.*, **59**, 1105 (1960); *Chem. Abstr.*, **55**, 24914 (1961).
1323. I. H. Pan, *J. Formosan Med. Assoc.*, **60**, 269 (1961); *Chem. Abstr.*, **56**, 774 (1962).
1324. T. Okabayashi, M. Ide, A. Yoshimoto and M. Otsubo, *Chem. Pharm. Bull.*, **13**, 610 (1965).
1325. T. J. Bond, K. L. Young and T. Andrus, *Appl. Microbiol.*, **20**, 536 (1970); *Chem. Abstr.*, **74**, 1427 (1971).
1326. P. O. Milch, *Diss. Abstr. Int. B*, **31**, 4514 (1971); *Chem. Abstr.*, **75**, 45960 (1971).
1327. Y. S. Kondratev and A. G. Skavronskaya, *Genetika*, **8**, 112 (1972); *Chem. Abstr.*, **77**, 148161 (1972).
1328. P. J. F. Henderson, *Biochem. J.*, **135**, 101 (1973).
1329. C. L. Barker, *Diss. Abstr. Int. B*, **34**, 3142 (1974); *Chem. Abstr.*, **81**, 115163 (1974).
1330. M. I. Kenaga, R. Ichikawa and S. Kondo, *J. Mol. Biol.*, **92**, 341 (1975).
1331. Y. Ishii and S. Kondo, *Mutat. Res.*, **27**, 27 (1975); *Chem. Abstr.*, **82**, 108712 (1975).
1332. I. Mifuchi and T. Morita, *Med. Biol.*, **64**, 101 (1962).
1333. I. Mifuchi, M. Hosoi, Y. Yanagihara and M. Nishida, *Gann*, **54**, 205 (1963).
1334. I. Mifuchi, T. Morita, Y. Yanagihara, M. Hosoi and M. Nishida, *Jap. J. Microbiol.*, **7**, 69 (1963); *Chem. Abstr.*, **61**, 997 (1964).
1335. T. Morita and I. Mifuchi, *Jap. J. Microbiol.*, **9**, 123 (1965).
1336. T. Morita, *Med. Biol.*, **72**, 166 (1966).
1337. J. M. Klein, *Diss. Abstr. Int. B*, **29**, 479 (1968); *Chem. Abstr.*, **70**, 17807 (1969).
1338. T. Morita, I. Mifuchi and T. Sugimura, *Igaku To Seibutsugaku*, **77**, 241 (1968); *Chem. Abstr.*, **70**, 65541 (1969).
1339. S. Nagai, *Mutat. Res.*, **7**, 333 (1969); *Chem. Abstr.*, **71**, 58044 (1969).
1340. S. S. Epstein, J. A. St., *Toxicol. Appl. Pharmacol.*, **15**, 451 (1969); *Chem. Abstr.*, **71**, 99185 (1969).
1341. T. Morita and I. Mifuchi, *Biochem. Biophys. Res. Commun.*, **38**, 191 (1970).
1342. H. Yamaguchi, A. Tatare and T. Naito, *Idengaku Zasshi*, **50**, 307 (1975); *Chem. Abstr.*, **84**, 101612 (1976).
1343. M. Okuda, *Toho Igakkai Zasshi*, **18**, 743 (1971); *Chem. Abstr.*, **77**, 147942 (1972).
1344. I. Morita, *Fukuoka Igaku Zasshi*, **62**, 760 (1971); *Chem. Abstr.*, **76**, 55063 (1972).
1345. T. Morita, I. Hirota and I. Mifuchi, *Igaku To Seibutsugaku*, **84**, 209 (1972); *Chem. Abstr.*, **77**, 137269 (1972).

1346. T. Morita, I. Hirota and I. Mifuchi, *Igaku To Seibutsugaku*, **84**, 285 (1972); *Chem. Abstr.*, **78**, 53209 (1973).
1347. T. Morita, I. Hirota, M. Fukanagu and I. Mifuchi, *Igaku To Seibutsugaku*, **84**, 225 (1972); *Chem. Abstr.*, **78**, 12057 (1973).
1348. T. Morita and I. Mifuchi, *Gann*, **65**, 27 (1974).
1349. H. Yamaguchi, A. Tatara and T. Naito, *Idengaku Zasshi*, **50**, 307 (1975); *Chem. Abstr.*, **84**, 101612 (1976).
1350. A. Tatara and T. Naito, *Idengaku Zasshi*, **50**, 307 (1975); *Chem. Abstr.*, **84**, 101612 (1976).
1351. T. Morita, M. Fukunaga and I. Mifuchi, *Gann*, **66**, 697 (1975).
1352. S. Nakanishi, *Nara Joshi Daigaku Seibutsu Gakkaishi*, **24/25**, 10 (1975); *Chem. Abstr.*, **84**, 130886 (1976).
1353. S. Nagai, *Mutat. Res.*, **34**, 187 (1976); *Chem. Abstr.*, **84**, 116297 (1976).
1354. A. C. Zahalsky, M. M. Keane, S. H. Hutner, K. U. Lubart, M. Kittrell and A. Amsterdam, *J. Protozool.*, **10**, 421 (1963); *Chem. Abstr.*, **60**, 11090 (1964).
1355. A. C. Zahalsky and S. L. Marcus, *Nature*, **208**, 269 (1965).
1356. T. Mita, R. Tokuzen, F. Fukuoka and W. Nakahara, *Gann*, **56**, 293 (1965).
1357. T. Mita, R. Tokuzen, F. Fukuoka and W. Nakahara, *Gann*, **57**, 273 (1966).
1358. S. H. Hutner, A. C. Zahalsky and S. Aaronson, in *Biochemistry of Chloroplast*, ed. T. W. Goodwin, Vol. 2, p. 703, Academic Press, London, New York, 1967.
1359. T. Mita, Y. Kawazoe and M. Araki, *Gann*, **60**, 155 (1969).
1360. L. A. Cohen, *Diss. Abstr. Int. B*, **33**, 3474 (1973); *Chem. Abstr.*, **78**, 144157 (1973).
1361. W. Leon, F. S. Cruz and M. E. Vasconcellos, *J. Protozool.*, **22**, 277 (1975); *Chem. Abstr.*, **83**, 23254 (1975).
1362. W. Leon and S. M. Krassner, *J. Parasitol.*, **62**, 115 (1976); *Chem. Abstr.*, **85**, 41895 (1976).
1363. S. Mashima and Y. Ikeda, *Appl. Microbiol.*, **6**, 45 (1958); *Chem. Abstr.*, **52**, 8276 (1958).
1364. N. Suzuki and S. Okada, *Mutat. Res.*, **34**, 489 (1976); *Chem. Abstr.*, **84**, 130440 (1976).
1365. B. E. Matter, M. T. Ong and F. J. De Serres, *Gann*, **63**, 265 (1972).
1366. B. N. Ames, F. D. Lee and W. E. Durston, *Proc. Nat. Acad. Sci. U.S.A.*, **70**, 782 (1973).
1367. J. McCann, N. E. Spingarn, J. Koburt and B. N. Ames, *Proc. Nat. Acad. Sci. U.S.A.*, **72**, 979 (1975).
1368. R. Fahrig, *Mutat. Res.*, **31**, 381 (1975); *Chem. Abstr.*, **84**, 85010 (1976).
1369. J. T. MacGregor and L. E. Sacks, *Mutat. Res.*, **38**, 271 (1976); *Chem. Abstr.*, **85**, 72866 (1976).
1370. R. Fahrig, *Umsch. Wiss. Tech.*, **76**, 224 (1976); *Chem. Abstr.*, **85**, 882 (1976).
1371. Y. Iwamoto and I. Mifuchi, *Proc. 37th Annu. Meet. Jap. Cancer Assoc., Tokyo, 1978*, **1978**, 283.
1372. H. Yoshikura, T. Kuchino and T. Matsushima, *Cancer Lett.*, **7**, 203 (1979).
1373. J. W. Lightbown and F. L. Jackson, *Biochem. J.*, **63**, 130 (1956).
1374. F. L. Jackson and J. W. Lightbown, *Biochem. J.*, **69**, 63 (1958).
1375. M. Avron, *Biochem. J.*, **78**, 735 (1961).
1376. M. Kogut and J. W. Lightbown, *Biochem. J.*, **84**, 368 (1962).
1377. J. L. Howland, *Biochim. Biophys. Acta*, **73**, 665 (1963); *Chem. Abstr.*, **59**, 10358 (1963).
1378. M. Luckner and C. Ritter, *Tetrahedron Lett.*, **1965**, 741.
1379. J. R. Brandon, J. R. Brocklehurst and C. P. Lee, *Biochemistry*, **11**, 1150 (1972).
1380. G. N. Pershin, V. V. Nesvadba and Z. K. Shatilova, *Farmakol. Toksikol.*, **16**, 25 (1953); *Chem. Abstr.*, **47**, 12466 (1953).
1381. S. Koshimura, A. Hamada, T. Otaki and K. Deguchi, *Annu. Rep. Res. Inst. Tuberc., Kanawaza Univ.*, **12**, 5 (1954); *Chem. Abstr.*, **49**, 9159 (1955).
1382. S. Sakai, K. Minoda, S. Akagi and N. Okoti, *J. Sci. Res. Inst. (Tokyo)*, **51**, 91 (1957); *Chem. Abstr.*, **51**, 16941 (1957).
1383. K. Miura, M. Ikeda, T. Ohashi, I. Okada and Y. Igarashi, *Yakugaku Zasshi*, **84**, 537 (1964); *Chem. Abstr.*, **61**, 12523 (1964).
1384. A. Taketo, H. Sawada and Y. Takagi, *Biochem. Biophys. Res. Commun.*, **15**, 256 (1964); *Chem. Abstr.*, **61**, 980 (1964).
1385. K. Miura and I. Okada, *Chem. Pharm. Bull.*, **13**, 525 (1965).
1386. H. Katoe, H. Iwana, Y. Takase and M. Shimizu, *Arzneim.-Forsch.*, **17**, 1030 (1967); *Chem. Abstr.*, **67**, 107051 (1967).
1387. M. Shimizu, S. Nakamura and Y. Takase, *Chem. Pharm. Bull.*, **17**, 2330 (1969).
1388. F. Fukuoka, T. Sugimura and S. Sakai, *Gann*, **48**, 65 (1957).

1389. K. Sato, T. Kuroki and H. Sato, *Proc. Soc. Exp. Biol.*, **134**, 281 (1970); *Chem. Abstr.*, **73**, 53930 (1970).
1390. H. I. Hadler and T. M. Cao, *Lancet*, **1**, 397 (1978).
1391. T. Ono, T. Tomaru and F. Fukuoka, *Gann*, **50**, 189 (1959).
1392. T. Tomaru, M. Ohashi, and F. Fukuoka, *Gann*, **52**, 89 (1961).
1393. Y. Shirasu, Y. Hayashi and F. Fukuoka, *Gann*, **51**, 341 (1960).
1394. R. Tokuzen, M. Araki, M. Saneyoshi and F. Fukuoka, *Gann*, **61**, 601 (1970).
1395. C. A. Benassi, *Gazz. Chim. Ital.*, **91**, 1104 (1961); *Chem. Abstr.*, **56**, 15420 (1962).
1396. L. I. Kurkul'tseva and A. Zikiryaev, *Nauch. Tr. Tashkent Gos. Univ.*, **334**, 26 (1968); *Chem. Abstr.*, **74**, 63372 (1971).
1397. A. S. Sadykov, O. S. Otroshchenko, N. E. Pavlovskaya and E. L. Rempel, *Vopr. Fiziol. Biokhim. Khlop.*, **1**, 111 (1969); *Chem. Abstr.*, **73**, 129884 (1970).
1398. J. E. Biaglow, B. Jacobson and C. Koch, *Biochem. Biophys. Res. Commun.*, **70**, 1316 (1976).
1399. C. Kaneko, H. Fujii, S. Kawai, A. Yamamoto, K. Hashiba, T. Kimata and M. Somei, *Chem. Pharm. Bull.*, **28**, 1157 (1980).
1400. T. Kinoshita, T. Onoue, M. Watanabe and S. Furukawa, *Chem. Pharm. Bull.*, **28**, 795 (1980).

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Subject Index

Notes on the use of this index

As in Part I, compounds which appear in the tables do not appear in the Subject Index unless they also appear in the text of the chapters. For Chapter 1 compounds appear generally under their full systematic name. Prefixes such as *o-*, *m-*, *p-*, *cis* and *trans* are ignored when the alphabetical order is determined. For Chapters 2 and 3 compounds appear largely under the major class, e.g.

1,2-Dihydroquinoline, 1-benzoyl-2-cyano,

or

4-Aminoquinoline *N*-oxide, 6-chloro,

but simple derivatives of quinoline occur throughout the index.

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