$-\overset{+}{N}\equiv N \quad -CN_2$

The chemistry of
diazonium and diazo groups
Part 1

THE CHEMISTRY OF FUNCTIONAL GROUPS

A series of advanced treatises under the general editorship of
Professor Saul Patai

The chemistry of alkenes (2 volumes)
The chemistry of the carbonyl group (2 volumes)
The chemistry of the ether linkage
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The chemistry of cyanates and their thio derivatives (2 parts)
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The chemistry of diazonium and diazo groups

Part 1

Edited by

SAUL PATAI

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Contributing authors

W. Ando	Chemistry Department, The University of Tsukuba, Niiharigun, Ibaraki 300–31, Japan
D. A. Ben-Efraim	The Weizmann Institute of Science, Rehovot, Israel
C. F. Cooper	Department of Chemistry, University of Missouri-Rolla, Rolla, Mo. 65401, USA
A. J. Fry	Wesleyan University, Middletown, Connecticut, USA
A. F. Hegarty	Chemistry Department, University College, Cork, Ireland
E. S. Lewis	Department of Chemistry, Rice University, Houston, Texas, USA
G. Linstrumelle	Équipe de Recherche No. 12 du CNRS, Laboratoire de Chimie, École Normale Supérieure, Paris, France
J. F. McGarrity	Institute of Organic Chemistry, University of Lausanne, Lausanne, Switzerland
J. B. Moffat	Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada
H. M. Niemeyer	Institute of Organic Chemistry, University of Lausanne, Lausanne, Switzerland
M. Regitz	Department of Chemistry, University of Kaiserslautern, D-6750, Federal Republic of Germany
K. Schank	Fachbereich 14.1 Organische Chemie, Universität des Saarlandes, D-6600 Saarbrücken, Germany
R. Shaw	1162 Quince Avenue, Sunnyvale, California 94087, USA
P. J. Smith	Department of Chemistry and Chemical Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada
S. Sorriso	Istituto di Chimica Fisica, Università di Perugia, 06100 Perugia, Italy
V. Štěrba	Organic Chemistry Department, Institute of Chemical Technology, 532 10 Pardubice, Czechoslovakia
K. C. Westaway	Department of Chemistry, Laurentian University, Sudbury, Ontario, Canada
D. Whittaker	Department of Organic Chemistry, University of Liverpool, England
D. S. Wulfman	Department of Chemistry, University of Missouri-Rolla, Rolla, Mo. 65401, USA

Foreword

The present volume, 'The Chemistry of Diazonium and Diazo Groups' is, on the whole, organized and presented according to the general lines described in the 'Preface to the Series', printed on the following pages.

Some difficulty arose in the presentation owing to the fact that while the two groups treated, i.e. the diazo group and the diazonium group, are closely related and even occur in equilibrium with each other, their chemical behaviour and characteristics differ from each other considerably. Moreover, the material which had to be covered proved to be much more extensive than originally surmised. For these reasons, some of the subjects had to be divided into two or more chapters; for instance, the synthetic applications of diazonium and diazo groups are treated in two separate chapters and even so each of these turned out to be very large. Similarly, the syntheses of the different title compounds are discussed in three separate chapters.

The plan of the present volume also included a chapter on 'Biological and Pharmaceutical Effects' which, however, failed to materialize. It is hoped that this will appear in one of the supplementary volumes to the series.

Jerusalem, February 1977 SAUL PATAI

The Chemistry of Functional Groups
Preface to the series

The series 'The Chemistry of Functional Groups' is planned to cover in each volume all aspects of the chemistry of one of the important functional groups in organic chemistry. The emphasis is laid on the functional group treated and on the effects which it exerts on the chemical and physical properties, primarily in the immediate vicinity of the group in question, and secondarily on the behaviour of the whole molecule. For instance, the volume *The Chemistry of the Ether Linkage* deals with reactions in which the C—O—C group is involved, as well as with the effects of the C—O—C group on the reactions of alkyl or aryl groups connected to the ether oxygen. It is the purpose of the volume to give a complete coverage of all properties and reactions of ethers in as far as these depend on the presence of the ether group but the primary subject matter is not the whole molecule, but the C—O—C functional group.

A further restriction in the treatment of the various functional groups in these volumes is that material included in easily and generally available secondary or tertiary sources, such as Chemical Reviews, Quarterly Reviews, Organic Reactions, various 'Advances' and 'Progress' series as well as textbooks (i.e. in books which are usually found in the chemical libraries of universities and research institutes) should not, as a rule, be repeated in detail, unless it is necessary for the balanced treatment of the subject. Therefore each of the authors is asked *not* to give an encyclopaedic coverage of his subject, but to concentrate on the most important recent developments and mainly on material that has not been adequately covered by reviews or other secondary sources by the time of writing of the chapter, and to address himself to a reader who is assumed to be at a fairly advanced post-graduate level.

With these restrictions, it is realized that no plan can be devised for a volume that would give a *complete* coverage of the subject with *no* overlap between chapters, while at the same time preserving the readability of the text. The Editor set himself the goal of attaining *reasonable* coverage with *moderate* overlap, with a minimum of cross-references between the chapters of each volume. In this manner, sufficient freedom is given to each author to produce readable quasi-monographic chapters.

The general plan of each volume includes the following main sections:

(a) An introductory chapter dealing with the general and theoretical aspects of the group.

(b) One or more chapters dealing with the formation of the functional group in question, either from groups present in the molecule, or by introducing the new group directly or indirectly.

(c) Chapters describing the characterization and characteristics of the functional groups, i.e. a chapter dealing with qualitative and quantitative methods of determination including chemical and physical methods, ultraviolet, infrared, nuclear magnetic resonance and mass spectra: a chapter dealing with activating and directive effects exerted by the group and/or a chapter on the basicity, acidity or complex-forming ability of the group (if applicable).

(d) Chapters on the reactions, transformations and rearrangements which the functional group can undergo, either alone or in conjunction with other reagents.

(e) Special topics which do not fit any of the above sections, such as photochemistry, radiation chemistry, biochemical formations and reactions. Depending on the nature of each functional group treated, these special topics may include short monographs on related functional groups on which no separate volume is planned (e.g. a chapter on 'Thioketones' is included in the volume *The Chemistry of the Carbonyl Group*, and a chapter on 'Ketenes' is included in the volume *The Chemistry of Alkenes*). In other cases certain compounds, though containing only the functional group of the title, may have special features so as to be best treated in a separate chapter, as e.g. 'Polyethers' in *The Chemistry of the Ether Linkage*, or 'Tetraaminoethylenes' in *The Chemistry of the Amino Group*.

This plan entails that the breadth, depth and thought-provoking nature of each chapter will differ with the views and inclinations of the author and the presentation will necessarily be somewhat uneven. Moreover, a serious problem is caused by authors who deliver their manuscript late or not at all. In order to overcome this problem at least to some extent, it was decided to publish certain volumes in several parts, without giving consideration to the originally planned logical order of the chapters. If after the appearance of the originally planned parts of a volume it is found that either owing to non-delivery of chapters, or to new developments in the subject, sufficient material has accumulated for publication of a supplementary volume, containing material on related functional groups, this will be done as soon as possible.

The overall plan of the volumes in the series 'The Chemistry of Functional Groups' includes the titles listed below:

The Chemistry of Alkenes (*two volumes*)
The Chemistry of the Carbonyl Group (*two volumes*)
The Chemistry of the Ether Linkage
The Chemistry of the Amino Group
The Chemistry of the Nitro and Nitroso Group (*two parts*)
The Chemistry of Carboxylic Acids and Esters
The Chemistry of the Carbon–Nitrogen Double Bond
The Chemistry of the Cyano Group
The Chemistry of Amides
The Chemistry of the Hydroxyl Group (*two parts*)
The Chemistry of the Azido Group
The Chemistry of Acyl Halides
The Chemistry of the Carbon–Halogen Bond (*two parts*)
The Chemistry of Quinonoid Compounds (*two parts*)
The Chemistry of the Thiol Group (*two parts*)
The Chemistry of Amidines and Imidates
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The Chemistry of Cyanates and their Thio Derivatives
The Chemistry of Diazonium and Diazo Groups
Supplement A: The Chemistry of Double-Bonded Functional Groups (*two parts*)

Titles in press:
The Chemistry of the Carbon–Carbon Triple Bond
Supplement B: The Chemistry of Acid Derivatives

Future volumes planned include:
The Chemistry of Cumulenes and Heterocumulenes
The Chemistry of Organometallic Compounds
The Chemistry of Sulphur-containing Compounds
Supplement C: The Chemistry of Triple-bonded Functional Groups
Supplement D: The Chemistry of Halides and Pseudo-halides
Supplement E: The Chemistry of $-NH_2$*,* $-OH$*, and* $-SH$ *Groups and their Derivatives*

Advice or criticism regarding the plan and execution of this series will be welcomed by the Editor.

The publication of this series would never have started, let alone continued, without the support of many persons. First and foremost among these is Dr Arnold Weissberger, whose reassurance and trust encouraged me to tackle this task, and who continues to help and advise me. The efficient and patient cooperation of several staff-members of the Publisher also rendered me invaluable aid (but unfortunately their code of ethics does not allow me to thank them by name). Many of my friends and colleagues in Israel and overseas helped me in the solution of various major and minor matters, and my thanks are due to all of them, especially to Professor Z. Rappoport. Carrying out such a long-range project would be quite impossible without the non-professional but none the less essential participation and partnership of my wife.

The Hebrew University
Jerusalem, ISRAEL.

SAUL PATAI

Contents

CHAPTER 1

General and theoretical aspects of the diazonium and diazo groups

J. B. MOFFAT

Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada

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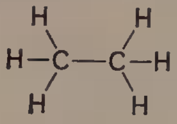
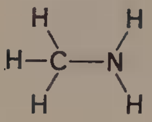
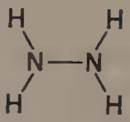
I. INTRODUCTION

In discussing the chemistry of molecules containing the NN bond and, in particular, in this first chapter, the general and theoretical aspects of such molecules, it seems reasonable to establish the scenario by comparing and contrasting such groups with other groups of importance in organic chemistry.

One would be hard pressed to find more logical candidates for comparison with molecules containing the N_2 group than those of C_2 and CN. Indeed such a ubiquitous trio of organic chemistry involving two homonuclear and one heteronuclear bond, the latter formed from the two different elements of the former, almost invite sociological comparison with parents and offspring. The C_2, CN and N_2 groups contain 12, 13 and 14 electrons, respectively, and the hierarchy of bonding can be conceived as beginning with the so-called single bond, so that we have as the simplest example for each group:





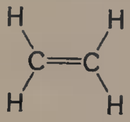


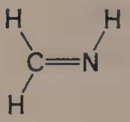
The first line of Table 1 compares average bond lengths for the central bonds of each of these molecules, and, not surprisingly, in view of the extra proton in the nitrogen nucleus as compared to carbon, the bond lengths decrease as one passes from the C—C to the N—N bond.

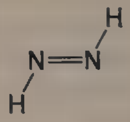
TABLE 1. Average bond lengths (Å) in molecules containing CC, CN and NN groups

Bond label	CC	CN	NN
Single	1·537	1·472	1·451
Double	1·335	1·32	1·25
Triple	1·202	1·157	1·098 (N_2)
	1·312 (C_2)	1·172 (CN)	

Removal of a hydrogen atom from each of the central atoms in the molecules above produces the trio of molecules with central double bonds,







Again the same trend in bond lengths (line 2, Table 1) is observed as in the case of the corresponding single-bonded molecules. However, in addition, in all cases shown, formation of the double bond results in a decrease in the bond length.

Continuation of the dehydrogenation process yields

$$H{-}C{\equiv}C{-}H \qquad H{-}C{\equiv}N \qquad N{\equiv}N$$

with the same gradation in bond lengths being maintained from C≡C to N≡N, as well as a further decrease in bond length in each case on formation of the triple bond. Extraction of the remaining hydrogen atoms from acetylene and hydrogen cyanide produces an increase in bond length, signalling a discontinuity in electronic structures. However, for each type of bond (single bonded, etc.) it is clear from the table that the NN bond length is, in each case, the lowest of the three shown.

The foregoing comparison may be extended to encompass bond energies, and average values for these are given in Table 2. Examination of the table shows that the two lowest bond energies listed are 37 and 61 kcal/mol, those for the N—N and N=N bonds respectively, while the highest value is 225 kcal/mol for the dissociation of the nitrogen molecule. In fact, with the exception of CO which has a dissociation energy of 256 kcal/mol, N_2 has the highest dissociation energy of any diatomic molecule.

TABLE 2. Average bond energies (kcal/mol) of CC, CN and NN bonds

Bond label	CC	CN	NN
Single	83	73	37
Double	146	112	61
Triple	200	213	225 (N_2)
	144 (C_2)	188 (CN)	

Consistent with these experimental observations are the conclusions derivable from simple molecular orbital theory for the electron configurations of C_2, CN and N_2, and their singly-ionized forms (Table 3). The difference between the number of bonding orbitals and the number of antibonding orbitals, sometimes called the bond order, can be seen to increase from C_2^+ to N_2, thereby suggesting that the strength of the bond in N_2 should not be unexpected.

TABLE 3. Electron configurations[a] of C_2, CN and N_2 molecules and their singly-ionized forms

Number of electrons	Molecule	Lowest electron configuration	State	P_b	P_a	Difference	D_0^0 (volts)
11	C_2^+	$KK(\sigma_g 2S)^2(\sigma_u 2s)^2(\pi_u 2P)^3$		$2\frac{1}{2}$	1	$1\frac{1}{2}$	
12	C_2, CN^+	$KK(\sigma_g 2S)^2(\sigma_u 2S)^2(\pi_u 2P)^4$	$^1\Sigma_g^+$	3	1	2	(3·6)
13	C_2^-, CN, N_2^+	$KK(\sigma_g 2S)^2(\sigma_u 2S)^2(\pi_u 2P)^4\sigma_g 2P$	$^2\Sigma_g^+$	$3\frac{1}{2}$	1	$2\frac{1}{2}$	6·34
14	CN^-, N_2	$KK(\sigma_g 2S)^2(\sigma_u 2S)^2(\pi_u 2P)^4$-$(\sigma_g 2P)^2$	$^1\Sigma_g^+$	4	1	3	7·37
15	N_2^-	$KK(\sigma_g 2S)^2(\sigma_u 2S)^2(\pi_u 2P)^4$-$(\sigma_g 2P)^2\ \pi_g 2P$	$^2\pi_g$	4	$1\frac{1}{2}$	$2\frac{1}{2}$	

P_b = Number of bonding electron pairs.
P_a = Number of antibonding electron pairs.
D_0^0 = Dissociation energy.

[a] G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed., D. Van Nostrand Co. Inc. Princeton, N.J. (1950).

Energy and geometry parameters relating to the ionization of the diatomic species C_2, N_2 and CN are given in Table 4. Again, although limited data are available, a consistent pattern is followed, N_2 is observed to have a high ionization energy and would be predicted to have a relatively high electron affinity.

TABLE 4. Energy and geometry parameters[a] for ionized forms of C_2, N_2 and CN

Molecule	Ionization energy (kcal/mol)	Electron affinity (kcal/mol)	Bond lengths (Å)		
			XY^-	XY	XY^+
C_2		71·5		1·24	
CN	348·9	88·1	1·07	1·18	1·17
N_2	359·3			1·10	1·12

[a] K. Watanabe, T. Nakayama and J. Mottl, *J. Quant. Spect. and Energy Transfer*, **2**, 369 (1962).

The theoretical aspects, and related physicochemical properties of molecules containing the N=N bond will be developed, in the following sections, by considering individual molecules and their substituted derivatives, each representative of a particular type of azo or diazo compound. The simplest relatives of N_2 will be considered first, CNN being taken as a hypothetical precursor of diazomethane, and N_2H^+ and N_2H being considered as prototypes of the diimide bond. The discussion on CNN is followed by sections on diazomethane itself and the two of its structural isomeric forms, nitrilimine and diazirine, which contain the N=N bond. Relevant information on substituted diazirines is also included.

Section III discusses the results of theoretical studies of diimide and its mono- and di-substituted forms as well as being concerned with related experimental work on these molecules. Although not strictly within the bounds of the title of this volume, diimides have been included here both for completeness and purposes of comparison in discussions of the NN bond.

In all cases, where available, spectral data and the results of theoretical calculations are given, together with some thermochemical and kinetic data, particularly where the latter may assist in understanding the structure and properties of the molecule. In general each section is developed historically, in order to permit the appropriate assessment of the data to be made by the reader wishing to use them, and also to indicate to the researcher topics which require further study.

II. DIAZO COMPOUNDS

A. The Prototype, CNN

Molecules containing two nitrogen atoms joined together and with one of these nitrogen atoms attached to a single carbon atom are referred to as diazoalkanes (R_2CNN). A number of extensive reviews of this subject[1, 2] have been published in the previous decade, in addition to several since 1970, some as recent as 1972[3–6]. There has been much interest in diazoalkanes for many years, particularly because of their usefulness as intermediates, and more recently as a consequence of work on the reactivity and structure of carbenes (R_2C:), which are intermediates in the photolysis and thermolysis of diazoalkanes.

The parent species of the diazoalkanes can be viewed, at least from the theoretical point of view, as diazomethylene, CNN. Robinson and McCarty, Jr[7], following the photolysis of diazomethane in a krypton matrix, observed a feature in the spectra at 4240 Å and tentatively suggested that this might be assigned to CNN or to HCNN. At about the same time, Goldfarb and Pimentel[8] observed features at 4182 and 3968 Å, following the photolysis of diazomethane isolated in a nitrogen matrix, which they too considered must be due to a reactive species, presumably CNN, since these features vanished when the sample was warmed. In 1966 the results of the first complete spectral study on CNN, prepared by the photolysis of matrix-isolated cyanogen azide with 2100–2800 Å radiation, were reported by Milligan and Jacox[9]. They first suggested the following mechanism for the production of diazomethylene from cyanogen azide:

$$N_3CN + h\nu\ (\lambda < 2800\ \text{Å}) \longrightarrow N_3^{\bullet} + {\bullet}CN \tag{1}$$

$$N_3^{\bullet} + {\bullet}CN \longrightarrow N_3NC \tag{2}$$

$$N_3NC \longrightarrow 2\,N_2 + C \tag{3a}$$

$$N_3NC \longrightarrow N_2 + CNN \tag{3b}$$

However, observations on the systems containing ^{15}N led them to modify their conclusions to suggest that the principal mode of formation of the CNN is by the attack of a carbon atom on a nitrogen molecule.

Diazomethylene was deduced to possess a triplet electronic ground state with a linear structure. The carbon–nitrogen bond was found to have approximately triple-bond character and the nitrogen–nitrogen bond approximately double-bond character, with the length of the former being estimated as 1·15 Å, and that of the latter as 1·25 Å.

More recently, CNN was prepared by trapping carbon atoms in a pure N_2 matrix[10] and medium-intensity bands of $^{12}CN_2$ (in a N_2 matrix) were observed at 2858, 1253 and 394 cm^{-1}, which shifted to 2836, 1232 and 392 cm^{-1} when ^{13}C was vaporized. Stretching force constants of 19·5 and 14·7 mdyn/Å were calculated for the CN and NN bonds, respectively.

What appears to be the only theoretical work done on CNN was reported by Thomson[11] in 1973. Using the linear molecules program ALCHEMY[12] he performed restricted Hartree–Fock calculations for the CNN configuration, $^3\Sigma^-$, $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(6\sigma)^2(1\pi)^4(7\sigma)^2(2\pi)^2$. Calculated energies, geometries and atomic populations are reported in Table 5.

TABLE 5. Calculated energies[a] and structure of CNN[11]

				Total atomic populations		
Basis set	Energy	R(NN)	R(CN)	C	N	N
Double zeta	−146·59094	2·565	2·220	5·72	7·43	6·85
Double zeta + polarization	−146·68096	2·530	2·190	6·12	6·92	6·96

[a] Energies are in hartrees and bond lengths in bohrs: 1 hartree = 627·7 kcal/mol; 1 bohr = 0·529 Å.

In addition a dissociation energy (to atoms) of 0·198 hartree and a dipole moment of 1·022 D were calculated for CNN, with the convention that the right-hand nitrogen atom is positive.

The calculated bond lengths are in reasonable agreement with the estimates of Milligan and Jacox[9]. The atomic populations are seen to be particularly sensitive to the size and nature of the basis set. Thomson also calculated the dissociation energies for NCN, NCC and CNC to be 0·212, 0·270 and 0·273 hartrees, respectively. As expected the calculations suggest that CNN is less stable than any of these latter three species.

B. *Diazomethane* (H_2CNN)

1. Introduction

Diazomethane is the simplest diazoalkane and as such has served as the prototype for many studies, both experimental and theoretical. From a classical point of view it may be considered as a resonance hybrid of a variety of planar forms:

$$\overset{-}{C}H_2{-}\overset{+}{N}{\equiv}N \qquad \text{(a)}$$

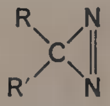
$$\overset{-}{C}H_2{-}N{=}N^+ \qquad \text{(b)}$$

$$\overset{+}{C}H_2{-}N{=}N^- \qquad \text{(c)}$$

$$CH_2{=}\overset{+}{N}{=}N^- \qquad \text{(d)}$$

Hence it is not unreasonable to expect diazomethane to be capable of assuming the properties of a carbene source, or an acid or a base, or an electrophile or a nucleophile, or a 1,3-dipole[5].

For many years there was considerable controversy concerning the structure of diazomethane until electron diffraction[13] and microwave spectroscopic experiments[14] showed the arrangement of carbon and nitrogen atoms to be linear and the overall structure to be planar. In 1960 the chemical evidence for the linear structure of diazomethane was provided by Paulsen[15], and Schmitz and Ohme[16] in the form of independent syntheses of the first diazirines,



which are isoelectronic with their corresponding diazoalkanes.

2. Theoretical studies

The first calculations[17] of the electronic structure employed the simple Hückel molecular orbital method to calculate a resonance energy of 0·6β and, at least within the assumptions of the method, values of the bond lengths and dipole moment in reasonable agreement with experiment. Hoffmann[18] some years later applied his extended Hückel technique to calculations on the excited states of diazomethane. Yoshida and Kobazashi have calculated the electronic spectra of diazomethane by the ASMO–LCAO–SCF–CI[19] and INDO–SCF–MO–CI[20] methods. Brintzinger[21] has suggested a qualitative description of the chemical bonds in diazomethane. What appears to be the first *ab initio* study of diazomethane was that performed by André and coworkers[22]. Apparently, however, an error in geometry unfortunately invalidates the results. Bastide and Henri-Rousseau[23] have done CNDO calculations to examine the transition between the linear and a bent form of diazomethane, the CNN angle in the latter was taken as 75°. A rotational barrier of 22 kcal was calculated and an interpretation[24] of orientation effects in 1,3-dipolar addition reactions was proposed. Hart[25] suggested that seven isomers of diazomethane are, in principle, possible, and carried out *ab initio* calculations using the LW [533; 3] Gaussian lobe basis set, on five of these structural isomers, diazomethane itself being included. Caballol and coworkers[26] employed the INDO technique to obtain wavefunctions for the $^1A_1$, $^1A''$ and $^3A''$ states of diazomethane. The ground-state geometry was taken from Herzberg[27] and the excited state geometries were obtained from the ground-state geometry by bending the CNN angle in the molecular and bisector planes. The planar structures were found to be more stable and the CNN angle was found to be 158° and 152° for the first excited singlet and triplet state, respectively. Two minima of depth −14·9 and −13·9 kcal/mol were found in the electrostatic potentials for ground-state diazomethane, the former at the carbon end and the latter at the nitrogen end of the molecule. These authors argue that this agrees with the experimental results which suggest a carbon attack[5]. In the case of the first excited $^1A''$ singlet state, protonation is predicted to occur within the molecular plane with a single minimum (−23·6 kcal/mol) appearing in the neighbourhood of the terminal nitrogen. Electrostatic potential results for diazomethane in the triplet state are quite similar to those for the singlet state, the well depth being −24·4 kcal/mol in the triplet case.

Leroy and Sana[28] have employed the Gaussian −70 programme of Hehre and coworkers[29] and a variety of basis sets to calculate the electronic structure and some thermodynamic properties of this compound. With the contracted Gaussian basis of Clementi, a total electronic energy of −147·18569 hartree, and bond energies of 104 and 181 kcal/mol for the CN and NN bonds, respectively, were obtained. In these calculations the geometry of diazomethane determined experimentally by Cox and coworkers[30] was employed. With a 4-31G basis set, Leroy and Sana[28] calculated the dipole moment to be 1·52 D to be compared with an experimental value of 1·40 D [30], and a total electronic energy of −147·60552 hartree.

The energy of formation at 0 K was obtained by the use of the equation

$$\Delta E_{\mathrm{f}}\,(0\ \mathrm{K}) = E_0^0 = \Delta E_{\mathrm{f}}^{\mathrm{th}} + \tfrac{1}{2}\sum_i h\nu_i$$

where $\Delta E_{\mathrm{f}}^{\mathrm{th}}$, the theoretical energy of formation was taken to be that calculated with the 4–31G basis set, and the ν_i are the frequencies of the nine normal modes for which the values from Moore and Pimentel[31] were employed. The energy of formation at 25 °C

$$\Delta E_{\mathrm{f}}\,(298{\cdot}16\ \mathrm{K}) = E^0 = E_0^0 + (E^0 - E_0^0)$$

was then obtained by using the previously calculated value for E_0^0, together with the value of $E^0 - E_0^0$ found by Moore and Pimentel[31]. The heat of atomization (ΔH_{a}) at 298·16 K was calculated from the experimental values of the heats of atomization of the elements[32].

In addition Leroy and Sana[28] calculated values for the thermodynamic functions mentioned above by another method, namely that proposed by Hehre and coworkers[33] in which use is made of reactions and their calculated energies in which the molecule of interest, in this case diazomethane, is involved either as a reactant or as a product. The two such reactions selected by Leroy and Sana are

(a) $$2\,\mathrm{CH_2N_2} + \mathrm{NH_3} = (\mathrm{CH_3})_2\mathrm{NH} + 2\,\mathrm{N_2}$$

$$\Delta E^{\mathrm{th}} = -145{,}260\ \mathrm{kcal}$$

(b) $$\mathrm{CH_2N_2} + \mathrm{NH_3} = \mathrm{CH_3NH_2} + \mathrm{N_2}$$

$$\Delta E^{\mathrm{th}} = -72{,}064\ \mathrm{kcal}$$

So that correlation effects could be considered to cancel out, both the C—H and N—H bonds had to be assumed equivalent, as well as the C—N bonds in all molecules in which they were present. The energy of formation of diazomethane can then be obtained from

$$\Delta E^{\mathrm{th}} = \sum |k_i\, N_i| \Delta E_{\mathrm{f}i}$$

or, more specifically for each of the reactions (a) and (b)

$$\text{(a)} \qquad \Delta E^{\text{th}} = 2\Delta E_f^{\text{exp}}(\text{N}_2)+\Delta E_f^{\text{exp}}[(\text{CH}_3)_2\text{NH}] - \Delta E_f^{\text{exp}}(\text{NH}_3)-2\Delta E_f^{\text{th}}(\text{CH}_2\text{N}_2)$$

$$\text{(b)} \qquad \Delta E^{\text{th}} = \Delta E_f^{\text{exp}}(\text{N}_2)+\Delta E_f^{\text{exp}}[(\text{CH}_3)\text{NH}_2] - \Delta E_f^{\text{exp}}(\text{NH}_3)-\Delta E_f^{\text{th}}(\text{CH}_2\text{N}_2)$$

where ΔE_f^{exp} is an energy of formation referenced to 0 K and corrected for the zero point energy. Table 6 reports the values obtained by Leroy and Sana for the thermodynamic functions of diazomethane. A value of 78 kcal/mol was also found for the CH bond energy. The calculated value for the heat of formation of diazomethane at 298·16 K (63·8 kcal/mol) may be compared with that obtained experimentally (51–60 kcal/mol)[34] (see also Table 8).

TABLE 6. Calculated thermodynamic properties of diazomethane (kcal/mol)[28]. Reproduced by permission of Springer-Verlag

	ΔE_f^{th}	ΔE_f (0 K)	ΔE_f (298·16 K)	ΔH_a (298·16 K)
Method 1	55·26	58·85	61·74	440·56
Method 2				
Equation (a)	57·45	61·03	63·91	438·39
Equation (b)	60·26	62·83	65·72	436·58
Average value	57·66	60·90	63·79	438·51

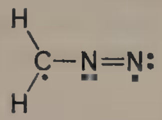
Leroy and Sana have also performed geometry optimizations within the STO-3G basis. Their results together with those for the force constants are compared with the experimental values of Moore and Pimentel in Table 7.

TABLE 7. Nuclear configuration and force constants of diazomethane (dyne/cm and erg/rad²). Reproduced by permission of Springer-Verlag

	CN	NN	CH	HCH	Reference
Calculated length (Å) or angle (deg)	1·282	1·189	1·078	121·7	28
Experimental	(1·300)	(1·139)	(1·075)	(126·0)	31
Force constant					
Calculated	$12{\cdot}53\times10^5$	$17{\cdot}48\times10^5$	—	$3{\cdot}60\times10^{-11}$	28
Experimental	$8{\cdot}3\times10^5$	$16{\cdot}9\times10^5$	—	$0{\cdot}63\times10^{-11}$	31

Leroy and Sana, in discussing the significance of their *ab initio* calculations in respect of the structure and bonding of diazomethane, note that the C—N and N—N bonds in diazomethane have the characteristics expected of a double and a triple bond respectively, and hence the molecule behaves as one possessing six π electrons. Four of these six electrons form a π bond extending over three centres, while the remaining two are essentially localized on the two nitrogen atoms. These authors conclude that the most important structural forms are those labelled (a) and (d) in Section II.B.1.

Walch and Goddard[35] have very recently reported on the results of *ab initio* generalized valence bond (GVB) and configuration interaction (CI) calculations (using a double-zeta basis) on the ground and low-lying excited states of diazomethane. All calculations employed the experimental geometry for the ground state as found by Cox, Thomas and Sheridan[30]: $R_{CH} = 1{\cdot}077$ Å, $R_{CN} = 1{\cdot}300$ Å, $R_{NN} = 1{\cdot}139$ Å and $\angle HCH = 126{\cdot}1°$. In contrast to the conclusion of Leroy and Sana, Walch and Goddard conclude that the calculated wavefunction is basically that of a singlet biradical with strong bonding between the radical π orbitals on the C and terminal N resulting from the interaction with the π pair on the central N:



Further, Walch and Goddard suggest that the GVB model of diazomethane would support a mechanism based on a biradical attack in the 1,3-addition of diazomethane to olefins, analogous to that in ozone rather than the usual mechanism dependent on the dipolar nature of diazomethane.

Results of theoretical studies, in which both diazomethane and diazirine are considered, are discussed in the section on diazirine.

3. Thermochemical properties

Foster and Beauchamp[36] have concluded that the proton affinity (PA) of diazomethane can be ordered with that of ammonia, azomethane and methylamine in the following way:

$$PA(NH_3) < PA(CH_2N_2) < PA(CH_3N{=}NCH_3) < PA(CH_3NH_2)$$

Consequently they place the heat of formation of diazomethane as greater than 64 kcal/mol but less than 73 kcal/mol.

Table 8 summarizes the various values suggested for the heat of formation of diazomethane.

TABLE 8. Heat of formation of diazomethane

Method	ΔH_f (25 °C) (kcal/mol)	Reference
Kinetics	67+	*a*
Thermochemistry	64–77	*b*
Group additivity	71	*c*
Appearance potential	49	*d*
Photodissociation	51+	*e*
Proton affinity	64–73	*f*
Theoretical	64	*g*

[a] D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962).

[b] J. C. Hassler and D. W. Setser, *J. Amer. Chem. Soc.*, **87**, 3793 (1965).

[c] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

[d] G. S. Paulett and R. Ettinger, *J. Chem Phys.*, **39**, 825, 3534 (1963); **41**, 2557 (1964).

[e] A. H. Laufer and H. Okabe, *J. Amer. Chem. Soc.*, **93**, 4137 (1971).

[f] Reference 36.

[g] Reference 28.

C. Isomers of Diazomethane

As Hart[25] has pointed out, diazomethane is unique among small molecules in having six known or suspected structural isomers.

H_2CNN

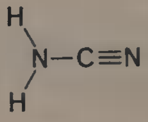
Diazomethane

HCNNH

Nitrilimine
(isodiazomethane)

$CNNH_2$

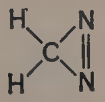
Isocyanamide



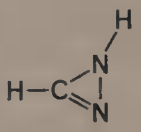
Cyanamide

H—N=C=N—H

Carbodiimide



Diazirine

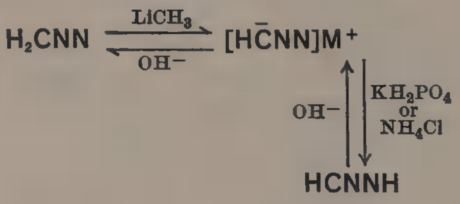


Isodiazirine

Of these isomers, diazirine and cyanamide have been prepared, and are stable molecules at room temperature. Derivatives of isodiazomethane, carbodiimide and isocyanamide are known and there is some evidence that isocyanamide has been prepared[37, 38]. Carbodiimide and isodiazirine have apparently not yet been prepared. Isodiazomethane, although not stable at room temperature, has been prepared[39–41]. Only the diazo isomers, namely isodiazomethane, diazirine and isocyanamide, will be discussed here.

1. Nitrilimine

Investigations of the reaction of triphenylmethyl sodium on diazomethane by Müller and coworkers in 1934[39] led to the discovery of this isomer of diazomethane. Anselme[42] has summarized the properties of isodiazomethane as they were known in 1966. The preparation involves the acidification at −80 °C of an ether suspension of diazomethyl anion ($[CH{-}N{=}N]^-M^+$), with an aqueous solution of potassium dihydrogen phosphate or ammonium chloride, as in



$$\begin{tikzcd} H_2CNN \arrow[r, shift left, "LiCH_3"] & {[H\bar{C}NN]M^+} \arrow[l, shift left, "OH^-"] \arrow[d, shift left, "KH_2PO_4 \text{ or } NH_4Cl"] \\ & HCNNH \arrow[u, shift left, "OH^-"] \end{tikzcd}$$

where M^+ may be Li^+, Na^+ $(C_6H_5)_3\overset{+}{P}CH_3$. Isodiazomethane, a pale yellow liquid, is then obtained by evaporation of the solvent at −50 °C *in vacuo*. Decomposition begins to occur at 15 °C and the compound explodes at 35–40 °C[40]. A maximum occurs at 247 nm in the ultraviolet spectrum, compared to absorption at 412 nm and 321 nm with diazomethane and diazirine, respectively. No infrared spectra have yet been reported, but it appears from molecular weight determinations in benzene that isodiazomethane is monomeric[41]. The formation of isodiazomethane by acidic hydrolysis of $[CH{-}N{=}N]^-M^+$ may be explained through the assumption of a kinetically controlled reaction, by which protonation occurs rapidly at the more nucleophilic nitrogen (presumably the terminal nitrogen) to give the thermodynamically less stable isomer.

Apparently the only theoretical work which has been done on isodiazomethane is that by Hart[25] mentioned previously. Results of calculations on isocyanamide were also reported at that time. The total electronic energies were obtained as −147·2425, −147·2868 and −147·3386 hartree for isodiazomethane, diazomethane and isocyanamide, respectively. This would imply that isocyanamide is more stable than isodiazomethane or diazomethane by approximately 63 and 34 kcal/mol, respectively. Indeed, Müller, Beutler and Zeeh[43] now suggest that the compound previously labelled isodiazomethane may in fact be isocyanamide. If this be so it is of interest to seek out any evidence for the existence of nitrilimine. Mills and Thompson[44], in a report in 1954 on the vibration–rotation bands of diazomethane, note that a peculiarity in the results for the band near 2100 cm^{-1} leads to the suggestion that this may be due to nitrilimine. On the other hand, Moore and Pimentel[45], 10 years later, find no evidence for any tautomeric form of diazomethane. More recently however, Ogilvie[46], again on the basis of an unexplained infrared band observed at 2169 cm^{-1} in the photolysis of diazomethane (gas phase and an argon matrix), has postulated the existence of nitrilimine.

Hart[25] has calculated the total electronic energy of the anions $[HCNN]^-$ and $[CNNH]^-$ as −146·6488 and −146·6389 hartree, respectively, making the former $[HCNN]^-$ more stable than $[CNNH]^-$ by approximately 6 kcal/mol. Calculations, assuming the entropies of these anions are equal, yield a value of $2{\cdot}3 \times 10^4$ for the equilibrium constant K for the equilibration of the two anions. Hart has calculated electrostatic potential maps for the two anions. For $[CNNH]^-$ there are minima of −225·0 and −187·0 kcal/mol in the region of the nitrogen and carbon lone pairs, respectively, while for $[HCNN]^-$ the corresponding values are −191·0 and −229·0 kcal/mol. These results suggest that protonation of $[CNNH^-]$ is more likely to occur at the nitrogen atom to give isocyanamide as the product while protonation of $[HCNN]^-$ should occur at the carbon atom to give diazomethane. These values indicate that the difference in proton affinity for nitrogen over carbon in $[CNNH]^-$ is exactly reversed in $[HCNN]^-$. Protonation at the 'secondary' nucleophilic site in each anion generates a common intermediate, nitrilimine. Hence it is conceivable that a feasible tautomeric pathway could involve a quickly attained equilibrium (involving proton gain and loss) through nitrilimine as an intermediate:

$$\mathrm{CN\bar{N}H} \underset{-\mathrm{H}^+}{\overset{\mathrm{H}^+}{\rightleftharpoons}} \mathrm{HCNNH} \underset{-\mathrm{H}^+}{\overset{\mathrm{H}^+}{\rightleftharpoons}} \mathrm{H\bar{C}NN}$$

A hypothetical reaction mechanism for the production of isocyanamide from diazomethane can then be constructed as shown in Figure 1. The anion tautomerism could occur through nitrilimine or directly as a single step (broken line). Unfortunately there is very little experimental evidence to support any mechanism. Of course a variety of different possibilities for such a mechanism exist. The formation of a dianion (CNN^{2-}) intermediate or the formation of a cyclic transition state involving a water molecule cannot be excluded. With the suggestion from Walch and Goddard[35] of a diradical structure for diazomethane, various mechanisms involving radicals become more reasonable. As Hart[25] points out, although his calculations suggest that isocyanamide is more stable than diazomethane, the experimental evidence suggests that diazomethane is thermodynamically the more stable. Since geometry optimization was performed with isocyanamide but not diazomethane, it is probable that the energy of the latter is not at the minimum value.

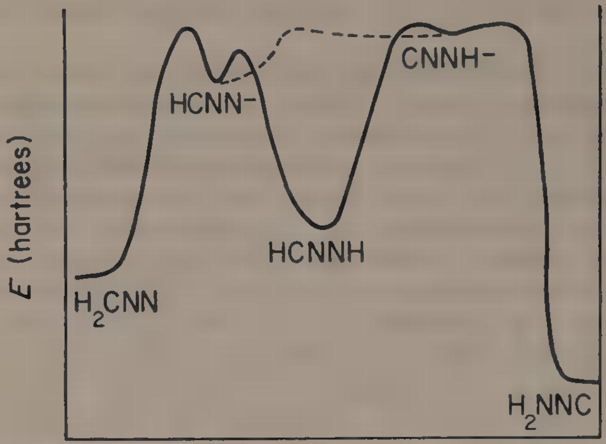


FIGURE 1. Total electronic energy changes in a hypothetical reaction mechanism for the production of isocyanamide from diazomethane. Reproduced by permission of the *Australian Journal of Chemistry.*

2. Diazirine and derivatives

a. *Spectra, structure and thermochemistry.* The cyclic isomers of diazoalkanes (diazirines) were first prepared in 1960 independently by Paulsen[47] and Schmitz and Ohme[48]. Studzinskii and Korobitsyna[49] have briefly considered the subject of diazirines as part of a review on aliphatic diazo compounds. Shortly thereafter the molecular structure, dipole moment and quadrupole coupling constants of diazirine were determined[50] from the rotational spectrum in the frequency region 7·8–41 GHz. Measurements on $H_2{}^{13}CN_2$ and $H_2C\,{}^{14}N\,{}^{15}N$ permitted interatomic distances of 1·228, 1·482 and 1·09 Å to be calculated for NN, CN and CH, respectively. The HCH, NCN and NCH angles were given as 117°, 48°57′ and 118°24′ and the dipole moment as 1·59 debye.

Schmitz and Ohme[51] and Graham[52] report the syntheses, by two different methods, of diazirine itself. Diazirine is a colourless gas at room temperature and has a boiling point of −14 °C. Graham[52] reports a number of sharp, regularly spaced peaks between 282 and 324 nm in the gas-phase ultraviolet spectrum and remarks on the striking similarity in shape of the spectrum with that of 2,3-diazabicyclo[2.2.1]-2-heptene[53]. The proton n.m.r. spectrum in carbon tetrachloride solution at 0 °C is a singlet at +241 Hz (relative to external benzene), a relatively high-field absorption for methylene protons, which is consistent with a strained three-membered ring structure. In the infrared spectrum of diazirine, Ettinger[54] found strong absorption in the 1600 cm⁻¹ region, which he assigned to double-bond NN stretching. In comparison, Le Fèvre and coworkers[55, 56] concluded that the —N=N— linkage, in a simple environment found in a series of azo compounds, has a characteristic frequency about 1580 cm⁻¹. Values of the thermodynamic functions for diazirine (ideal gas, 1 atm) as calculated by Ettinger[54] are given in Table 9. In a brief preliminary note, Merritt[57] has reported on the ultraviolet spectrum of diazirine under high dispersion, and finds the 0–0 band at 30,964 cm^{-1}. A number of frequencies in the ground and upper state are also found and tentatively identified.

The mass spectra and appearance potentials of diazirine and diazomethane have been determined[58] and the heat of formation of diazirine estimated to be 79·3 kcal/mol as compared with 49·3 kcal/mol for diazomethane. By the use of bond energies the strain energy associated with the diazirine ring structure was estimated to be about 22 kcal/mol. The heats of formation of the ions $CH_2N_2^+$ and CHN_2^+ were also estimated to be 314 and 355 kcal/mol, respectively.

TABLE 9. Thermodynamic functions (cal mol^{-1} deg^{-1}) for diazirine[54] (ideal gas, 1 atm)

T (K)	$-(G^0-H^0_0)/T$	C^0_p	S^0	$(H^0-H^0_0)/T$
298·15	48·44	10·19	56·87	8·43
400	51·01	12·39	60·17	9·16
600	55·05	15·94	65·91	10·87
800	58·39	18·35	70·85	12·45
1000	61·32	20·04	75·14	13·81

That the cyclic isomer is more stable than the linear isomer is readily seen from the difference in the estimated heats of formation, approximately 30 kcal/mol. The difference is also evident in the reaction chemistry, the diazoalkanes being some of the most reactive substances known in organic chemistry while diazirines are much more stable. Graham[52] notes that diazirine is decomposed relatively slowly by sulphuric acid with liberation of a molecule of nitrogen. It is stable to *t*-butoxide ion in *t*-butyl alcohol and, although storable in glass, is decomposed by ultraviolet radiation. Apparently it can be handled safely at room temperature as a liquid or a gas although, as a consequence of the lack of agreement on this point, it is advisable to take suitable precautions.

Bell[59] has suggested that a different set of assumptions concerning the processes occurring in the mass spectrometer ion source will yield values of ΔH_f differing from those of Paulett and Ettinger[58] but more in accord with the results of other experiments. The production of CH_2^+ from CH_2N_2 (either diazirine or diazomethane) can be expressed by

$$A(CH_2^+) = \Delta H_f(CH_2^+) - \Delta H_f(CH_2N_2)$$

where $A(CH_2^+)$ is the appearance potential of CH_2^+ from the particular isomer under consideration. Hence $\Delta H_f(CH_2N_2)$ can be obtained from the experimental appearance potential if a value for $\Delta H_f(CH_2^+)$ is available. Bell argues that the value of 333 kcal/mol[60] used by Paulett and Ettinger for $\Delta H_f(CH_2^+)$ is an older one, and in a previous application[61] has led to the conclusion that the major product in an ion–molecule reaction is formed via an endothermic process, whereas if the value suggested by Bell is used the process becomes exothermic. The ionization potential of $CH_2(^3\Sigma_g^-)$ to give $CH_2^+(^2\pi)$, probably the ion ground state, is 240 kcal/mol[62]. Bell suggests that a very probable value for ΔH_f of $CH_2(^1A_1)$ is 85 kcal/mol, on the basis of kinetic and thermochemical experiments[63–65]. Jordan and Longuet-Higgins[66] have calculated a value of 10 kcal/mol for the separation of the $CH_2(^1A_1)$ state from the ground state $CH_2(^3\Sigma_g^-)$. Hence $\Delta H_f[CH_2(^3\Sigma_g^-)] = 75$ kcal/mol and $\Delta H_f[CH_2^+(^2\pi)] =$ 315 kcal/mol. If a correction of 40 kcal/mol is applied to allow for the possibility that CH_2^+ will not be formed in the $^2\pi$ state in electron-impact experiments[67] but rather in the higher energy $^4\Sigma_u^-$ state[62], then $\Delta H_f[CH_2^+(^4\Sigma_u^-)]$ is 355 kcal/mol. Table 10 summarizes Bell's values, with two heats of formation for each of CH_2N_2, $CH_2N_2^+$ and CHN_2^+ from each isomer, calculated on the assumption (i) that $A(CH_2^+)$ corresponds to a process yielding $CH_2^+(^4\Sigma_u^-)$, or (ii) that $A(CH_2^+)$ corresponds to a process giving $CH_2^+(^2\pi)$.

TABLE 10. Appearance potentials and calculated thermochemical values[59] (kcal/mol)

		Diazomethane	Diazirine
$A(CH_2^+)$ [58]		284	254
$A(CH_2N_2^+)$ [redacted]		208	235
$A(CHN_2^+)$ [58]		341	327
$\Delta H_f(CH_2N_2)$	(i)	71	101
	(ii)	31	61
$\Delta H_f(CH_2N_2^+)$	(i)	279	336
	(ii)	239	296
$\Delta H_f(CHN_2^+)$	(i)	360	276
	(ii)	320	336

Differentiation between values labelled (i) and (ii) is given in the text.

Bell favours the value of 71 kcal/mol for ΔH_f (diazomethane), since kinetic studies[63] suggest that the value should be greater than 67 kcal/mol, and the value of 61 kcal/mol for ΔH_f (diazirine) on the basis that the value of 101 kcal/mol would cause the reaction to yield CH_2 and N_2 to be 16 kcal/mol exothermic, and this would seem to conflict with the experimentally known relative thermal stability of diazirine compared to diazomethane.

Paulett and Ettinger[68], in their reply to Bell, argue that his estimate of 75 kcal/mol for the heat of formation of the ground state of methylene is too low and present evidence to support a value of 95 ± 5 kcal/mol. They present values of 104 and 134 kcal/mol for the heats of formation of diazomethane and diazirine, respectively, in the case where the $A(CH_2^+)$ corresponds to processes in which CH_2^+ is generated in an excited state.

Lau[69] has reported an absorption maximum of 30,989 cm^{-1} for diazirine, and notes a red shift when the spectra of derivatives of diazirine were obtained in solution, which leads him to suggest that the electronic transition is a $\pi^*-\pi$ transition.

Following up on his earlier note, Merritt[70] provides further details of his work on the electronic absorption spectra of *n*-diazirine, N_1^{15}-diazirine, d_1-diazirine and d_2-diazirine. Merritt notes that, as in diimide, the diazirine molecule contains two adjacent nitrogen atoms, each with a lone pair of electrons. Hence a splitting of the degeneracy in the electronic spectrum resulting from the perturbation of the lone-pair electron orbitals would be expected. Merritt reports two systems, separated by approximately 220 cm^{-1}, at 30,970 cm^{-1} and 31,187 cm^{-1}, both of which are present at 14 K.

b. *Theoretical studies.* What appears to be the first quantum chemical study of diazirine was done by Hoffman[71] using his extended Hückel calculations (EXH). The experimentally determined geometry of Pierce and Dobyns[50] was employed to calculate that diazomethane is 70 kcal/mol more stable than diazirine and that the ionization potentials of diazomethane and diazirine are 11·96 and 12·78 eV, respectively, compared with the Paulett and Ettinger[58] experimental values of 9·03 and 10·18 eV, respectively. The relative simplicity of the EXH method must, of course, be kept in mind. Frey and Stevens[72] and Amrich and Bell[73] have shown that the major primary photochemical reaction in the 3200 Å photolysis of diazirines is probably direct elimination of nitrogen to form a carbene, while a minor pathway is rearrangement to form the diazo compound.

The b_2 orbital is $C—N_1$ and $C—N_2$ bonding but $N_1—N_2$ antibonding. The antibonding a_2 orbital is only $N_1—N_2$ antibonding. Hence the $a_2 \leftarrow b_2$ excitation (to which the 3200 Å transition is assigned) weakens the $C—N_1$ and $C—N_2$ bonding more than that of N—N, and the breaking of one or both of these bonds is consistent with the known photochemistry of the molecule.

In a study of the photolysis of diazirine in a nitrogen matrix, Moore and Pimentel[74] showed that the product diazomethane was formed from the reaction of methylene (from diazirine) and matrix N_2. No diazomethane was found in the gas phase photolysis of diazirine. Hoffmann employed calculations on two simple models to obtain information on the path of the isomerization. Starting with diazirine geometry, a simple $C—N_2$ bond lengthening, keeping $C—N_1$ and $N_1—N_2$ constant was studied. In addition, using the diazomethane structure, and holding all bond lengths fixed, combinations of changes in CN_1N_2 and HCN_1 bond angles were considered, but with N_1 and N_2 constrained to remain in the original plane of the ring. A number of features were observed from the results of the calculations. The A_2 excited state of diazomethane prefers to be planar, and correlates with the B_1 excited state of diazirine. The A_1 excited state of diazomethane has a lower relative energy with a bent CNN skeleton. The results of photochemical experiments[73] appear to require the involvement of more than one excited state of diazomethane in the rearrangement. Hoffmann suggests that one possible pathway then involves the conversion of some of the excited B_1 diazirine into the second excited state, A_1, of diazomethane, and return from that excited state to the ground state without internal conversion to the A_2 excited state. The application of Woodward–Hoffmann rules to the concerted decomposition of diazomethane and diazirine to methylene and N_2 leads to the conclusion that the first excited state of diazirine (B_1) and that of diazomethane (A_2) may decompose only to an A_1 or B_1 methylene and an electronically excited nitrogen molecule.

Snyder and Basch[75], as part of a paper in which heats of reaction are calculated from self-consistent field energies of closed-shell molecules, have included diazomethane and diazirine among the many molecules considered. Table 11 summarizes

TABLE 11. Calculated and experimental data for diazirine and diazomethane[75]

	Diazirine		Diazomethane	
E_{DZ} (hartree)	−147·7287		−147·7702	
$-V/2T$ (hartree)	0·99960		1·00006	
E_{vib} (hartree)	0·0321 [54]		0·0306 [27]	
E_T (hartree)	−147·6938		−147·7368	
$E_{corr\text{-}intra}$ (hartree)	−0·7014		−0·7071	
ΔH_f^0 (298 K) (kcal/mol)	[+101] [59]		[+71] [59]	
Reactions	Theory	Experimental	Theory	Experimental
ΔH^0_{298} ($H_2 + CH_2N_2 = CH_4 + N_2$) (kcal)	−119·6	[−118·8]	−92·2	[−88·8]
ΔH^0_{298} ($4\ H_2 + CH_2N_2 = CH_4 + 2\ NH_3$) (kcal)	−162·5 −142·9	[−141·0]	−135·1 −102·3	[−110·0]
ΔH^0_{298} ($2\ CH_4 + CH_2N_2 = C_2H_6 + CH_4 + N_2$) (kcal)	−97·2	[−103·3]	−69·8	[−73·3]

their various results for these two molecules, with experimental geometries employed throughout. To facilitate the calculations it was assumed that the sum of the electronic correlation energy and the difference of the electronic energy in the Hartree–Fock and the double-zeta basis did not change in a reaction having closed-shell reactants and products. The second set of values given for the complete hydrogenation reaction in Table 11 results from the inclusion of estimates for interatomic and intraatomic correlation energy.

Kochanski and Lehn[76] employ the IB MOL programme for *ab initio* SCF–LCAO–MO calculations using a basis set of gaussian functions on diazirine in its experimental configuration[50]. Table 12, column 1, contains some of their calculated

TABLE 12. Calculated and experimental data[a] for diazirine

	Kochanski and Lehn[76]	Lombardi, Robin and coworkers[77, 78]			
T	147·6529				
V_{nn}	63·8985				
V_{ne}	−472·6353				
V_{ee}	113·3859				
E_{tot}	−147·6980 [−148·3469][b]		−147·7287		
Orbital energies				Overlap and type	
$1a_1$	−15·7282	$1a_1$	−15·6895		
$1b_2$	−15·7266	$1b_1$	−15·6879		
$2a_1$	−11·3530	$2a_1$	−11·3193		
$3a_1$	−1·5467	$3a_1$	−1·5253		
$4a_1$	−0·9521	$4a_1$	−0·9385	0·205	C—$H_{1,2}$σ and +0·205 N—Nσ
$2b_2$	−0·8744	$2b_1$	−0·8540	−0·809	N—Nσ
$1b_1$	−0·7112(π)	$1b_2$	−0·6970	+0·210	C—$H_{1,2}$π
$5a_1$	−0·6776	$5a_1$	−0·6687	+0·186	N—Nσ
$6a_1$	−0·5897	$6a_1$	−0·5777	+0·057	C—Nσ and −0·001 N—N l.p.
$2b_1$	−0·5111(π)	$2b_2$	−0·4920	+0·352	N—Nπ
$3b_2$	−0·4347	$3b_1$	−0·4180	−0·228	N—N l.p.
		$1a_2$	+0·0937		
Total atomic populations					
N_1, N_2	7·163		7·054		
C	6·188		6·304		
H_1, H_2	0·743		0·795		
Binding energy	0·223 [0·6719][b]				
Dipole moment	2·47 D [1·59 D] [50]		2·34 D		
Ionization potential	11·83 eV [10·18 eV] [58]				

[a] All energies in hartrees.
[b] Estimated from heat of formation.[58]

results. The MO's $2b_2$, $6a_1$ and $3b_2$ which are strongly localized on the nitrogen atoms contribute at the same time weakly to the C—N bonds and strongly to the nitrogen lone pairs. Both $2b_2$ and $6a_1$ contribute strongly to the description of the lone pairs.

The C and N atoms have the following charge distributions:

C: $1s^{1\cdot98}$ $2s^{1\cdot22}$ $2p\sigma^{1\cdot73}$ $2p\pi^{1\cdot25}$

N: $1s^{1\cdot98}$ $2s^{1\cdot89}$ $2p\sigma^{2\cdot32}$ $2p\pi^{0\cdot97}$

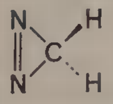
From this it may be concluded that the N atoms are σ acceptors and very weak π donors, while C is a π acceptor. Overlap populations show that the C—N bonds in diazirine are much weaker than the C—C single bonds in cyclopropene. The N=N bond is weakly σ antibonding and π bonding (MO's $1b_1$ and $2b_1$) so that the N=N double bond is weak. The low-lying $2b_2$ MO results from the antisymmetric mixing of two nitrogen lone pairs mostly N(2s) in character. $6a_1$ is weakly N—N bonding which contradicts the result from overlap population which implied that $6a_1$ was of weakly N—N antibonding character. $3b_2$ contributes to the nitrogen lone pairs as well as to the C—N bonds. There is no pure lone pair MO. All MO's contributing to the lone pairs also contribute to some extent to the ring bonds.

An experimental study of the lower $n \rightarrow \pi^*$ excitation in difluorodiazirine, F_2CN_2, has been performed by Lombardi and coworkers[77] and a supporting calculation on both diazirine and F_2CN_2 has been done[78]. Calculations were performed using a gaussian-type orbital (GTO) basis set, using a total of 125 primitive GTO's which were contracted to 50 gaussian-type functions. This basis is equivalent to a so-called Double Zeta basis, in which each AO is represented by two Slater-type orbitals. Hencher and Bauer's structural data[87] were employed.

The calculated results[78] for F_2CN_2 are given in Table 13. The two MO's $9a_1$ and $4b_1$ represent the two 'non-bonding' orbitals conventionally assigned to the azo group, but mutual interaction separates them by 3·8 eV. The $n \rightarrow \pi^*$ transition originates at $4b_1$, and terminates at the π^* MO, $2a_2$. The computed singlet–singlet and singlet–triplet excitations are 3·99 and 3·07 eV, respectively, compared to the observation of the excited singlet at 3·7 eV. Analysis of the MO's involved in the transition shows that n is nearly equally distributed among the C—N—N atoms of the ring, but that π^* is completely localized on the N atoms. Consequently the n–π^* excitation involves the transfer of about $\frac{1}{3}$ electron from the CF_2 group to the N=N group of difluorodiazirine.

The results of the *ab initio* calculation by Robin and coworkers[78] on diazirine are included in Table 12 for convenience in comparison with the earlier work of Kochanski and Lehn[76]. In addition, Tables 12 and 13 also include some of the results obtained in comparison with photoelectron spectral data of both diazirine and F_2CN_2. The agreement between their observed and calculated (using 92% of the Koopmans' Theorem value) ionization potentials for both these molecules was found to be quite acceptable.

Bloor and Maksic[80] calculated diamagnetic susceptibilities and quadrupole moments of diazirine using the CNDO/2D and SCC (self-consistent charge) semi-empirical methods. The molecule was oriented as shown:



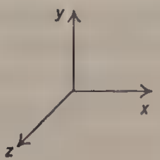


TABLE 13. Calculated and experimental data for difluorodiazirine[78]

		Overlap and type[79]	
Total energy (a.u.)	−345·3999		
$-V/2T$	0·99961		
Orbital energies			
$1a_1$	−27·3726		
$1b_2$	−27·3726		
$2a_1$	−15·7494		
$1b_1$	−15·7483		
$3a_1$	−11·5465		
$4a_1$	−1·7715		
$2b_2$	−1·6915		
$5a_1$	−1·5702		
$2b_1$	−0·9790	−0·581	N—Nσ
$6a_1$	−0·9763	+0·158	N—Nσ
$3b_2$	−0·8569	+0·100	C—Fσ
$7a_1$	−0·8447	+0·195	N—Nσ
$3b_1$	−0·7741	−0·207	N—Nσ
$1a_2$	−0·7306	−0·042	F—F
$8a_1$	−0·7107	+0·081	N—Nσ
$4b_2$	−0·7017	−0·145	F—F
$9a_1$	−0·6251	+0·039	N—N l.p. and −0·071 C—$F_{1,2}\sigma$
$5b_2$	−0·5800 (π)	+0·354	N—Nπ
$4b_1$	−0·4851	−0·255	N—N l.p.
$2a_2$	+0·0221 (π*)		
5b	+0·2568		
$10a_1$	+0·2705		
$6b_1$	+0·2970		
Dipole moment	0·082 D		
Quadrupole coupling constants[a]			
$x_{\alpha\alpha}$ (N)	−0·614		
$x_{\beta\beta}$ (N)	−2·452		
$x_{\gamma\gamma}$ (N)	+3·066		
n	0·599		
Net charges			
C	+0·544		
N	−0·018		
F	−0·255		
Second moments of the electronic charge			
$\langle x^2 \rangle$	41·4323[b]		
$\langle y^2 \rangle$	97·2931		
$\langle z^2 \rangle$	136·2211		

[a] Values in Mc/sec computed in the principal axes system using a nuclear quadrupole moment of $Q(^{14}N) = 1{\cdot}60 \times 10^{-26}$ cm^2.

[b] z is the two-fold rotation axis, x is perpendicular to z in the CN_2 plane and y is perpendicular to the CN_2 plane.

Tables 14 and 15 list the electronic second moments and the molecular quadrupole moments calculated by the two methods and compare these with the *ab initio* results[81]. Unfortunately there do not appear to be any experimental data for diazirine with which to compare the calculated values. However, with other molecules where such experimental data are available, agreement between such data and calculated values is very good for the second moments, but not as satisfactory with molecular quadrupole moments, the former agreement being ascribed by the authors more to the insensitivity of the quantities mentioned than to the high quality of the calculated wavefunctions.

TABLE 14. Second moments of the electronic-charge distribution (10^{-16} *e* cm^2) of diazirine[80]

	CNDO/2D	SCCMO	*ab initio*[81]
$\langle x^2 \rangle$	15·81	15·60	15·48
$\langle y^2 \rangle$	9·27	9·47	9·62
$\langle z^2 \rangle$	4·94	4·89	5·08
$\langle r^2 \rangle$	30·02	29·96	30·22

TABLE 15. Molecular quadrupole moments (10^{-26} Fr cm^2) (Fr = e.s.u. of charge) of diazirine[80]

	CNDO/2D	SCCMO	*ab initio*[81]
Q_{xx}	−0·81	0·54	2·01
Q_{yy}	−2·44	−4·02	−4·76
Q_{zz}	3·25	3·48	2·75

The results of MINDO/2 and EXH calculations[82, 83] on diazirine and its dimethyl derivative are shown in Table 16. Haselbach and coworkers[82] note that the orbital sequence for diazirine calculated by the MINDO/2 technique differs from that obtained by Robin and coworkers[78] in the order of the orbitals $a_1(n_+)$ and $a_1(\sigma)$, and point out that it is known that for unsaturated systems MINDO/2 yields σ orbitals with somewhat high energies. Hence the positioning of $a_1(\sigma)$ between $b_1(\pi)$ and $a_1(n_+)$ in Table 16 should be considered a consequence of the use of the MINDO/2 method.

TABLE 16. MINDO/2 calculated orbital energies (hartrees) for diazirine and 3,3-dimethyldiazirine

Diazirine[82]	3,3-Dimethyldiazirine[83]
0·5751 $b_1(\pi)$	0·3572 $b_2(n_-)$
0·4943 $a_1(n_+)$	0·3862 $b_1(\pi)$
0·4322 $a_1(\sigma)$	0·4212 $a_1(\sigma)$
0·4105 $b_1(\pi)$	0·4392 $a_1(n_+)$
0·3848 $b_2(n_-)$	0·4502 $b_1(\pi)$

The vertical ionization potentials $I_V(J)$ of dimethyldiazirine as determined by photoelectron spectroscopy[82] are given as 9·76, 12·11 and 13·31 eV, or 0·3587, 0·4450 and 0·4891 hartrees.

3. Substituted diazirines

a. *Spectra and structure.* Although earlier workers[47, 48, 51, 52] had proposed methods for the preparation of diazirine and substituted diazirines, it appears that Mitsch[84] was the first to prepare perfluorodiazirine (F_2CN_2), a precursor of CF_2. He and his coworkers subsequently measured[85] the infrared spectrum of F_2CN_2 from 4000 to 250 cm^{-1} and the Raman spectrum from 2700 to 100 cm^{-1} in order to establish its structure. The frequencies of the infrared and Raman bands for the fundamental modes expected for the diazirine and diazomethane structures were calculated and these were compared with the measured fundamental vibration frequencies of F_2CN_2, shown in Table 17. The match between those values predicted for the diazirine structure and those observed is quite convincing.

TABLE 17. Summary of fundamental vibration frequencies of F_2CN_2[85]. Reprinted, with permission, from Hencher and Bauer, *J. Amer. Chem. Soc.*, **87**, 1186 (1965). Copyright by the American Chemical Society

Symmetry	Frequency (cm^{-1})	
A_1	ν_1	1563
	ν_2	1282
	ν_3	805
	ν_4	502
A_2	ν_5	451
B_1	ν_6	1248
	ν_7	481
B_2	ν_8	1091
	ν_9	544

Simmons and coworkers[86] studied the ultraviolet absorption spectrum of CF_2N_2 in the 3750–3000 Å region under high resolution and confirmed the conclusions from the infrared and Raman work[85], that the molecule did indeed possess a cyclic C_{2V} structure. The results of the two studies agree quite well, as can be seen from Table 18, except for ν_3. ν_1 and ν_4 may be described as the symmetric NN stretch and symmetric CF_2 deformation, respectively. Hence it appears that the most significant change in geometry between the two electronic states is a stretching of the nitrogen–nitrogen bond which expands the ring and alters the FCF angle.

TABLE 18. Comparison of the vibrational assignment for the A_1 species in CF_2N_2 as found from the infrared[85], Raman[85] and ultraviolet[86] spectra

Vibration	Infrared (vapour) (cm^{-1})	Raman (liquid) (cm^{-1})	Ultraviolet (vapour)	
			ν'' (cm^{-1})	ν' (cm^{-1})
ν_1	1563	1560	1564·0	1436·9
ν_2	1282	1280	1282·9	
ν_3	805	804	775·0	643·3
ν_4	502	500	500·2	516·6

Hencher and Bauer[87] completed the puzzle by providing interatomic distances and bond angles from electron diffraction experiments on the vapour. They confirmed the C_{2V} symmetry in which the planes of CF_2 and CN_2 are mutually perpendicular with C—F = 1·315 Å, C—N = 1·426 Å, N═N = 1·293 Å, ∠FCF = 111·84°, ∠NCN = 53·95°. Comparison of these values for perfluorodiazirine with those for diazirine shows that the C—N distance is shorter (1·426 vs 1·482 Å) and the N═N distance is longer (1·293 vs 1·228 Å) in the former than in the latter by about 0·06 Å. These are summarized in Table 19. Hencher and Bauer compare the C—F distance and the ∠FCF for F_2CN_2, 1·315 Å and 111·84°, respectively, with those found for perfluorocarbene (F_2C:)[88], 1·300 Å and 104·9°, respectively, and rationalize the differences on the basis of the greater extent of delocalization of the carbon valence electrons in the radical. In addition, the compression of the charge density around the carbon atom and hence the shortening of adjacent bond lengths when F is substituted for H on a carbon atom has been observed with many other molecules. The introduction of F atoms affects not only the adjacent C—F bond lengths, but also adjacent bonds are shortened, as is observed in the present examples, where the C—N distance in F_2CN_2 is smaller than in H_2CN_2. The longer N=N bond in F_2CN_2 than in H_2CN_2 cannot be due primarily to the presence of a three-atom ring since the C—C distance in cyclopropene is 1·525 Å[89], close to that found in cyclopropane[90], while C=C is 1·286 Å, less than the C=C distance in ethylene. To be consistent with these changes, it would be anticipated that the N=N distance in F_2CN_2 (1·293 Å) would be less than that in N_2F_2 (1·224 Å)[91], which it is not.

TABLE 19. Nuclear configuration of diazirine and perfluorodiazirine

Parameter	F_2CN_2 [87]	H_2CN_2 [50]
C—F	1·315 Å	
C—H		1·09 Å
C—N	1·426 Å	1·482 Å
∠NCN	53·95°	48·9°
∠FCF	111·84°	
∠HCH		117° (±2)
N=N	1·293 Å	1·228 Å
F · · · F	2·178 Å	
N · · · F	2·374 Å	

Robertson and Merritt[92], continuing the work on diazirines already begun in their laboratory, obtained the ultraviolet absorption spectra, at high resolution, for 3-bromo- and 3-chloro-3-methyldiazirine. These compounds were prepared by the method of Graham[52]. Two electronic systems are found for these two substituted diazirines, separated by 63 cm^{-1} in 3-bromo-3-methyldiazirine (BMD) and 137 cm^{-1} in 3-chloro-3-methyldiazirine (CMD), again providing evidence for the splitting of the degeneracy of the lone-pair nitrogen electrons as observed with diazirine[70]. The strong progression is the symmetrical NN stretching frequency at 1412 cm^{-1} in BMD and 1454 cm^{-1} in CMD. Spectra of solutions of BMD and CMD in benzene, ethanol and chlorobenzene showed a blue shift of approximately 30 cm^{-1} as the solvent was changed from less polar to more polar, which indicates that the transition is $\pi^* \leftarrow n$.

The vapour-phase infrared spectra of BMD and CMD were measured in the 250–4000 cm^{-1} region by Mitchell and Merritt[93]. The N=N stretching vibrations in BMD and CMD are 1571·3 and 1573·4 cm^{-1}, respectively, little changed from 1626 cm^{-1} in diazirine[54] and 1563 cm^{-1} in difluorodiazirine[85]. The symmetric and antisymmetric C—N stretching vibrations were assigned as 991 and 807 cm^{-1} in diazirine[54], and 1282 and 1091 cm^{-1} in difluorodiazirine[85], a considerable shift. Mitchell and Merritt assign the symmetric C—N stretching vibration to 1071·6 cm^{-1} in CMD and 1090·9 cm^{-1} in BMD and the antisymmetric vibration to 858 and 868 cm^{-1} in BMD and CMD, respectively.

Since Hencher and Bauer[87] had found that the C—N and N=N bond lengths of F_2CN_2 differ by an unexpectedly large amount (0·06 Å) from their corresponding values in H_2CN_2, then it might be expected that other substituents would alter the ring geometry but to a lesser degree. Hence Wollrab and coworkers[94] observed the rotational spectra for dimethyldiazirine to test this hypothesis. Their measured structural parameters are given in Table 20. The N=N and C—N distances in diazirine and DMD are quite similar, indicating that methyl substitution has little, if any, effect on the ring structure. A dipole moment of 2·19 D (± 0·07) was obtained from the Stark shift. The internal rotation splittings for $(CH_3)_2CN_2$ yield a barrier to internal rotation of 1129 ± 20 cal/mol and an angle of 120·4 ± 0·4° between the top axes. The quadrupole coupling constants (MHz) are $\chi_{aa} = -0·94 \pm 0·8$, $\chi_{bb} = 3·20 \pm 0·4$, $\chi_{cc} = -2·27 \pm 0·4$, with the *a* axis being that passing through the ring carbon atom and bisecting the N=N bond, the *C* axis passing through the ring carbon atom and running parallel to the N=N bond.

TABLE 20. Structure parameters of dimethyldiazirine (DMD)[94], difluorodiazirine (DFD)[87], diazirine (D)[50] methyldiazirine (MD)[95] and 3-chloro-3-methyldiazirine (CMD)[96]

Bond	DMD	DFD	D	MD	CMD
		Bond length (Å)			
C—C	1·499			1·501	1·498
C—N	1·490	1·426	1·482	1·481	(1·462)
N=N	1·235	1·293	1·228	1·235	1·241
C—H_s	1·080			1·098	(1·09)
C—H_a	1·100		1·09	1·096	
		Bond angle			
∠NCN	(48·9°)[a]	53·95°	48·9°	49·3°	50·2°
∠NNC	(65·5°)[a]				
∠CCC	119·7°				
∠FCF		111·8°			
∠HCH			117°		

[a] Assumed from the structure of diazirine[50].

H_s, H_a: symmetric (in-plane) and asymmetric (out-of-plane) hydrogen positions, respectively.

Continuing their examination of the effect of substituents on the diazirine ring, Scharpen and coworkers[95] obtained the rotational spectra of CH_3CHN_2 and CD_3CHN_2 (methyldiazirine). Their results are shown in Table 20 for convenience in comparison of the values of the various parameters. The N=N bond length is the same as that found in dimethyldiazirine although the CN bonds may be slightly shorter. The internal rotation splittings gave a methyl group rotation barrier of 773·9 cal/mol. Quadrupole coupling constants (MHz) of $\chi_{aa} = +0·48 \pm 0·8$, $\chi_{bb} = -2·53 \pm 0·4$ and $\chi_{cc} = +2·05 \pm 0·4$ were obtained with the *a* axis along the CN bond and the *b* axis parallel to the N=N bond. A dipole moment of 2·03 ± 0·07 D was calculated.

A third paper, this time on CMD, was published by Wollrab and Scharpen[96], and the structural parameters are added to Table 20 for convenient comparison. The N=N bond length is only slightly larger than the same parameter in the methyl-substituted diazirines[94, 95]. The barrier to internal rotation of the methyl group is

1689 ± 10 cal/mol. The chlorine quadrupole coupling constants (MHz) are $\chi_{aa} = -66{\cdot}51$, $\chi_{bb} = 32{\cdot}91$ and $\chi_{cc} = 33{\cdot}60$ with the *ab* plane being the molecular symmetry plane containing the two carbon atoms, the chlorine atom and H_8. The *c* axis is normal to this plane.

Mitchell and Merritt[97] measured the vapour and solid-phase infrared spectra for 3,3-dimethyldiazirine and 3,3-dimethyl-d_6-diazirine in the 250–4000 cm^{-1} region. The NN stretching frequency (solid phase) was 1586 cm^{-1}, while the symmetric and antisymmetric C—N stretching vibrations were assigned to 1136 and 788·1 cm^{-1}, respectively.

Lombardi, Klemperer, Robin, Basch and Kuebler (LKRBK)[77] carried out both an experimental and theoretical study of the lower $n \rightarrow \pi^*$ excitation in difluorodiazirine, F_2CN_2 (DFD). They note that no microwave spectrum has been observed for DFD which may be due to a vanishingly small ground-state dipole moment. Using the results of Hencher and Bauer[87] they are able to establish the changes in the N—N and F—F distances on excitation, and hence the molecular structure of F_2CN_2 in the $n \rightarrow \pi^*$ excited state. Such changes are given as $+0{\cdot}060 \pm 0{\cdot}005$ and $-0{\cdot}034 \pm 0{\cdot}005$ Å for NN and FF, respectively, yielding 1·343 Å and 2·144 Å, respectively, for the $n \rightarrow \pi^*$ excited state bond distances. These authors point out that since the spectrum is sensitive only to the change in the N=N distance on excitation, their results cannot confirm or deny the large value previously found[87] by electron diffraction for the N=N bond length in DFD. LKRBK estimate a value of $\mu' = 1{\cdot}5 \pm 0{\cdot}2$ D for the $n \rightarrow \pi^*$ excited-state dipole moment of DFD and a value of only 0·082 D for that in the ground state. Discussion of the theoretical studies of LKRBK on DFD has been given in the appropriate section of this chapter. However, it may be desirable to summarize those portions of their theoretical results which relate particularly to their experimental work. The orbital energies are summarized in Table 13 of the theoretical studies section (II.C.2.b) to which reference may be made. Orbitals $4b_1$ and $9a_1$, the highest occupied and the third highest occupied, have energies of $-0{\cdot}4851$ and $-0{\cdot}6251$ hartrees, respectively, and represent the two 'non-bonding' orbitals associated with the —N=N— group. As has been observed repeatedly experimentally in the diazirines, their mutual interaction separates them, in this case by 0·14 hartrees or 3·8 eV. The $n \rightarrow \pi^*$ transition involves the passage of an electron from $4b_1$ to the π^* molecular orbital, $2a_2$. Using the virtual orbital approximation yields a calculated singlet–singlet $n \rightarrow \pi^*$ excitation energy of 3·99 eV compared to their observed value of 3·7 eV.

LKRBK note that the electronic spectrum of a polyatomic molecule is normally severely blue-shifted on substituting the hydrogens by fluorine, and hence it is surprising to find the $n \rightarrow \pi^*$ band of F_2CN_2 (3·7 eV) to the red of that of H_2CN_2 (3·95 eV). However their calculations predict the correct relative ordering of the $n \rightarrow \pi^*$ bands of diazirine (4·17 eV) and difluorodiazirine (3·99 eV).

The bond length changes on excitation may be rationalized by examining the nature of the molecular orbitals (MO). The $9a_1$ MO tends to draw the two nitrogen atoms together while the $4b_1$ MO acts in an opposing fashion. Hence, in an $n \rightarrow \pi^*$, the promotion of an electron from the $4b_1$ MO would be expected to cause the N=N distance to shorten, but promotion occurs to the $2a_2$ π^* MO which is more N=N antibonding than $4b_1$. Consequently the increased N=N distance in the upper state can be rationalized.

LKRBK also argue that the second band system observed in the vibronic spectra of diazirines by themselves and others[92] could not be the second $n \rightarrow \pi^*$ transition ($9a_1 \rightarrow 2a_2$) for two reasons. One, their MO energies would have the two $n \rightarrow \pi^*$ transitions separated by approximately 20,000 cm^{-1}, a value of the order of 100-times larger than that observed experimentally. Secondly, symmetry considerations would suggest that the second $n \rightarrow \pi^*$ transition is forbidden. LKRKB tentatively assign the second system in the diazirines to the $\pi \rightarrow \pi^*$ triplet state.

Robertson and Merritt[98] measured the high-resolution electronic absorption spectrum of 3,3′-dimethyldiazirine (DMD), and two superimposed electronic systems were again observed, the weak second origin is 126 cm^{-1} to the red of the strong origin of the allowed singlet–singlet $\pi^* \leftarrow n$ system. In addition, a third electronic system was observed in the 3900–4200 Å region, which these authors take as the triplet–singlet $\pi^* \leftarrow n$ transition. The N=N stretching vibration is again the most prominent feature in all systems. The high-resolution electronic absorption spectrum of 3-methyldiazirine[99] was also obtained. Results somewhat similar to those for DMD were obtained, the two electronic systems again being observed, this time separated by 92 cm^{-1}. The N=N stretching vibration was again prominent near 1499 cm^{-1}.

Correlations of bond stretching frequencies, bond lengths and dissociation energies, as advanced by Bernstein[100], have been pursued by McKean and co-workers[101] for a large variety of molecules among which are the diazirines. CH dissociation energies (D^0_{298}) of 110·8 and 98·4 kcal were predicted for diazirine and dimethyldiazirine, respectively.

The 3920 Å absorption spectrum of difluorodiazirine was reinvestigated by Hepburn and Hollas[102] and changes in structural parameters for the ground to the excited state were calculated as 0·036 and −0·038 Å for the NN and FF bond lengths, respectively, which may be compared to +0·06 and −0·034 Å for NN and FF, respectively, as found by LKRBK[77]. Hepburn and Hollas also conclude that there is no positive evidence for a second electronic system in the 3520 Å region.

Accurate values of the ^{14}N nuclear quadrupole coupling constants (MHz) have been measured by Pochan and Flygare[103], as $\chi_{aa} = +0{\cdot}196$, $\chi_{bb} = -3{\cdot}010$, $\chi_{cc} = +2{\cdot}814$, all $\pm 0{\cdot}150$, where the a axis is coincident with the molecular symmetry axis and b is in the plane of the molecule. These values are in fair agreement with the calculated results of LKRBK[77], $\chi_{aa} = -0{\cdot}8$ MHz, $\chi_{bb} = -1{\cdot}88$ MHz, $\chi_{cc} = +2{\cdot}69$ MHz. Walsh orbitals having sp orbitals in the plane of the ring (one pointing away from the N and containing a lone pair of electrons; the other entering into a C—N σ bond) were used with unhybridized p_z and p_y orbitals to describe the ^{14}N field gradients.

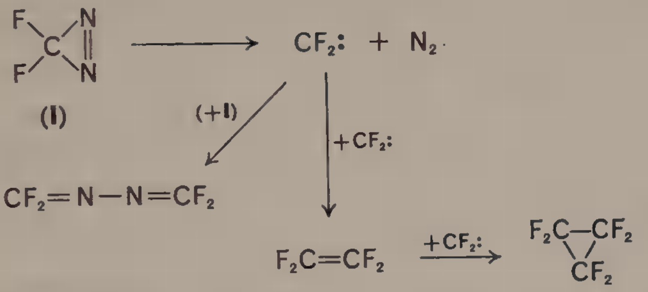
b. *Kinetics of thermal decomposition.* Relatively little work had been done on the thermal decomposition of aliphatic diazo compounds, presumably because of their instability, until the discovery of convenient preparative procedures for various substituted diazirines. Since these compounds appeared to be more stable than the corresponding diazo compounds, there followed a substantial amount of work on their decomposition. This section will deal primarily with the physicochemical aspects of such decompositions.

Frey and Stevens[104] have investigated the thermal decomposition of dimethyldiazirine (DMD) in the temperature range from 124 to 174 °C, and have found this reaction, producing propene and nitrogen, to be homogeneous and first order. Below 100 torr, the first-order rate constant decreases with pressure, but at 100 torr it has essentially attained its high-pressure limit. At an initial pressure of 4 torr, the measured first-order rate constants yield an activation energy of 33·2 kcal/mol. At this pressure and 145·1 °C, $k = 3{\cdot}47 \times 10^{-4}$ sec^{-1}. At sufficiently high pressures the rate constant of a unimolecular reaction should be independent of pressure, and consequently the authors propose that this reaction is probably unimolecular. Further, no departure from first-order kinetics was observed even in runs carried to more than 80% decomposition. Since propene is known to be an inhibitor of radical-chain reactions, and since the rate of decomposition of dimethyldiazirine is not affected by the accumulation of propene in the system, it was concluded that it was unlikely that any chain reaction is involved. Hence it was presumed that the decomposition is a true unimolecular reaction. These authors considered two possible mechanisms, first, a 1,2-hydrogen shift and a C—N scission to form a diradical as an intermediate, followed by a breaking of the remaining CN bond and, second, a concerted mechanism in which N_2 is released and dimethylcarbene is formed as an intermediate, followed by the rearrangement to propene. The authors argue that the first mechanism is unlikely on energetic grounds.

Bottomley and Nyberg[105] have also investigated the gas-phase thermal decomposition of DMD, but in the temperature range 60–70 °C and at pressures of 200 torr, at very slow rates using precision gas-volumetric techniques. Their results and those of Frey and Stevens[104], after adjustment for pressure differences, fit a single Arrhenius activation energy equation. They also conclude that the reaction is homogeneous. Bottomley and Nyberg[105] argue for a mechanism in which dimethyldiazomethane is formed as an intermediate, since the high value of the pre-exponential factor (10^{14}) is taken to indicate a transition state considerably 'looser' (i.e. higher entropy) than the initial configuration, especially when a rigid cyclic structure is broken.

The thermal decomposition of difluorodiazirine (DFD) yields primarily nitrogen, tetrafluoroethylene, hexafluorocyclopropane and perfluoro-2,3-diaza-1,3-butadiene, with traces of other fluorine-containing compounds[84, 106].

The reactions may be represented as a series of competitive consecutive steps:



(1)

By decomposing at a partial pressure of 50 torr in the presence of a 3-molar excess of C_2F_4, the side reactions were minimized and decomposition occurred primarily to form difluorocarbene and nitrogen. Such primary decomposition appeared to be unimolecular and homogeneous in the temperature range of 123–170 °C and total pressure of 100–800 torr. The rate constant was pressure dependent in this range. At a total initial pressure of 200 torr and 141·0 °C the rate constant was $1{\cdot}27 \times 10^{-4}$ $\sec^{-1}$. At the same pressure the pre-exponential factor was $10^{13{\cdot}1}$ and the activation energy 32·2 kcal/mol. Neuvar and Mitsch[107] also prefer a mechanism involving difluorodiazomethane as an intermediate prior to loss of nitrogen.

In order to determine the effect of the electronegative chlorine atom on the decomposition of diazirines and to confirm that the decomposition was unimolecular, by following the reaction in the fall-off region, the thermal decomposition of 3-chloro-3-methyldiazirine (CMD) was investigated[108]. In the temperature region of 106–170 °C, CMD undergoes a first-order decomposition, which is probably unimolecular, to form vinyl chloride and nitrogen. No other products were detected. Low-pressure experiments were performed at an initial reactant pressure of 4 torr and at nine temperatures ranging from 107 to 170 °C. At 147 °C the rate constant was $3{\cdot}50 \times 10^{-3}$ $\sec^{-1}$, the pre-exponential factor $10^{11{\cdot}7}$, and the activation energy 27·2 kcal/mol. In order to study the effect of pressure perfluoropropane was added as an inert gas. For a reaction mixture which consisted initially of 50 torr of CMD and 300 torr of perfluoropropane, and temperatures between 110 and 148 °C, an Arrhenius expression was obtained for k_∞ which contained $10^{14\cdot1}$ as a pre-exponential factor and 31·1 kcal/mol as an activation energy. These authors retain their belief that the decompositions proceed via the formation of a carbene. Substitution in the 3-position of a chlorine atom should lead to some stabilization of the resulting carbene as compared with its hydrogen or alkyl analogue. The energy of activation for DMD was 33·2 kcal/mol (4 torr) which probably could be adjusted to 34 kcal/mol to correspond to k_∞. The difference between this value and that of 31 kcal/mol obtained from CMD would suggest a significant stabilizing effect of the chlorine atom. Bridge and coworkers[108] take the pre-exponential factor of $10^{14\cdot1}$ as indicating that the decomposition has a relatively small entropy of activation, and hence that in the transition state no new free rotations have developed. They consequently favour a cyclic intermediate in which both C—N bonds are weakened and N=N strengthened.

The thermal decomposition of 3,3-tetramethylenediazirine, 3,3-pentamethylenediazirine and 3,3-diethyldiazirine was also investigated by Frey and Scaplehorn[109]. The decompositions may be represented as follows:

3,3-Tetramethylenediazirine

(100–139 °C)

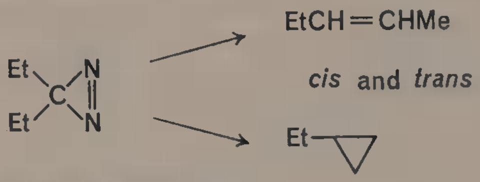
$k = 10^{13\cdot40} \exp(-30{,}500/RT)\ \text{sec}^{-1}$
$P_{i,\,\text{reactant}} = 7$ torr

3,3-Pentamethylenediazirine

(101–137 °C)

$k = 10^{13\cdot34} \exp(-30{,}870/RT)\ \text{sec}^{-1}$
$P_{i,\,\text{reactant}} = 5$ torr

3,3-Diethyldiazirine

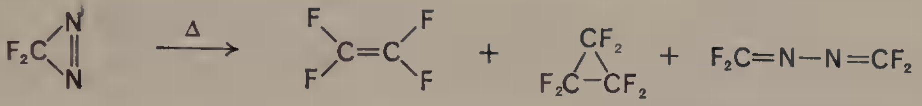


(118–149 °C)

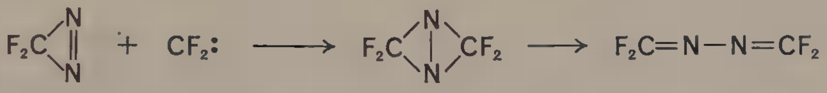
$k = 10^{13\cdot73} \exp(-31{,}890/RT)\ \text{sec}^{-1}$
$P_{i,\,\text{reactant}} = 10$ torr

In all cases the reactions were homogeneous and first order, and probably unimolecular.

Although it does not properly fall under the heading of kinetics of thermal decomposition, nevertheless it seems appropriate to take note of a study of the polymerization of difluorodiazirine (DFD)[110] because of the information which such work may provide concerning possible reaction intermediates. Pyrolysis or ultraviolet pyrolysis of difluorodiazirine in the presence of boron trifluoride produced polydifluoromethylene. Unlike Frey, Ogden and Mitsch[110] favour the formation of a linear intermediate rather than the concerted elimination of nitrogen in the decomposition of DFD. Under certain conditions tetrafluoro-2,3-diazabuta-1,3-diene, tetrafluorethylene and perfluorocyclopropane are formed from the decomposition of DFD:



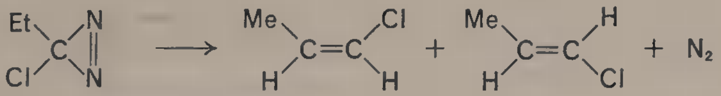
Tetrafluoro-2,3-diazabuta-1,3-diene could be derived from reaction of difluorocarbene with the linear intermediate or by insertion of difluorocarbene into the difluorodiazirine double bond, followed by rearrangement:



However, Ogden and Mitsch[110] could find no examples of insertion of difluorocarbene into an N=N bond, and consequently favoured the linear intermediate.

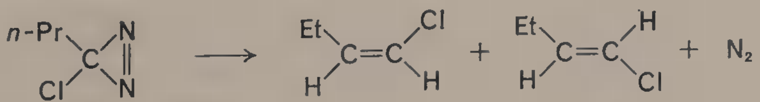
Continuing their studies of the thermal decomposition of diazirines, Frey and Liu[111] investigated 3-chloro-3-ethyldiazirine, 3-chloro-3-*n*-propyldiazirine, 3-chloro-3-isopropyldiazirine and 3-chloro-3-*t*-butyldiazirine. The overall decomposition reactions are given below:

3-Chloro-3-ethyldiazirine



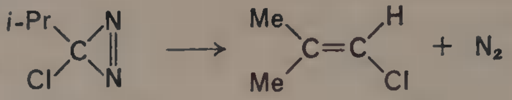
$k = 10^{13\cdot985} \exp(-30{,}450/RT)\ \mathrm{sec}^{-1}$
(20 torr of diazirine and 60 torr of *n*-butane; 103–145 °C)

3-Chloro-3-*n*-propyldiazirine



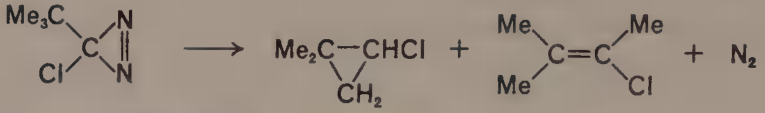
$k = 10^{13\cdot98} \exp(-30{,}980/RT)\ \mathrm{sec}^{-1}$
(10 torr diazirine and 20 torr butane; 105–149 °C)

3-Chloro-3-isopropyldiazirine



$k = 10^{14 \cdot 01} \exp(-30{,}590/RT)$ sec^{-1}
(10 torr diazirine and 20 torr butane; 107–145 °C)

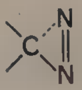
3-Chloro-3-*t*-butyldiazirine



$k = 10^{13 \cdot 36} \exp(-29{,}500/RT)$ sec^{-1}
(4 torr diazirine; 105–148 °C)

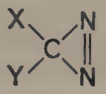
The values of the free energy of activation ($\Delta G^{\ddagger}$) for decomposition of all the alkylchlorodiazirines fall within the range $28 \cdot 75 \pm 0 \cdot 3$ kcal/mol and the authors again interpret this as supporting the intermediate formation of a carbene by a concerted elimination of nitrogen.

The thermal decomposition of 3-chloro- and 3-bromo-3-phenyldiazirines (BPP) has been investigated in several solvents over the 60–110 °C temperature range[112]. In this temperature range, 3-chloro-3-phenyldiazirine (CPD) decomposes unimolecularly to yield nitrogen and the corresponding carbene. This carbene can either react with diazirine to give dimeric product or with the solvent to yield the appropriate compounds. The average activation energies for CPD and BPD are 27·8 and 27·4 kcal/mol respectively, the former being averaged over that obtained in three different solvents. The former value represents a decrease in activation energy of about 3 kcal/mol from that found for 3-chloro-3-methyldiazirine[108] and this is suggested to reflect the resonance stabilization effects of the phenyl group on the transition state of diazirine decomposition. The pre-exponential factors in both cases are approximately 10^{14}, suggesting a typically unimolecular reaction with a relatively tight transition state. The results of Liu and Toriyama[112] also show that the rate of decomposition changes very little as the solvent is varied, which appears to indicate that the transition state of the rate-determining step is likely to be more radical than ionic. Further, the substituent effects are interpreted as supporting a radical intermediate such as



In a second paper Liu and Toriyama[113] have examined the effect of *para* substituents on the thermal decomposition of a series of 3-chloro-3-aryldiazirines in various solvents. A summary of their results, together with those of previous workers, is given in Table 21. They find, in agreement with the data previously discussed in this section, that the thermal decomposition of diazirines is unimolecular with a pre-exponential factor of approximately $10^{13 \cdot 7}$. Each of the solvents used (cyclohexene, diethyleneglycol monoethyl ether and dimethyl sulphoxide) gave similar organic products and all the free energies of activation are approximately $26 \cdot 0 \pm 0 \cdot 3$ kcal/mol.

TABLE 21. Summary of kinetic data for the thermal decomposition of substituted diazirines[113]



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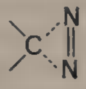
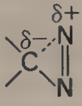
Reference	X	Y	State	log *A*	*E* (kcal/mol)	$\Delta S^{\ddagger}$ (cal mol^{-1} deg^{-1})
107	Fluoro	Fluoro	Vapour	13·40	32·50	0·5
109	Ethyl	Ethyl	Vapour	13·73	31·89	2·0
108	Chloro	Methyl	Vapour	14·14	31·07	3·9
111	Chloro	Ethyl	Vapour	13·99	30·45	3·2
111	Chloro	*n*-Propyl	Vapour	13·98	30·98	3·2
111	Chloro	*i*-Propyl	Vapour	14·01	30·59	3·3
111	Chloro	*t*-Butyl	Vapour	13·36	29·50	0·3
112	Chloro	Trichloromethyl	CCl_4	13·80	29·20	2·3
112	Chloro	Phenyl	Cyclohexene	13·87	28·00	2·6
113	Chloro	*p*-Methoxyphenyl	Cyclohexene	13·41	26·49	0·5
113	Chloro	*p*-Tolyl	Cyclohexene	13·94	27·87	2·9
113	Chloro	*p*-Chlorophenyl	Cyclohexene	13·81	27·72	2·3
113	Chloro	*p*-Nitrophenyl	Cyclohexene	13·80	27·85	2·3
112	Bromo	Phenyl	Cyclohexene	13·75	27·36	2·1

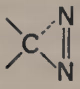
Although the substituent effects on the rates of reaction are small, nevertheless the following order can be discerned: $p\text{-}CH_3O > p\text{-}CH_3 > p\text{-}Cl > H \simeq p\text{-}NO_2$. Liu and Toriyama employ these results in an attempt to select one of



(I)

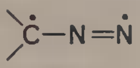


(II)

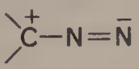


(III)

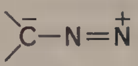
as the most likely transition state. The order of substituent effects would be expected to be the reverse of that observed if the charge separated transition state **II** is invoked. Further, the lack of solvent effects renders **II** unlikely as a transition state in the thermal decomposition of diazirines. In view of the suggestion of Schmitz[114] that a mechanism passing through transition state **I** would require the carbon atom in that state to tend towards a sextet, and consequently that such a transition cannot be stabilized by withdrawal of electrons, Liu and Toriyama conclude that the order $p\text{-}CH_3O > p\text{-}CH_3 > H > p\text{-}Cl > p\text{-}NO_2$ would be expected, thus ruling against state **I** in the present case. Liu and Toriyama as a result conclude that transition state **III** is most probable and consider three possible structures for that state:



(IIIa)



(IIIb)



(IIIc)

State **IIIc** is believed to be unlikely in view of the known relative electronegativities of nitrogen and carbon atoms. The free radical form may be classified as an S radical[115] in which the observed properties are shifted in the same direction with donor and acceptor substituents. The likely order of contribution of different substituents to structure **IIIb** would, however, be identical to the observed order. Consequently these authors believe that the transition state of 3-chloro-3-*p*-methoxyphenyldiazirine would be stabilized through both structures **IIIa** and **b**, and hence might be expected to exhibit the most rapid decomposition. Since 3-chloro-3-*p*-tolyl-phenyldiazirine has less resonance ability, both transition states **IIIa** and **b** will be involved to a lesser extent. With 3-chloro-3-*p*-chlorophenyldiazirine, **IIIa** would then be the expected transition state, and its rate would be expected to be lower. Although structure **IIIa** is relatively equally stabilized by the *p*-NO_2 as by the *p*-CH_3O substituent, since *p*-NO_2 is strongly electronegative **IIIb** is not likely, and the stabilizing effect from **IIIa** may be largely erased so that the observed rate is similar to that of the unsubstituted compound. Liu and Toriyama conclude that the most likely mechanism is one involving the breaking of one of the C—N bonds leading to a diradical (**IIIa**) and a diazomethane (**IIIb**) intermediate, the contribution of the latter probably being small due to the lack of solvent effects. As has been noted earlier in this chapter (Section II.B.2) Walch and Goddard[35] obtained wavefunctions for diazomethane which lead them to suggest a singlet biradical structure for the ground state of diazomethane.

Although the recent calculations by Tschuikow-Roux and Jung[116] on a three-centre decomposition reaction for perfluorodiazirine might be included in the section on theoretical studies of diazirines, they are included here because results of such calculations do provide information on a possible decomposition mechanism. These authors begin with the stable configuration for perfluorodiazirine, that is, with the NCN plane perpendicular to the FCF plane. The molecule is then perturbed within one of three models where the ∠NCN bending mode is used as the reaction coordinate. In model **I**, the C—N bonds and the N—N bond are taken to have half-bond orders and bond order 2·5, respectively. The C—F bond distance and the ∠FCF remain unchanged from the initial state. In model **II**, the total bond order is taken as fixed, the C—N bonds and N—N bond then have half-bond orders and bond order 3, respectively. The ∠FCF is chosen as the average of that in perfluorodiazirine and the CF_2 radical. The CF_2 bond distance is unchanged from the initial value. Model **III** retains the assumption of conservation of total bond order but postulates that the fractional decrease in bond order of a bond being partially broken is equal to $\Delta n = 1/3$, the fraction of the number of bonds undergoing changes in the ring opening. Consequently, 2/3 and 8/3 bond orders are assigned to the C—N and N—N bonds, respectively. The CF bond lengths and ∠FCF are used as in model **II**. Basically what is then required is the minimum energy corresponding to each of these sets of constraints, and these are calculated as 60·3, 75·6 and 32·7 kcal/mol, for models **I**, **II**, and **III**, respectively, compared to the experimental activation energy of 32·2 kcal/mol[107]. Model **III** apparently is the most appropriate and in support yields a calculated pre-exponential factor in reasonable agreement with the experimental value. It should be emphasized, however, that however interesting such results may be, they do not provide sufficient information to permit a discrimination between a thermal decomposition mechanism involving a linear intermediate and one involving a concerted elimination of nitrogen. However, the weight of evidence presented in this section appears to favour a linear intermediate in the decomposition of diazirines.

III. DIIMIDES (DIAZENES)

As indicated in the introduction to this chapter, although not strictly speaking within the purview of this chapter, diimides have been included for purposes of comparison and completeness. Reference should also be made to the chapter by Dr M. B. Robin on 'Electronic Structures' which appeared in the volume on *The Chemistry of the Hydrazo, Azo and Azoxy Groups* in the present series. It is hoped that the present discussion will supplement, rather than duplicate, the information given in the chapter mentioned above.

A. The Prototypes, N_2H^+ and N_2H

The molecular ion, N_2H^+, may quite reasonably be considered as representing the simplest azo or diazo compound. In 1974 Turner[117] reported the discovery of three closely spaced new interstellar lines near 93·174 GHz. Green and coworkers[118] suggested the molecular ion N_2H^+ to be an excellent candidate for the carrier of Turner's lines and, assuming the ion to be linear, have performed *ab initio* calculations, using a double-zeta basis set, as a function of r(NN) and r(NH), the nitrogen–nitrogen and nitrogen–hydrogen bond lengths. The minimum energy was found when $r(\mathrm{NN}) = 1{\cdot}099$ Å and $r(\mathrm{NH}) = 1{\cdot}041$ Å, and the frequency of the $J = 1 \rightarrow 0$ rotational transition was calculated to be $92{\cdot}2 \pm 1{\cdot}8$ GHz, in good agreement with the observed value given previously. Similarly the quadrupole coupling constant for the outer nitrogen, deduced from observations as $-5{\cdot}7$ MHz, was calculated to be $-5{\cdot}3 \pm 0{\cdot}5$ MHz, while that for the inner nitrogen was calculated as $-1{\cdot}2 \pm 0{\cdot}5$ MHz, a contribution to the hyperfine structure too small to be resolved in the sources so far observed. However, the agreement between the aforementioned experimental and calculated values seems to provide rather good evidence for the association of Turner's lines with N_2H^+.

Even more recently, Hillier and Kendrick[119] have extended the previous calculations on N_2H^+. Restricted Hartree–Fock (RHF) calculations of the electronic ground state of N_2H^+ were performed with inclusions of nitrogen d and hydrogen p polarization functions.

Large-scale configuration interaction calculations were then performed including single and double excitations from the RHF configuration and again assuming the molecule to be linear. Values of 93·1 GHz, $-4{\cdot}70$ MHz and $-1{\cdot}00$ MHz were obtained from the calculations for the frequency of the $J = 1 \rightarrow 0$ rotational transition (actually B_e rather than B_0 was calculated), the quadrupole constant for the outer nitrogen and that for the inner nitrogen, respectively. Quite obviously the agreement of the first value with experiment is considerably improved, while that of the second suffers some degradation. The inclusion of correlation alters other calculated values, of course, and $-109{\cdot}414325$ hartrees, 1·097 Å and 1·031 Å are found for the total electronic energy, r(NN) and r(NH), respectively, as compared with $-109{\cdot}163339$ hartree, 1·065 Å and 1·023 Å, respectively, obtained with the RHF calculations.

Vasudevan and coworkers[120] have carried out extensive calculations on N_2H^+. Their calculated equilibrium values compared with those mentioned previously and with those of Forsen and Roos[121] are provided in Table 22. Vasudevan and coworkers performed calculations as a function of NH and NN distances as well as the HNN angle, and found N_2H^+ to be linear in its ground state.

Ab initio molecular orbital calculations have also been performed[122] on the free radical HNN, using the restricted open-shell method of Roothaan[123] with the extended 4–31G basis set of Pople and coworkers[124]. Standard molecular exponents were used for HNN• and N_2, but the energy used for the H atom was that obtained with optimum atomic exponents. The internuclear separations of NN and NH were calculated as 1·18 and 1·020 Å, respectively, and the H—N—N angle was obtained as 118°. The HNN• radical was calculated to be less stable than an H atom and an N_2 molecule in their ground states, the radical having a dissociation energy of

TABLE 22. Calculated equilibrium parameters for N_2H^+

r(NH) (Å)	r(NN) (Å)	NH Stretching force constant (mdyn/A)	Total electronic energy (hartree)	Dissociation energy (eV)	Proton affinity (kcal/mol)	Reference
1·041	1·099	—	—	—	—	118
1·031	1·097	—	−109·414325 (CI)	—	—	119
1·023	1·065	—	−109·163339 (RHF)	—	—	119
1·026	1·093	7·1	−109·0748 (SCF)	5·48	126·5	120
1·027	1·093[a]	4·9	−109·2443 (CI)	5·46	126·0	120
1·024	1·093[a]	—	−108·967	—	127·7	121
—	1·077	—	−109·157[b]	—	123	121

[a] Assumed.

[b] With d-type polarization functions.

−9·0 kcal/mol. The activation energy for the decomposition of HNN• to N_2 and H was found as 22·6 kcal/mol.

Very recent *ab initio* SCF and CI calculations[125] on the ground and excited states of the HNN radical, using a bond length for N—H of 1·058 Å and either 1·093 Å or 1·199 Å for N—N, predicted the ground state to be non-linear with a H—N—N angle of 124° and a binding energy of 2·2 kcal/mol.

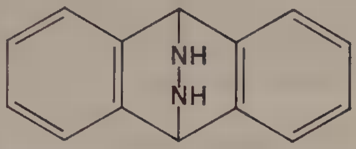
B. Diimide (Diazene)

1. Introduction

Although the molecular ion, N_2H^+, may be taken as the simplest representative of the class of molecules containing the NN bond, the molecule H—N=N—H, diimide (or diazene) is perhaps a more appropriate candidate for this position, since it is the simplest uncharged molecule of this type. Like diazomethane, as discussed earlier, diimide has a number of possible isomers, the *cis* and *trans* form, and 1,1-dihydrodiazine ($H_2\overset{+}{N}{=}\overset{-}{N}$). Diimide is the parent molecule of the azo compounds. The unsymmetrically substituted diazenes, of which 1,1-dihydrodiazine is the parent compound, are both important and interesting molecules. Lemal[126] has pointed out that these unstable isomers of azo compounds might be expected to lose molecular nitrogen with ease and hence serve as an important method for producing carbon–carbon bonds, as azo compounds do. However, as a consequence of their instability, other reactions appear to occur preferentially. Nevertheless, the properties and reactions of 1,1-disubstituted diazenes remain of importance in chemistry. Unfortunately, discussion of these compounds would lead us too far afield of the intention of this volume. Hence, attention will be limited to 1,1-dihydrodiazine itself for comparison with the *cis* and *trans* forms of diimide. A comprehensive review of nitrenes of which Reference 126 is a part has been published previously.

The nomenclature unfortunately presents some difficulty. Lemal[126] has pointed out that N_2H_2 is an aminonitrene, but prefers to label R_2N_2, where the two R atoms or groups are attached to the same nitrogen, as 1,1-disubstituted diazene, or simply diazenes. Hünig and coworkers[127] suggest that the systematic name diazene would be appropriate if NH was analogously named 'azene'. They employ diimine in preference to diimide on the basis of less ambiguity and continued association with the older literature. In the present article, diimide and diazene will be employed interchangeably where no confusion can arise.

Although a number of workers believed that they had direct or indirect chemical evidence for the existence of diimide, it was not until 1958 that Foner and Hudson[128] first detected diimide by mass spectrometry as an *m/e* 30 peak during the decomposition of hydrazoic acid or hydrazine in an electric discharge under reduced pressure. A fast-flow system was used and the diimide was detected downstream from the discharge. Foner and Hudson also showed that N_2H_2 could be trapped at -196 °C as a yellow solid consisting of ammonia and N_2H_2, and regenerated in the gas phase on warming. Thermal decomposition of anthracene-9,10-biimine at 100 °C *in vacuo*



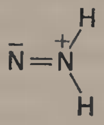
at the inlet of a mass spectrometer also apparently produces diimide[129], thereby suggesting a relatively high thermal stability for diimide. In contrast, diimide cannot be detected during the thermal decomposition of hydrazine in argon at 1470–2770 °C[130]. Photodecomposition of hydrazine[131] with vacuum ultraviolet radiation and the combustion of hydrazine at low pressure[132] has also led to the observation of diimide.

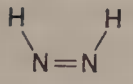
2. Spectroscopy and structure

The various nuclear configurations which are, in principle, possible for N_2H_2 are shown below:

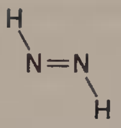
$H{-}N{=}N{-}H$

linear

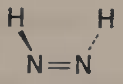




planar, *cis*



planar, *trans*



non-planar

One of the prime tasks of the spectroscopists was not only to determine in which of these forms diimide exists in its most stable form, but also to elucidate the nature of the electronic states, and in particular the electronic ground state. The next section attempts to trace the development of the answers for these and other questions, and to indicate those which remain unanswered at this time.

Walsh[133], in his interesting and far-reaching semi-quantitative predictions of shapes, spectra, and the electronic orbitals of polyatomic molecules, suggested that diimide would possess a planar non-linear structure. Wheland and Chen[134] assumed NH and NN distances to be 1·014 Å and 1·23 Å, respectively, and calculated, using simple, semi-empirical, LCAO–MO theory with overlap integrals neglected, a value of 100° for the most stable NNH angle. With the assumption that the *cis–trans* isomerization passes through a planar intermediate in which one NNH angle is 180°, whereas the other is allowed to take on whatever value leads to the most stable configuration, an activation energy of 33 kcal/mol was calculated for an activated complex in which the NNH angle that is not equal to 180° has the value of 76°.

Blau and coworkers[135, 136] obtained the infrared spectrum of solid diimide between 350 and 4900 cm^{-1} and that of the gas in the 3200 to 1300 cm^{-1} regions by decomposition of hydrazine with a microwave discharge. Infrared bands were observed at 3205, 3095, 2898, 1821, 1495, 1406 and 1362 cm^{-1}. They deduced that the solid at liquid nitrogen temperature has a planar structure and that the molecule appears to be primarily in the *cis* form, with molecular parameters of NH, NN and $\angle$HNN, being assumed as 1·014 Å, 1·230 Å and 100°, respectively. Unfortunately, the structure of the molecule in the gaseous state could not be unambiguously determined from the spectrum.

Dows and coworkers[137] investigated spectra of glow discharge decomposition products of HN_3 after condensation at 90 K and during slow warming. Absorptions at 860 and 3230 cm^{-1} were attributed to N_2H_2. Three prominent absorptions at 1290, 1325 and 3080 cm^{-1} observed in the photolysis of NH_3 in solid nitrogen were attributed[138] to intermediates D, E and F, respectively, possibly corresponding to NH_2, N_2H_2 and NH, respectively. It was established[139] that species D contained two hydrogen atoms but it was not possible to distinguish between the amine radical, *cis*- and *trans*-diimide, or NH_2N_3. Milligan and Jacox[140] propose that D and E may be N_2H_2 or $HN{=}N{-}N{=}NH$. Emission features near 3000 cm^{-1} from an ammonia–oxygen flame[141] were interpreted as due to NH_2, but with N_2H_2 as an alternate possibility. Rosengren and Pimentel[142] produced diimide by photolysing hydrazoic acid, both unlabelled and labelled with deuterium and ^{15}N, in solid nitrogen at 20 K. To *trans*-diimide the following features were positively assigned: 1285·8 cm^{-1} (HNNH), 1480·5 and 1058 cm^{-1} (HNND), 946·2 cm^{-1} (DNND). The only other absorptions which displayed isotopic frequency patterns appropriate to diimide were bands at 1279 and 3074 cm^{-1} which they assigned to *cis*-HNNH.

Trombetti[143] examined the infrared spectrum of N_2H_2 vapour in the 3100 cm^{-1} region and the vacuum ultraviolet spectra of both N_2H_2 and N_2D_2, and concluded from an analysis of the former spectrum that N_2H_2 in the ground state has a planar *trans* conformation with $r_{N-N} = 1{\cdot}238$ and $\angle N{-}N{-}H = 109°$, assuming r_{N-H} to be between 1·05 and 1·08 Å. Trombetti attributes five bands to diimide in the discharge products (77 K) of N_2H_4 (3095, 2950, 2900, 1404 and 1359 cm^{-1}) and N_2D_4 (2521, 2291, 2199, 1032 and 999 cm^{-1}). Trombetti interpreted his results in terms of a *trans* structure only, assigning the three infrared active fundamentals of *trans*-N_2H_2 at 3095, 1404 and 1359 cm^{-1} (2291, 1032 and 999 cm^{-1} for N_2D_2). The remaining bands were tentatively assigned as combinations involving unobserved Raman-active fundamentals which were deduced to be 1552 and 1496 cm^{-1} (1498 and 1167 cm^{-1} for N_2D_2). Trombetti also observed two electronic band systems near 3500 and 1730 Å and, from intensity variations in the 1730 Å system, decided that the ground state is a triplet (^3B_g) and that the first excited state may have a B_u symmetry. Trombetti[144] has also measured the infrared spectra of solid N_2H_2 and N_2D_2 from 600 to 4000 cm^{-1} at liquid nitrogen temperature. For both compounds five bands were observed and tentatively assigned to the three allowed fundamentals (N_2H_2: 1359, 1404, 3095; N_2D_2: 999, 1032, 2291 cm^{-1}) and to two combination bands (N_2H_2: 1496, 1552; N_2D_2: 1167, 1498 cm^{-1}) of *trans*-diimide.

Bondybey and Nibler[145] have prepared N_2H_2 as a discharge product of N_2H_4 and have studied the infrared and Raman spectra for both solid and matrix isolated

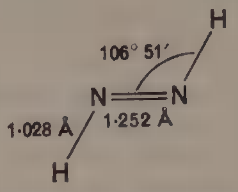
HNNH, HNND and DNND. The five in-plane vibrations of isolated *trans*-HNNH have all been determined: Raman A_g modes, 3128, 1583 and 1529 cm^{-1}; infrared B_u modes, 3131 and 1286 cm^{-1}. Isotopic substitution established the characteristic NN stretch as the 1529 cm^{-1} band. The A_u out-of-plane torsion was not definitely assigned but could be a weak infrared feature observed at 832 cm^{-1}. No evidence of *cis*-diimide was detected. Dilution studies of the solid discharge products showed that a number of hydrogen-bonded complexes form between HNNH and NH_3, and Bondybey and Nibler suggest that their work indicates that the earlier interpretations[136, 143] of the solid spectra in terms of 'isolated' *trans*- and *cis*-diimide must be discounted. These authors also conclude that their results are not inconsistent with Trombetti's conclusion that the electronic ground state of N_2H_2 is a triplet.

The infrared absorption spectrum of diimide in the 3·2 μm region has been re-examined at higher resolution than previously employed[146], and that of dideuterodiimide (N_2D_2) at 4·3 μm was also obtained for the first time. The following geometrical parameters were obtained for the planar *trans* conformation of diimide: $r_{N-H} = 1{\cdot}028$ Å, $r_{N-N} = 1{\cdot}252$ Å, $\angle N-N-H = 106°51'$. It is interesting to note that this N—N bond distance is the same as in azomethane, while ∠N—N—H is lower than ∠N—N—C in the same molecule by approximately 5 degrees[147, 148]. Carlotti and coworkers[146] argue that the evidence provided on line intensities agrees with the intensity alternation which would be expected for an A_g or A_u ground state. This disagrees with the earlier conclusions of Trombetti[143], whose spectral data were recently confirmed by Willis and Back[149]. Hence Carlotti and coworkers offer the possibility that the ultraviolet and the infrared spectra may not have the same lower state. They speculate that it may be possible that planar *trans*-diimide converts slowly to a less stable *cis* form which absorbs in the ultraviolet, so that an explanation for the apparently long lifetime of the ultraviolet absorption could be provided.

Back and coworkers[150] have examined the absorption spectra of N_2H_2 and N_2D_2 in the gas phase in the region 3000–4300 Å. The spectra were attributed to the $^1B_g \leftarrow {}^1A_g$ ($\pi^* \leftarrow n_+$) transition of *trans*-diimide, which the authors suggest may be allowed as a consequence of vibronic interaction. From Franck–Condon calculations the H—N=N angle in the upper state was calculated to be 132°, or 25 degrees larger than the ground-state value and the increase in the N=N bond length was given as approximately 0·05 Å. As these authors point out, it might be expected that diimide becomes non-planar in its first excited singlet state. However, if the excited state of diimide were non-planar, progressions in the spectra corresponding to excitation of the ν_4' torsional vibration should be observed, but there are no unassigned bands of significant intensity.

The near-ultraviolet absorption spectrum of diimide in liquid ammonia at −50 °C has been measured[151]. At this temperature the diimide and ammonia should exist as a pale yellow liquid. Compared with the gas-phase spectrum, the absorption of diimide in ammonia is shifted to the red by approximately 500 Å, broadened considerably, and the sharp vibrational structure found for the gas phase essentially disappears. These effects are attributed to a strong interaction between ammonia and diimide, possibly through hydrogen bonding. A complementary experiment with diazomethane, in which a much smaller shift to the red was observed, leads Back and Willis to conclude that the bonding of the diimide hydrogens to the NH_3 lone pairs is much more important than the bonding of the NH_3 hydrogens to the lone pairs of azomethane or diimide, which might be expected from the strong intramolecular interaction between the two lone pairs in azo compounds which make them less available for intermolecular interactions.

A brief summary of this section may be both appropriate and useful. The evidence would appear to favour the planar *trans* configuration of diimide as its most stable structure with values for the geometrical parameters as shown:



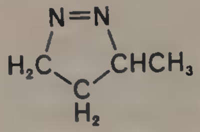
The electronic ground state appears to be a singlet and the first excited state apparently possesses a planar structure with an N=N—H angle widened to 132°.

3. Theoretical studies

The first theoretical studies of diimide were those of Walsh[133] and Wheland and Chen[134]. The results and conclusions of these authors have been briefly described in the previous section and only brief additional references will be made to them here. In 1953, Walsh[133] predicted from the number of electrons in the molecule for the then unknown N_2H_2, a planar bent ground state, existing in either a *cis* or a *trans* form. Wheland[134] could not distinguish between the *cis* and *trans* forms because of the assumptions made in his calculations, but he did find the most stable NNH angle to be about 100° and an activation energy of 33 kcal/mol for the *cis–trans* isomerization.

The spectroscopic studies in the mid-60's on the structure of diimide prompted Alster and Burnell[152] to carry out extended Hückel (EXH) calculations on the *cis–trans* thermal isomerization of N_2H_2. They considered three possible activated complexes: (i) an asymmetric bent structure in which one NNH angle was held at 180° while the other NNH angle was varied to produce the most stable configuration (lowest electronic energy), (ii) a 90° twisted structure in which one NNH bond is held at 90° to the second NNH bond and both angles are varied to minimize the energy, (iii) the linear N_2H_2 structure. The NN and NH bond distances were held fixed at 1·22 and 1·03 Å, respectively. Values of 128° in the *cis*, *trans* and asymmetric bent geometries and 143° in the 90° twisted structure for the NNH angle were found to minimize the energy. Energy differences from the *cis* form, which these calculations predicted to be of lowest energy, are 8·5, 11·6, 16·6 and 20·6 kcal/mol for the *trans*, asymmetric bent, 90° twist and linear forms, respectively. Hence the 8·5 kcal/mol corresponds to the *cis–trans* transition energy and the remaining values to the predicted activation energies for the isomerization of the *cis* form.

Very shortly after, Robin and coworkers[153] published the results of their work on the electronic states of azoalkanes. They performed *ab initio* calculations in a Gaussian-type orbital (GTO) basis with limited configuration interaction, and, in addition, measured the electronic spectra of a series of *trans*-azoalkanes, R—N=N—R, where R was CH_3, C_2H_5, $(CH_3)_2CH$ and $(CH_3)_3C$, also *trans*-difluorodiazirine and one *cis*-azoalkane, 3-methyl-1-pyrazoline,



In their calculations, *cis*- and *trans*-HN=NH were taken to have planar structures with ∠NNH = 112°39′, $D(N—H)$ = 1·021 Å and $D(N=N)$ = 1·240 Å. Two basis sets were employed, a conventional 'energy-minimized' gaussian basis and an augmented GTO basis. The authors note that it appears that the energy-minimized basis yields excited states of unusually high energies due to a neglect of the tails of the wavefunctions. It is predicted that in the case of *trans*-diimide, the lowest excited triplet state will lie below the singlet ground state when calculated in the energy-minimized basis, but 2 eV above it when calculated in the augmented basis. Consequently their calculations primarily employed the augmented basis. Ionization potentials of 10·97 and 10·46 eV were calculated for *cis*- and *trans*-diimide, respectively, compared to the Foner and Hudson[128] value of 9·85 eV.

Gordon and Fisher[154], as part of a study of the isomerization mechanism of diazacumulenes using the INDO method, examined diimide and difluorodiimide. In both cases the *cis* form was found to be thermodynamically more stable than the *trans* form by 4·5 and 4·1 kcal/mol for diimide and difluorodiimide, respectively. Activation energies of 46 and 72 kcal/mol are predicted for inversion and rotation on one nitrogen, respectively, if only singlet states are involved with diimide. A triplet isomerization proceeding by a rotation around the double bond has a calculated activation energy of 40 kcal/mol for diimide. For difluorodiimide the calculated singlet and triplet activation energies are 68 and 52 kcal/mol, respectively.

SCF–LCAO–MO calculations using Gaussian functions and employing the IBMOL program with a basis set consisting of 9s and 5p for N and C and 4s for H were reported by Lehn and Munsch[155]. The bond lengths of diimide were taken from the results of Blau and Hochheimer[136] and the NNH bond angles were optimized. The results are given in Table 23. The *trans* form is found to be more stable than the *cis* by 10·5 kcal/mol. Thermal *trans*-to-*cis* isomerization by inversion at one nitrogen (activation energy of 50 kcal/mol) is predicted, the activation energy for rotation around the N=N bond being substantially higher at 84·1 kcal/mol. Veillard, Lehn and Munsch[156] had pointed out earlier that nitrogen inversion is accompanied by a 2s → 2p electronic population transfer at the inverting nitrogen atom. With diimide a decrease of approximately 0·3 and 0·1 electron was observed for the nitrogen 2s and hydrogen (on the inverting nitrogen) 1s populations, respectively. Simultaneously the population of the nitrogen 2p orbital lying in the direction of the lone pair increases by 0·47 electron. From a comparison of population changes on inversion in other molecules the authors conclude that a high inversion barrier corresponds to a large population transfer.

TABLE 23. Computed angles and energies for diimide[155]

Symmetry groups	Conformation	Optimized NNH angle	Total energy (hartree)	Energy barriers (kcal/mol)
C_{2h}	*trans*	70°	−109·924240	
C_{2V}	*cis*	63°	−109·907558	*cis–trans* = 10·5
C_h	bent (b)	68°	−109·844374	b-*trans* = 50·1
$D_{\infty h}$	linear (l)	0°	−109·737979	l-*trans* = 116·9
C_2	perpendicular (perp)	56° [a]	−109·790334	perp-*trans* = 84·1

[a] Angle not optimized.

Schaad and Kinser (SK)[157] point out that diimide gives *cis* addition of hydrogen to a double bond, which is usually interpreted in terms of a cyclic transition state, which seems to imply a *cis* structure for diimide or perhaps an easy interconversion between the *cis* and *trans* forms. With this in mind, calculations were done employing a minimal basis of Slater-type orbitals (1s for each hydrogen and 1s, 2s, $2p_x$, $2p_y$, $2p_z$ for each nitrogen and carbon atom) expressed in terms of normalized gaussian functions. In their calculations on the various forms of diimide, SK optimized bond angles and bond lengths. The same conformations of diimide as those studied by Lehn and Munsch[155] were also considered by Schaad and Kinser, except that in place of the perpendicular form, a twisted form with a variable out-of-plane angle was employed. Only the closed-shell singlet states of the electronic configurations were considered.

Table 24 shows the results of Schaad and Kinser for the various configurations. When the configurations yielding the lowest energies had been found, the bond lengths and angles were varied to minimize the energy of that configuration. The lowest energy configurations found were:

cis: $(1a_1)^2(1b_2)^2(2a_1)^2(2b_2)^2(3a_1)^2(4a_1)^2(1b_1)^2(3b_2)^2$

trans: $(1a_g)^2(1b_u)^2(2a_g)^2(2b_u)^2(3a_g)^2(3b_u)^2(1a_u)^2(4a_g)^2$

Table 24 summarizes the values of the total electronic energy and bond angles and lengths for the optimum geometries. The table indicates that the *trans* structure is 7·6 kcal/mol lower in energy than that of the *cis* and the lowest energy path for the *trans–cis* isomerization involves the bent conformation with an activation energy of 72·4 kcal/mol. These authors employ group frequencies to calculate statistical mechanical values of various thermodynamic functions. It turns out that the ΔG_{298} value for *cis–trans* isomerization is 7·5 kcal/mol yielding a value of $2{\cdot}7 \times 10^5$ (25 °C) for the equilibrium constant, $K = [trans]/[cis]$, which implies that approximately $2{\cdot}2 \times 10^{18}$ molecules of *cis* isomer are present per mole. Hence, double bond reduction could take place only with the *cis* isomer which is replenished through equilibrium with the *trans* form.

TABLE 24. Total electronic energy and geometrical parameters for conformation of N_2H_2 [157]

Conformation	Electronic energy (kcal/mol)	Bond lengths (Å)		Bond angles	
		NN	NH	NNH	φ*
cis	−66,844·1	1·27	1·13	112°	0°
trans	−66,851·7	1·28	1·13	104°	180°
linear	−66,654·9	2·28	2·77	180°	—
twisted	−66,767·6	2·53	2·24	105°	90°
bent	−66,779·1	2·42	2·42 2·08	115° 180°	—

Wong and coworkers[158] performed LCAO–MO–SCF calculations employing a basis set of Gaussian lobe atomic wavefunctions on *trans*-diimide, *cis*-diimide and 1,1-dihydrodiazine in the expected closed-shell, ground-state, electronic configuration with full geometry optimization. In addition they made additional calculations for an open-shell configuration using one of Trombetti's experimentally measured geometries for *trans*-diimide. A summary of their results is given in Table 25. The *in situ* adjusted Gaussian lobe function calculations referred to in the table involve the determination of the long-range components of the 2s and 2p groups of nitrogen by the SCF procedure. The extended Gaussian lobe function calculation makes use of a basis in which a one-component s orbital and three one-component p orbitals centred at the middle of the NN axis have been added as supplementary functions.

Examination of the wavefunctions and coefficients of the molecular orbitals (MO) shows that the first two MO's are nitrogen 1s orbitals, and the remainder could approximately represent one σ_{NN} bond, two σ_{NH} sp^2 bonds, two sp^2 lone pairs, and one pure P_x NN bond.

TABLE 25. Results of Wong, Fink and Allen[158] for diimide

Basis set	Structure	Bond lengths		Bond angle	$E_{tot.}$
		NN	NH	HNN	(hartree)
SCF–LCAO–GLO	*trans*[a]	2·370	1·90	102·5°	–109·93017
in situ adjusted	*cis*[a]	2·353	1·91	115·5°	–109·92913
	$H_2N^+{=}N^-$[b]	2·403	1·89	122°	–109·92233
Extended GLO	*trans*	2·260	1·90	102·5°	–109·95274
	cis	2·353	1·91	115·5°	–109·94423
	$H_2N^+{=}N^-$	2·423	1·90	122°	–109·94145
Open shell	*trans*	2·340	2·01	109°	
^1B_g					–109·79297
^3B_g					–109·81556
Closed shell	*trans*	2·340	2·01	109°	
^1A_g					–109·9340

[a] Same electronic configurations as given by Schaad and Kinser[157].

[b] $(1A_1)^2(2A_1)^2(3A_1)^2(4A_1)^2(1B_2)^2(5A_1)^2(1B_1)^2(2B_2)^2$.

It is instructive to examine the ground-state molecular-orbital symmetries and order of occupancy. The $^1B_1$ of $H_2N^+{=}N^-$ and *cis*-N_2H_2. $1A_u$ of *trans*-N_2H_2 are all $2p_x\,\pi$ bonded molecular orbitals. The $2B_2$ in $H_2N^+{=}N^-$ is a pure $2p_z$ bonded with hydrogen atoms. In $3B_2$ of *cis*-N_2H_2, $4A_g$ of *trans*-N_2H_2, the molecular orbitals are hybrid orbitals mixing $2p_y$, $2p_z$, 2s, 1s of nitrogen and bonded to hydrogen atomic orbitals.

The theoretically predicted ionization potentials for *trans*-diimide, *cis*-diimide and 1,1-dihydrodiazine are 10·87, 10·84 and 9·95 eV, respectively, which may be compared with the experimental value of 9·85 eV [128]. Use of the relation

$$E(\text{binding}) = E(\text{total}) - \sum_i E_i\,(\text{atom})$$

where $\sum_i E_i\,(\text{atom}) = -109{\cdot}77432$ hartree for N_2H_2 yields binding energies of 4·85, 4·62 and 4·55 eV for *trans*-diimide, *cis*-diimide and $H_2N^+{=}N^-$, respectively. Hence all these species are predicted by Wong and coworkers to be possible, although diimide is thermodynamically unstable with respect to $N_2 + H_2$, as shown by Schaad and Kinser[157]. From Table 25 it is readily seen that the calculated order of stability places *trans*-diimide first, followed by *cis*-diimide, then $H_2N^+{=}N^-$ followed by the *trans* form in the triplet state. Hence a planar, *trans* structure for a ^1Ag electronic ground state is favoured.

Tinland[159] applied the CNDO/S method[160] to the *cis* and *trans* forms of diimide with the geometries of Robin and coworkers[153]. The computed ionization potentials of *cis*- and *trans*-diimide are 12·61 and 11·96 eV, respectively, and it is predicted that the *trans* form is more stable than the *cis* form by 0·47 eV. The general features of the shape of diimide, molecular energy levels and simple molecular orbital pictures as determined by extended Hückel calculations are presented by Gimarc[161]. Gimarc also makes use of symmetry arguments in discussing probable *cis–trans* isomerization mechanisms. In the *trans* isomer of N_2H_2, the highest occupied orbital is $3a'_g$ while in the *cis* isomer it is $2b_2$. On rotation from *trans* to *cis* through the non-planar transition state, the *trans* $3a'_g$ orbital moves much higher in energy to become a_2 in the *cis* form. On the other hand, the lowest unoccupied orbital in the *trans* form is b''_g which falls in energy to become $2b_2$ in the *cis* form on rotation from *trans* to *cis*. Hence the orbitals cross, and consequently the electrons in the highest occupied orbital ($3a'_g$) of *trans*-diimide, on rotation from *trans* to *cis* through the non-planar transition state, would have to transfer to the b orbital, which falls during rotation, to avoid moving to the higher energy. As Gimarc points out, this would be a violation of the principles of conservation of orbital symmetry[162]. In the C_s pathway the a, b symmetry is lost and $3a'_g$ can be converted directly to $2b_2$. Hence the planar C_s transition state for the N_2H_2 isomerization is strongly favoured since the linear state can be excluded on energetic grounds and the non-planar rotation by symmetry conditions.

The $n \rightarrow \pi^*$ transition energies and one-electron orbital energies for the *cis* and *trans* forms of diimide, as obtained from *ab initio* minimal basis SCF–CI calculations, are reported by Ditchfield and coworkers[163]. The minimal basis set of Slater-type atomic orbitals (STO) is replaced by a sum of four gaussian-type functions, one such sum for each STO. Wavefunctions, ψ_i^l, describing singly excited configurations are formed from the ground-state wavefunction by promoting electrons from doubly occupied orbitals ψ_i to virtual orbitals ψ_l. Mixing of configurations representing different singly excited virtual states is then performed. These authors calculate that the *trans* isomer should be more stable than the *cis* for the ground states.

Since the azo group contains two pairs of non-bonding electrons, there are two possible $n \rightarrow \pi^*$ transitions, although only one low-energy u.v. band is generally observed. If diimide exists in the *trans* form, then a relatively strong interaction between the lone pairs will occur, and consequently a large splitting in the energies of the two *n* orbitals, and finally two $n \rightarrow \pi^*$ transitions of quite different energies. Ditchfield and coworkers find a splitting between the two *n* orbitals of approximately 5–6 eV and 2·5–3·5 eV in the *trans* and *cis* compounds, respectively. The two $n \rightarrow \pi^*$ transitions in the *trans* compound are separated by about 6 eV, but only 2 eV in the *cis* compound. Values reported for the transition energies for diimide are 4·37 and 3·37 eV for *cis* and *trans* forms, respectively, to be compared with Trombetti's experimental value of 3·55 eV for the *trans* structure.

Genson and Christoffersen[164], continuing their work on *ab initio* calculations by a technique employing molecular fragments and employing the floating spherical gaussian orbitals of Chu and Frost[165] as basis functions, applied this method to a number of nitrogen-containing molecules, including diimide. Bond lengths of 2·30 and 1·911 bohr for N—N and N—H bond distances, respectively, were used. They too find that the *trans* form is the more stable with energy of −93·56754 hartree compared to −93·56048 hartree for the *cis* form. The value of $E(cis) - E(trans)$ was calculated as 4·52 kcal/mol.

Ab initio calculations were performed with the IBMOL-5 program, using a gaussian-type basis, on 1,1-dihydrodiazine and on *cis*- and *trans*-diimides by Wagniere[166]. The geometry of Robin and coworkers[153] was employed, namely $r(\text{NN}) = 1{\cdot}240$ Å, $r(\text{NH}) = 1{\cdot}021$ Å, $\angle(\text{NNH}) = 112°39'$. Calculations involved two basis sets (I and II), one with 11s and 7p on nitrogen and 6s on hydrogen contracted to a (5, 3/2) set, the other (II) with the same contracted basis, augmented by polarization functions in the plane of the molecule, p_x and p_y, on each hydrogen atom, and by diffuse s, p_x, p_y, p_z functions on each nitrogen atom. The lowest energies were, of course, obtained with basis set II and are listed below for the lowest closed-shell state:

cis-Diimide	– 109·96639 hartree
trans-Diimide	– 109·98092 hartree
1,1-Dihydrodiazine	– 109·95317 hartree

Calculations by Wagniere[166] on the excited states of the three molecules showed that the $^3A_2$ state of 1,1-dihydrodiazine lies 0·090 eV in energy below that of the closed-shell state $^1A_1$ (basis set II).

Hariharan and Pople[167] have carried out *ab initio* calculations intended to examine the influence of polarization functions on molecular orbital hydrogenation energies, and in so doing have used a 4–31G basis set, a 6–31G basis set and a 6–31G basis set with polarization functions added. The 4–31G set has an s inner-shell function which is a linear combination of four s-type gaussian functions and a valence shell (s and p) represented by inner (three-gaussian) and outer (one-gaussian) parts. For hydrogen, similar (31) s-type functions are used. The 6–31G basis set differs from the 4–31G set in improvement of the inner-shell function. Then a set of six single (uncontracted) d-gaussian functions is added to the 6–31G set for heavy atoms, the hydrogen functions being unmodified. This set is labelled 6–31G*. The basis set called 6–31G** is arrived at from the 6–31G* set by adding three p-polarization functions on each hydrogen atom. Bond lengths of 1·25 Å and 0·99 Å for NN and NH, respectively, 109·47° for the NNH bond angle, and the *trans* conformation, were employed for diimide. Total energies as follows were calculated with the various basis sets (hartree):

6–31G	– 109·92792
6–31G*	– 109·99123
6–31G**	– 109·99768

These values may be compared with – 109·81102 and – 109·79320 hartree for *trans*- and *cis*-diimide obtained earlier with the 4–31G set[168]. For the complete hydrogenation reaction

$$HN{=}NH + 2\,H_2 \longrightarrow 2\,NH_3$$

they calculated the following energies (kcal/mol):

4–31G	– 90·7
6–31G	– 91·0
6–31G**	– 81·4

Hence these authors suggest that the addition of d-functions (6–31G → 6–31G*) produces an energy lowering per N atom (in N_2H_2) or 19·9 kcal/mol while the inclusion of p-functions on hydrogen (6–31G* → 6–31G**) lowers the energy per hydrogen atom by 2·0 kcal/mol (for N_2H_2).

Baird and Swenson[169] have used the closed-shell SCF–LCAO–MO method with a minimal basis of Slater-type orbitals each represented by a linear combination of three gaussian-type orbitals (STO–3G) to calculate various properties of diimide in the ground, $^1(n, \pi^*)$, $^3(n, \pi^*)$ and $^3(\pi, \pi^*)$ states. In their work all N—H bond lengths were taken as 1·01 Å and the two H—N—N angles were assumed to be equal, while the N—N distance, the H—N—N bond angle, and the dihedral angle between the two N—H bonds were taken as variables. An absolute minimum is claimed for the *trans* conformation, with the *cis* isomer 5 kcal/mol higher in energy. Optimized geometries were obtained for the *trans*, *cis*, bent and twisted forms and these are shown in Table 26. A value of 98° was found for the dihedral angle of the twisted form at the maximum in their potential energy curves. Activation energies of 60 and 84 kcal/mol were found for the *trans* to *cis* isomerization through the planar and rotational transition states, respectively. These authors note also that the N—N bond lengths in the planar excited states, $^1(n, \pi^*)$ and $^3(n, \pi^*)$, do not differ greatly from those in the ground state, and attribute this to the fact that the highest occupied molecular orbital (HOMO) in both *cis* and *trans* diimide is N—N antibonding, so that removal of an electron from the n-MO of *cis* diimide increases the N—N overlap population by 0·21, which almost compensates for the decrease of 0·29 due to single occupancy of the π^* MO. As they also point out, ionization of the least tightly bound electron would be expected to produce a decrease in the central bond distance for diimide and azo compounds, an effect not often observed in polyatomic molecules.

TABLE 26. Optimized geometries (Å and degrees) for diimide[169]. Reproduced by permission of the National Research Council of Canada from the *Canadian Journal of Chemistry*, **51**, 3097–3101 (1973)

	trans		*cis*		Twisted		Bent	
State	N—N	Angle H—N—N	N—N	Angle H—N—N	N—N	Angle H—N—N	N—N	Angle H—N—N
Ground	1·21	109	1·21	115	1·24	124	1·21	110
$^1(n, \pi^*)$	1·26	121	1·22	133	1·22	127	1·24	116
$^3(n, \pi^*)$	1·26	120	1·22	132	1·26	117	1·24	118
$^3(\pi, \pi^*)$	1·42	105	1·42	114	1·36	128	1·38	108

It is interesting to note that Back, Willis and Ramsay[150], from their absorption spectral data and Franck–Condon calculations, predicted that the $^1(n, \pi^*)$ state of diimide would have an N—N bond length increased by 0·05 Å and an HNN angle 25° larger than the ground-state value, for the *trans* form. Baird and Swenson[169] calculated 0·05 Å and 12° for the corresponding increases, providing reasonably satisfactory agreement.

Calculations show that *trans* to *cis* isomerization through a rotational mechanism is preferred for both the $^3(n, \pi^*)$ and $^1(n, \pi^*)$ states of diimide with the activation energies being zero for both states, compared to 25 and 23 kcal/mol, respectively, for passage through the planar transition state. Rotational isomerization for the $^3(\pi, \pi^*)$ state should be symmetry-forbidden, and the *trans* to *cis* barriers are calculated to be 71 and 65 kcal/mol for the rotational and planar transition states, respectively.

In the course of analysing the photoelectron spectra of a number of azo compounds, Brogli and coworkers[170] have performed some extended Hückel and MINDO/2-type calculations on *cis*- and *trans*-diimide. From the latter type of calculations they have shown that the splitting for the nitrogen lone-pair orbital energies passes through a maximum at about 120° for the N—N—H angle in the *trans* form but a minimum at about 100° for the *cis* form. This appears to be supported, in part, by their spectral data. Gimarc[161] argued that such behaviour in *cis*-azo groups is due to a 'through-bond' interaction of the n_+-orbital with a lower lying N—N σ-orbital.

Merényi and coworkers[171] used the program REFLECT, which employs a basis set of gaussian orbitals, in this case four s-type orbitals on each hydrogen atom and seven s-type and three p-type on each nitrogen atom, to calculate barriers to rotation and inversion for diimide and its protonated form. The geometry of Lehn and Munsch[155] was used. Their results are summarized in Table 27. With both diimide and protonated diimide the inversional barrier is lower than the rotational barrier for isomerization, but the corresponding barriers for the protonated form are lower than those for the unprotonated form.

TABLE 27. Effect of protonation on the energies and barriers to rotation and inversion of diimide[171]

Form	Total energy (hartree)	Barrier (kcal/mol)
H—N=N—H		
trans	−109·8175	
cis	−109·8033	8·9(*c*–*t*)
planar bent	−109·7348	51·9[a]
twisted	−109·7044	71·0
H_2N^+=NH	−110·1360	
planar bent	−110·0880	30·1
twisted	−110·0325	64·9

[a] Relative to the energy of the *trans* isomer.

An extensive study[172] by means of *ab initio* SCF and CI methods has been carried out on both the ground and excited states of diimide for the purpose of investigating the ultraviolet spectrum of this molecule. The NN and NH distances were held fixed at 1·238 Å and 1·065 Å, respectively[158], and the NNH bond angle was varied from 90° to 170° for a variety of electronic configurations. An absolute minimum was obtained for the *trans* form with an energy of −109·9345 hartree, first ionization potential of 10·78 eV and *cis–trans* energy difference of 12·6 kcal/mol. A barrier to isomerization of 109 kcal/mol was calculated for the ground state by employing a linear configuration for the transition state.

The most recent reports of theoretical studies on diimide appear to be that of Vasudevan and coworkers[172], mentioned previously, and that of Winter and Pitzer[173]. In the latter work, both NH and NN bond distances and the NNH bond angle were varied to achieve a geometry optimization to 0·01 bohr and 0·3° for the bond distances and angle, respectively. Hartree–Fock calculations employed the 9S5P/4S gaussian basis set of Huzinaga[174] contracted to a [4s3p/2s] basis by Dunning[175]. A summary of geometries, energies and energy differences for all calculations of these and previous workers is shown in Table 28.

Ahlrichs and Staemmler[176] have published the results of *ab initio* calculations on the structure and geometry of the three isomers of N_2H_2, including 1,1-dihydrodiazine, and using gaussian basis sets with polarization functions. These authors refer to the work of Carlotti and coworkers[146] and Frost and coworkers[177] as establishing experimentally that diimide possesses a singlet ground state in a planar *trans* configuration. The latter authors have studied the photoelectron spectrum of N_2H_2 and conclude that they are probably observing the molecule in the singlet ground state.

The calculations of Ahlrichs and Staemmler, the results of which are summarized in Table 28, account for electron correlation by means of a configuration interaction (CI) computation based on the pair natural orbitals (PNO) of the respective pair correlation functions (PNO CI). This treatment is stated by these authors to be essentially equivalent to a configuration interaction calculation in which all doubly substituted configurations have been included with the Hartree–Fock function. In

TABLE 28. Geometries and energies for *cis*- and *trans*-diimide

Author		R_{NN} (Å)	R_{NH} [Å)	θ_{NNH} (degs)	E (hartree)	ΔE (kcal/mol) (*cis–trans*)	E_{act} (kcal/mol) (from *trans* form)	Reference
Wheland				100*			33	134
Alster and Burnelle		1·22	1·03	128*		8·5	12	152
Robin, Hart and Kuebler		1·240	1·021	112·7*				153
Gordon and Fisher						4·5	46 (i); 72 (r)	154
Lehn and Munsch	*cis*	1·230	1·014	117*	−109·9076	10·5	50 (i); 84 (r)	155
	trans	1·230	1·014	110*	−109·9242			
Schaad and Kinser	*cis*	1·27*	1·13*	112*	−106·5245	7·6	72 (i)	157
	trans	1·28*	1·13*	104*	−106·5365			
Wong, Fink and Allen	*cis*	1·245*	1·011*	115·5*	−109·9291	0·7		158
	trans	1·254*	1·005*	102·5*	−109·9302			
Wong, Fink and Allen	*cis*	1·245*	1·011*	115·5*	−109·9442	5·3		158
	trans	1·196*	1·005*	102·5*	−109·9527			
Tinland		1·240	1·021	112·7		10·8		159
Genson and Christoffersen	*cis*	1·217	1·011		−93·5605	4·5		164
	trans	1·217	1·011		−93·5675			
Wagniere	*cis*	1·240	1·021	112·7	−109·9664			166
	trans	1·240	1·021	112·7	−109·9809			
Radom, Hehre and Pople	*cis*	1·25	0·99	109·5	−109·7932	11·2		168
	trans	1·25	0·99	109·5	−109·8110			
Hariharan and Pople	*trans*	1·25	0·99	109·5	−109·9977			167
Baird and Swenson	*cis*	1·21	1·01	115	−108·5598	5	60 (i); 84 (r)	169
	trans	1·21	1·01	109	−108·5678			
Merényi, Wettermark and Roos	*cis*	1·230	1·014	117	−109·8033	8·9	52 (i); 71 (r)	171
	trans	1·230	1·014	110	−109·8175			
Vasudevan *et al.*	*cis*	1·238	1·065	111*	−109·9144	12·6	109 (linear *trans* state)	172
	trans	1·238	1·065	111*	−109·9345			
Winter and Pitzer	*cis*	1·238*	1·025*	116*	−109·9401	8·2		173
	trans	1·239*	1·017*	110*	−109·9531			
Ahlrichs and Staemmler	*trans*	1·207*	1·021*	109*	−110·3755	5·8	55	176
	cis	1·207*	1·032*	114*	−110·3665			

i = inversion; r = rotation; * = optimized variable.

addition, the coupled electron-pair approximation was employed to approximate the effect of unlinked cluster terms arising from the doubles (CEPA). The energy values given in Table 28 are those arising through the use of CEPA. Not included in the table are their values for H_2NN which are 1·221 Å, 1·012 Å, and 122·3° for the NN and NH distances and NNH angle, respectively. Their best energy for the triplet (ground) state of H_2NN is −110·3341 hartree (CEPA).

Ahlrichs and Staemmler find the *trans* isomer to be the most stable isomer with the *cis* isomer and H_2NN approximately 5·8 and 26·0 kcal/mol above the *trans* form. In addition their CEPA calculations yield a value for ΔE of 59·6 kcal/mol for the reaction

$$N_2H_2\ (\textit{trans}) \longrightarrow H + N_2 + H$$

so that the isomerization apparently competes with this process. Further, their value of 55 kcal/mol for the barrier to the *trans–cis* isomerization suggests that such isomerization is unlikely to be the first step of the decomposition of N_2H_2

$$2\ N_2H_2 \longrightarrow N_2H_4 + N_2$$

Unpublished work from this laboratory[178], in which a variety of molecules containing the NN bond have been compared using an STO–3G basis, will be referred to in more detail later. While not yielding energy values of Hartree–Fock quality, such calculations do have the advantage of being relatively inexpensively extended to larger molecules, thus permitting a comparison of a larger number of molecules possessing the NN bond. With this method, an energy of 7·3 kcal/mol was calculated for the *trans* to *cis* isomerization, with the *trans* possessing the lower energy of the two forms.

C. Disubstituted Diimides

1. N_2F_2

a. *Theoretical studies.* Next to diimide itself, probably the most studied diimide, from the point of view of theoretical calculations, has been difluorodiimide.

Extended Hückel calculations were employed by Kaufman and coworkers[179] to examine some properties of molecules containing nitrogen and fluorine, among them being *cis*- and *trans*-N_2F_2. The values given by Sanborn[188] for the structural parameters were used. Calculated N—F overlap populations of 0·34 and 0·32 for the *trans* and *cis* forms, respectively, and 1·09 and 1·16 for that of the N=N bond in the *trans* and *cis* forms, respectively, indicated that the N—F distance in *trans*-N_2F_2 should be shorter than that in *cis*-N_2F_2, while the N=N distance in *cis*-N_2F_2 should be shorter than that in *trans*-N_2F_2. In addition, their calculated total electronic energies suggested that the *cis* form should be more stable than the *trans*.

Ray and Narasimhan[180] have utilized extended Hückel theory to study the transition state in the isomerization of *trans*-N_2F_2 to *cis*-N_2F_2. The structural data of Bohn and Bauer[201] were employed in the calculations. Configurations generated by rotating one NF bond around the NN axis were considered. Two types of *trans* configurations were examined, one (T) in which the experimentally observed bond lengths and angles of the *trans* form were used, and the other (T′) in which those of the *cis* form (C) were employed. Likewise C′ refers to a hypothetical *cis* form in which the *trans* bond lengths and angles are used. Linear configurations, LT and LC, were also considered, in the former the N—N and N—F bond lengths of *trans*-N_2F_2 were used, while in the latter those of the *cis* form were employed.

Table 29 summarizes the calculated values of electronic energy. The calculated binding energy for *trans*-N_2F_2, 255·4 kcal/mol is in good agreement with the experimental value of 244·3 kcal/mol[193]. The *cis* (C) configuration is predicted to be more stable than the *trans* (T) by approximately 15 kcal/mol, compared with 3 kcal/mol found experimentally (Armstrong and Marantz). The T′ and C′ configurations have higher energies than the respective T and C forms. Barrier heights in the isomerization of *trans*- to *cis*-N_2F_2 are shown in Table 30. According to the results of extended Hückel calculations, of the three transition-state configurations considered, that achieved by a rotation around the N=N bond possesses the lowest energy.

TABLE 29. Total electronic energies for N_2F_2 as found by EXH method[180]

Configuration	Total energy (eV)	Binding energy (kcal/mol) Calculated	Binding energy (kcal/mol) Observed[193, 207]
T	−539·4168	255·41	244·3
C	−540·0626	270·33	247·3
T′	−539·1941		
C′	−539·6203		
LT	−531·7076		
LC	−531·8146		

TABLE 30. Barrier heights for *trans* → *cis* isomerization of N_2F_2 [180]

Transition state	Barrier height (kcal/mol)
rotation	47
LT	178
LC	176

Gordon and Fisher[154] have utilized the CNDO and INDO methods of Pople and coworkers[181] to calculate energies and structural parameters for N_2F_2, the latter being obtained by minimizing the energy. As can be seen from Table 31, the *trans* form is found to be 4·1 kcal/mol higher in energy than that of the *cis* form, in good agreement with the experimentally derived value of 3·0 kcal/mol found by Armstrong and Marantz[193]. If only singlet states are involved in the isomerization of *cis*- to *trans*-N_2F_2, then activation energies of 68 and 85 kcal/mol for inversion and rotation on one nitrogen, respectively, are found. If the transition form exists in a triplet state, then it is predicted that the lowest activation energy, 52 kcal/mol, will be achieved through rotational isomerization. In the singlet and triplet rotational transition states, dihedral angles of 100° and 70°, respectively, were calculated.

CNDO/2 calculations have also been performed on N_2F_2 by Herndon and coworkers[182]. Geometry optimization was also employed and gave 1·26 Å for the N—F distance in both the *cis* and *trans* forms (experimental: *cis*, 1·41 Å; *trans*, 1·40 Å[201]); and 112° and 109° for the FNN angle in the *cis* and *trans* molecules respectively (experimental: *cis*, 114°; *trans*, 106°[201]). In view of these results, these

TABLE 31. Total relative electronic energies and energy-optimized structural parameters for N_2F_2 as found with the CNDO and INDO methods[154]

State	Form	Geometrical parameters				Relative energy (kcal/mol)
		Bond lengths (Å)		Bond angles (degrees)		
		N—F	N=N	∠FNN	Dihedral	
Singlet	linear	1·25	1·20	—	—	143·8
Triplet	linear	1·25	1·20	—	—	128·6
Triplet	*cis*	1·23	1·30	111	0	98·5
Triplet	bent	1·25 (1·23)[a]	1·26	115	—	94·0
Singlet	*trans*	1·24	1·24	132	100	85·0
Singlet	bent	1·24 (1·23)[a]	1·22	114	—	67·7
Triplet	*trans*	1·24	1·27	119	180	66·7
Triplet	*trans*	1·24	1·30	113	70	52·0
Singlet	*trans*	1·25	1·25	109	180	4·1
Singlet	*cis*	1·25	1·24	116	0	0·0

[a] Bond lengths in brackets refer to the N—F lengths at the N—F which is bending.

workers varied the value of the β constant for fluorine in the CNDO method to bring the experimental and theoretical N—F distances for the *trans* into coincidence. Table 32 summarizes their results, which do not differ greatly from those of Gordon and Fisher[154] except in predicting an activation energy of 81·1 kcal/mol for the inversion mechanism.

Gimarc[161] applied the extended Hückel method to N_2F_2 and discussed the results primarily from the point of view of the molecular orbitals involved and the shapes of the molecule. For molecules like N_2F_2 which possess 24 valence electrons, the highest occupied orbitals for linear geometry would be the doubly degenerate upper

TABLE 32. CNDO/2 results for N_2F_2 [182] using adjusted β_F value of 14·07

Form	Geometrical parameters				Symmetry	Relative energy (kcal/mol)
	Bond lengths (Å)		Bond angles (degrees)			
	N—F	N=N	∠FNN	Dihedral		
trans	1·40	1·19	144	180	C_{2h}	155·2 (max)
linear	1·45	1·15	180	—	$D_{\infty h}$	106·8
trans	1·40	1·23	110	95	C_2	85·70 (max)
trans	1·393	1·19	112, 185	180	C_s	81·10 (max)
trans	1·40	1·23	110	90	C_2	79·65
bent	1·393 (1·393)	1·19	112	—	C_s	75·40
1,1-Difluoro	1·40	1·19	133	—	C_{2v}	39·0 (min)
trans	1·395	1·22	105	180	C_{2h}	3·14 (min)
cis	1·40	1·21	114	0	C_{2v}	0·00 (min)

π_g orbitals, $\pi_g(x)$ and $\pi_g(y)$. These are completely antibonding, being composed of p atomic orbitals antiparallel to each other, and each would contain a single electron only. The degeneracy of these $\pi_g(x)$ and $\pi_g(y)$ orbitals is removed when the molecule bends, the two levels becoming a_2 and b_2 for *cis*, and b_g'' and a_g' for *trans* bending, and these four orbitals can now contain p_z and s atomic orbitals as well as p_x or p_y. When *cis* bending occurs, the energy of the a_2 level changes very little from that of the $\pi_g(y)$, but the energy of the b_2 level decreases substantially below that of the linear $\pi_g(x)$, because the lower lobes of the F atom p_x atomic orbitals move from antibonding positions into favourable bonding positions with respect to the neighbouring N atom p_x orbitals. On the other hand, when *trans* bending occurs, b_g'' remains similar in energy to $\pi_g(y)$, but the a_g' level is lower in energy than $\pi_g(x)$, since the p_x orbitals on the F atoms move into bonding positions with respect to their neighbouring N atoms. As Gimarc points out, it is then the b_2(*cis*) and a_g'(*trans*) energy levels which give *cis* and *trans* shapes to N_2F_2.

In discussing the isomerization of N_2F_2, Gimarc notes that the rotational mechanism involves the crossing of highest filled and lowest unoccupied a and b orbitals. The principle of conservation of orbital symmetry consequently forbids the rotational mechanism. In the inversional mechanism the highest-filled a_g' orbital can convert into b_2 because a,b symmetry is lost.

Turner[183] has used the CNDO theory to calculate the total electronic energies of the *cis* and *trans* forms of N_2F_2 as a function of bond angle between 90° and 125°. Minimum energies of −78·6953 and −78·6958 hartree were found at 110° and 105° for the *cis* and *trans* forms, respectively. Within the limits of error of the calculation the energies are the same. The calculated rotational barrier (*trans* → *cis*) is 85·1 kcal/mol. Turner suggests, since no significant change occurs in the population analysis in passing from the *trans* to the *cis* form, that the origin of the barrier is probably not due to any alteration in chemical bonding but is simply an atom–atom repulsion.

The method and results of *ab initio* minimal basis SCF–CI calculations performed by Ditchfield and coworkers[163] on diimide have been discussed in a previous section. The same paper reported −11·4 and 5·67 eV for the energies of the *n* and π^* orbitals of *cis*-N_2F_2, and −10·05 and 5·87 eV for the corresponding orbitals of *trans*-N_2F_2, yielding vertical singlet $n \rightarrow \pi^*$ transition energies of 5·75 and 4·22 eV for the *cis* and *trans* forms, respectively.

Brundle and coworkers[184] have employed photoelectron spectroscopy and *ab initio* gaussian orbital calculations to study the effect of the substitution of fluorine for hydrogen in a planar molecule, which has been shown, at least in some cases, to have a much larger stabilizing effect on the σ MO's than on the π MO's. There is some difficulty in studying diimide and difluorodiimide for this purpose, as these authors point out, since there are no photoelectron data for *trans*-diimide and the photoelectron spectrum of *trans*-N_2F_2 may contain bands due to an isomeric impurity. However, Table 33 summarizes their calculated and experimental ionization potentials for these two molecules. The highest MO in N_2F_2, $7a_g$, contains some N—F σ-antibonding character in addition to the N—N antibonding lone-pair component. The agreement between the calculated energy of 13·92 eV and the experimental, 13·4 eV, is quite good. What the authors refer to as the perfluoro shift, or simply the change in orbital energies on substitution of fluorine for hydrogen, is +3·6 eV for the $4a_g$–$7a_g$ orbital pair. The $1a_u$ π MO of N_2H_2 is calculated to possess an energy of 13·07 eV, which correlates with the $2a_u$ level of N_2F_2 at 14·24 eV (calc.). The $1a_u$–$2a_u$ shift then is approximately +1·1 eV.

Companion and Hsia[185] have employed a bicentrically rescaled, energy-partitioned, version of the CNDO/2 method in a study of atomization of a variety of nitrogen fluoride molecules, including N_2F_2. The geometrical data of Bohn and Bauer[201] were employed. Calculated values for the heats of atomization were 217·1 and 216·0 kcal/mol for the *trans* and *cis* forms respectively, which may be compared with the experimental values[186] of 251·6 and 254·9 kcal/mol for the *trans* and *cis* forms, respectively. The electron affinity and first ionization energy were calculated as 2·00 and 14·62 eV for N_2F_2.

TABLE 33. Observed and calculated ionization potentials (eV) for N_2H_2 and *trans*-N_2F_2 [184]. Reprinted, with permission, from Brundle and coworkers, *J. Amer. Chem. Soc.*, 94, 1451 (1972). Copyright by the American Chemical Society

N_2H_2		N_2F_2			
Orbital	0·92 K.T.[a]	Orbital	0·92 K.T.[a]	Adiabatic IP	Vertical IP
$4a_g$	9·84	$7a_g$	13·92	12·8	13·4
$1a_u$	13·07	$2a_u$	14·24	13·65	14·1
$3b_u$	15·97	$6b_u$	16·60		
$3a_g$	17·42	$6a_g$	17·50		
$2b_u$	23·93	$1b_g$	18·57		
$2a_g$	34·80	$1a_u$	19·80	18·0	18·70
$1b_u$	391·4	$5b_u$	20·20		19·80
$1a_g$	391·5	$5a_g$	20·39		21·0
		$4b_u$	24·06	22·3	22·7
		$4a_g$	35·8		
		$3b_u$	42·4		
		$3a_g$	43·5		
		$2b_u$	396		
		$2a_g$	396		
		$1b_u$	661		
		$1a_g$	661		

[a] 0·92 K.T. refers to 92% of the value as given by Koopmans' theorem.

b. *Spectra and structure.* The electron diffraction pattern of a sample of N_2F_2 was determined in 1947 by Bauer[187], who assumed a 50–50% mixture of *cis* and *trans* isomers, and fitted the data with N—F and N=N bond lengths of 1·44 and 1·25 Å, respectively, and FNN bond angle 115°. Sanborn[188] prepared large amounts of N_2F_2 by maintaining an electric discharge in a stream of nitrogen trifluoride in the presence of mercury vapour. Two fractions were obtained by gas chromatographic separation on a silica-gel column held at a low temperature, each with a molecular weight of 66, but with quite different chemical reactivity. One fraction reacted with mercury and explosively with diborane, while the other did not, and the infrared spectra of the two fractions were different. Sanborn, from his infrared data, decided that the inactive form was *trans*-1,2-difluorodiazine (τ-1,2-DFD) and the active form was suggested to be 1,1-difluorodiazine (1,1-DFD). For the fraction suggested to be τ-1,2-DFD, three fundamental vibrations (cm^{-1}) of symmetry A_g (1010; N—F symmetric stretch; 1636, N=N stretch; 592, N=N—F symmetric bend), one of A_u (360, torsion) and two of B_u (989, N—F asymmetric stretch; 421, N=N—F asymmetric bend) were identified. On the other hand, 1,1-DFD gave three A_1 fundamentals (896, N—F symmetric stretch; 1524, N=N stretch; 552, F—N—F symmetric bend), one B_2 (737, out-of-plane bend) and two B_1 (952, N—F asymmetric stretch; 573, F—N—F symmetric bend). Sanborn provided chemical, mass spectral, dipole moment and infrared spectral evidence for the identification of his 'active' fraction of N_2F_2 as 1,1-DFD and not *cis*-1,2-difluorodiazine.

Ettinger and coworkers[189] agreed with Sanborn that the less active (lower boiling, −111·4 °C) isomer was the *trans* configuration, but argued that the structure of the more active (higher boiling, −105·7 °C) isomer was much more in doubt, for a variety of reasons. They provided alternative interpretations for Sanborn's experimental data and, in addition, noted that n.m.r. spectra of both the high- and low-boiling isomers showed only one nitrogen resonance, while two nitrogen resonances might be expected for 1,1-DFD. They noted also that the dipole moment change for the N=N stretching mode is not along the axis of the least moment of inertia, but is along an axis of intermediate moment. Consequently, a *cis* isomer as well as a 1,1-isomer could show only PR structure. Sanborn[190] while conceding that the shapes of the infrared bands did not preclude a *cis* isomer, insisted that the infrared band at 737 cm^{-1} in 'active' N_2F_2 must be a fundamental vibration, and can only be a bending fundamental, which would be, he argued, out of position for a *cis* isomer, but fitting perfectly for 1,1-DFD.

Herron and Dibeler[191], in their mass spectrometric study of N_2F_2, measured the appearance potentials of $N_2F_2^+$, N_2F^+ and NF^+ from the *trans* isomer as 13·1, 13·9 and 17·0 eV, respectively, while those from what they considered to be the *cis* isomer were, for N_2F^+ and NF^+, 14·0 and 16·9 eV, respectively. The *cis* isomer apparently does not produce a parent ion. Hence the appearance potentials of the normal fragment ions N_2F^+ and NF^+ are identical within experimental uncertainty (±0·2 eV) for both *cis*- and *trans*-N_2F_2. Herron and Dibeler reasoned that this information suggested a similarity in molecular structure and hence favoured the identification of the 'active' isomer as *cis*-1,2-DFD rather than 1,1-DFD. Heats of formation for the *cis* and *trans* isomers were reported as 16·4 and 19·4 kcal/mol, respectively with associated bond dissociation energies D(FN=NF) as 106 and 103 kcal/mol, respectively.

Measurements of the ^{19}F chemical shifts and splittings for the two isomers of N_2F_2 were reported by Noggle and coworkers[192]. An analysis of the $^{19}F\text{-}\{^{14}N\}^{13}$ double-resonance spectra for the reactive isomer indicated that both nitrogens in the molecule have the same chemical shift, thus providing strong evidence in favour of the *cis* structure for the 'active' isomer. Calculated and observed spectra agreed quite well when the *cis* and *trans* structures were assumed.

The heats of formation of the two isomeric forms of N_2F_2 were measured calorimetrically by Armstrong and Marantz[193], by reacting the N_2F_2 with ammonia.

$$N_2F_2(g)+8/3\ NH_3(g) = 2\ NH_4F(C)+4/3\ N_2(g)$$

Mean heats of reaction of 211·7 and 209·2 kcal/mol were measured for the *trans* and 'active' isomers, respectively. The difference in the heats of reaction of the two samples, adjusted for the purity of the samples, yields a heat of isomerization (active $\rightleftarrows$ *trans*), $\Delta H^0_{f298} = 3{\cdot}0$ kcal/mol, indicating that the 'active' form is more stable thermodynamically than the *trans* form. Use of $\Delta H^0_{f298}[NH_3(g)] = -11{\cdot}04$ kcal/mol[194], and $\Delta H^0_{f298}[NH_4F(c)] = -111{\cdot}0$ kcal/mol[195], produces values of 19·4 and 16·4 kcal/mol for ΔH^0_{f298} of the *trans* and 'active' isomers of N_2F_2, respectively. Armstrong and Marantz calculate the total binding energy of *trans*-N_2F_2 to be 244·3 kcal/mol, which, with the use of 107·9 kcal/mol for E(N=N), yields a value of 68·2 kcal/mol for E(N—F).

The microwave spectrum of the 'active' isomer of N_2F_2 was measured by Kuczkowski and Wilson[196], who concluded that the structure was planar and *cis* with NN and NF bond lengths of 1·214 and 1·384 Å, respectively, and FNN angle of 114·5°. A dipole moment of 0·16 D was obtained from the rotational Stark effect. Thus, by 1963, the evidence in favour of the *cis* structure for the 'active' isomer seemed strongly to outweigh any other previously held conclusion.

The gas-phase infrared and liquid-phase Raman spectra of *trans*-N_2F_2 has been measured by King and Overend[197], with the following vibrational assignments: $\nu_{NN} = 1522$, $s\nu_{NF} = 1010$, $s\delta_{NF} = 600$, $a\nu_{NF} = 990$, $a\delta_{NF} = 423$ and torsion = 363·5 cm^{-1}. These authors note that their assignment of the infrared spectrum is essentially the same as that of Sanborn[188]. In a subsequent paper[198] these same authors restudied some of the bands at higher resolution to obtain estimates of the rotational constants, which values are consistent with the values of Bauer[187] from electron diffraction measurements.

The Raman spectrum of gaseous *trans*-1,2-difluorodiazine has been reported by Shamir and Hyman[199]. The three symmetric vibrations were obtained and assigned as 1018 cm^{-1}, N—F symmetric stretch; 1523 cm^{-1}, N=N stretch, and 603 cm^{-1}, N=N—F symmetric bend, which agree quite well with those found by King and Overend[197] for the liquid, where in all cases the liquid-phase values are lower than those in the gas phase, as might be expected.

The Raman spectrum of *cis*-N_2F_2 was also measured by King and Overend[200]. A summary of their data, together with that of other workers, is given in Table 34.

TABLE 34. Vibrational assignment of *cis*- and *trans*-N_2F_2

cis-N_2F_2 (gas)[200]				*trans*-N_2F_2					
						Frequency (cm^{-1})			
		Frequency (cm^{-1})	Description			Gas[199]	Liquid[198]	Calc.[188]	Description
A_1	ν_1	1525	ν_{NN}	A_g	ν_1	1523	1522	1636	ν_{NN}
	ν_2	896	ν_{NF}		ν_2	1018	1010	1010	ν_{NF}
	ν_3	341	δ_{NF}		ν_3	603	600	592	δ_{NF}
A_2	ν_4	(550)	Torsion	A_u	ν_4	362	363·5	360	Torsion
B_1	ν_5	952	ν_{NF}	B_u	ν_5	990	990	989	ν_{NF}
	ν_6	737	δ_{NF}		ν_6	420	423	421	δ_{NF}

Bohn and Bauer[201] have determined the structures of *cis*- and *trans*-1,2-difluorodiazine from electron diffraction measurements, using sectored-microdensitometer data. The geometric configurations and interatomic distances were found to be essentially the same as those previously estimated on the basis of the visual technique. Table 35 records the structural parameters from the work of Bohn and Bauer[201] and Kuczkowski and Wilson[196]. The N=N and N—F distances as obtained by Bohn and Bauer[201] are similar to those expected for other molecules with N=N and N—F bonds. However, in the *trans* isomer, ∠NNF = 105·5° is surprisingly small. With the *cis* compound there is agreement between the two sets of data shown in Table 35 for the N=N bond distance and ∠NNF but not for the N—F bond distance. But the major structural difference between the *cis* and *trans* isomers is the larger ∠NNF in the former compound. This can be rationalized on the basis of a repulsion between the two F atoms in the *cis* isomer which are about 1 ångström closer together than in the *trans* form. The N=N bond length is also somewhat shorter in the *cis* form, while the N—F distance is slightly longer in the *cis* form.

Calculations of vibrational coupling effects and potential functions of both the *cis* and *trans* isomers have been made by Pearce and Levin[202] who employed the structural parameters of Bohn and Bauer[201], and compared their calculated results with the experimental data[198, 199, 200]. Calculated and observed frequencies agreed quite well in all cases.

TABLE 35. Structural parameters for *cis*- and *trans*-N_2F_2

	trans-N_2F_2	*cis*-N_2F_2	
	Bohn and Bauer[201]	Bohn and Bauer[201]	Kuczkowski and Wilson[196]
N=N (Å)	1·230	1·214	1·214
N—F (Å)	1·396	1·410	1·384
N · · · F (Å)	2·093	2·209	
F · · · F (Å)	3·339	2·381	
∠NNF (deg)	105·5	114·4	114·5

c. *Thermochemical properties*. Colburn and coworkers[203] were the first to report on the properties of N_2F_2. Their values for a variety of physical properties are given in Table 36. For comparison purposes the table is augmented by the data given in the review paper of Pankratov[204]. Colburn and coworkers[203] considered the *cis* isomer to be chemically more reactive, yet Lustig[205] found that the isomerization of the *trans* to the *cis* isomer took place below 100 °C nearly quantitatively in a static system. Lustig[205] points out that this isomerization is consistent with the heats of formation of Armstrong and Marantz[193] (see Table 36), which indicates that the *cis* isomer is thermodynamically more stable.

TABLE 36. Physical properties of *cis* and *trans* difluorodiimide[203]

	trans-Difluorodiimide	*cis*-Difluorodiimide
Vapour pressure	$\log P_{\text{torr}} = (-742{\cdot}3/T)+7{\cdot}470$	$\log P_{\text{torr}} = (-803{\cdot}0/T)+7{\cdot}675$
Boiling point (°C)	−111·4	−105·7
Heat of vaporization (cal/mol)	3400	3670
Critical temperature (°C)	−13	−1
Critical pressure, estimated (atm)	55	70
Melting point (°C)	−172	below −195
Heat of isomerization (kcal/mol)		27·5 ± 5·0 (est)[203]
Heat of formation ΔH_f^0 (kcal/mol)	19·4 [193]	16·4 [193] 25·3 [204] 20·5 (−105 °C) [204]

Pankratov[204] has determined the heat of formation of the 'active' *cis* isomer of N_2F_2 from reaction with acid potassium iodide solution. He obtained 25·3 ± 2·0 kcal/mol at 25 °C and 20·5 ± 2·0 kcal/mol at −105·7 °C (for the liquid isomer). Pankratov calculates a dissociation energy of 97·5 kcal/mol for the N=N bond in the *cis* isomer by using 61·14 kcal/mol for the heat of formation of NF and his value for N_2F_2.

d. *Kinetics of isomerization.* Binenboym and coworkers[206] have carried out experiments designed to provide information on the *cis–trans* isomerization of difluorodiimide under homogeneous conditions. As has been mentioned, the isomerization is catalysed by heated metal reaction vessels, and difluorodiimide also attacks glass at elevated temperatures. In the study by Binenboym and coworkers, N_2F_2, highly diluted in argon was heated in a single-pulse shock tube. Since the tube walls remain cold, the reaction can be studied under homogeneous conditions. The isomerization was studied between 297 and 342 °C and at pressures up to 1·6 atm. Vapour phase chromatography was employed to calculate *cis* and *trans* concentrations. The isomerization was identified as first-order with rate constants given by

$$k = 10^{14} \exp(-32{,}200/RT)\ \mathrm{sec}^{-1}$$

These authors point out that the pre-exponential factor is high and similar to that found with the carbon–carbon double-bond system[207]. However, their calculations of the energy required to decouple the π-bond overlap yielded 84 kcal/mol, much higher than their experimental value of 32 kcal/mol. Hence they conclude that the isomerization cannot take place by rotation and a decoupling of the π-bond overlap so that the transition state presumably retains its double-bond character. They tentatively suggest that a linear configuration in the transition state may be consistent with their results.

Apparently no further work on the *trans–cis* isomerization was done until, in 1974, Vedeneev and collaborators[208] reported on experiments done in a Teflon reactor from 100 to 150 °C and at initial *trans*-N_2F_2 pressures of 15, 25 and 32 torr. They report that an autoaccelerated reaction begins when the first trace of *cis*-N_2F_2 is formed. Values of $\Delta H = -2070 \pm 145$ cal/mol and $\Delta S = -1{\cdot}55 \pm 0{\cdot}37$ e.u. were obtained.

2. Tetrazene

Wiberg and coworkers have recently reported on the preparation[209] of tetrazene, N_4H_4, and its photoelectron spectrum[210] resulting from their earlier work on azo compounds.[211] Discussion of the work contained in the latter reference would lead us too far outside the domain of this volume.

These authors believe that N_4H_4 is $H_2N{-}N{=}N{-}NH_2$, probably, at least with their methods of preparation, in the *trans* form. Thermal decomposition produces N_2 and hydrazine by one route or alternative rearrangement to ammonium azide $NH_4^+\ N_3^-$, the former in about 75% yield and the latter 25%. Gaseous tetrazene is unstable at room temperature, whereas decomposition of solid tetrazene begins at approximately 0 °C. Their assignments of the bands of the photoelectron spectrum, plus CNDO/S calculations lead to the following orbitals and energies: π_3(8·51 eV), n_+(10·13 eV), π_2(11·67 eV), n_-(13·92 eV) and π_1(14·44 eV).

D. Monosubstituted Diimides

1. Introduction

Relatively little work, of either theoretical or experimental nature, had been reported on the physicochemical properties of the interesting molecules, $R{-}N{=}N{-}H$, until quite recently. A review[212] has been published in 1971 by Kosower. He states that, up to 1965, there were no reports of the direct observation of a monosubstituted diimide, although there were many descriptions of reactions in which $R{-}N{=}N{-}H$ had been invoked as an intermediate. Monosubstituted diimides (i) are oxygen sensitive, (ii) disappear via bimolecular reaction and (iii) react (often) with base. It is claimed that methyldiimide is the only monosubstituted diimide that can be readily isolated in pure form.

2. Spectra and structure

Absorption data are reported by Kosower for the monosubstituted diimides. The $n \rightarrow \pi^*$ bands fall between 3490 and 3750 Å for unconjugated systems and between 4030 and 4175 Å for conjugated compounds. Kosower notes that the absorption coefficients are all very low, between 18 and 100, thus implying a trans structure for all diimides listed. The $n \rightarrow \pi^*$ transition for trans $CH_3N{=}NCH_3$ appears at 3430 Å[212], while that for $CH_3N{=}NH$ is given as 3610 Å, thus suggesting that alkyl substitution for hydrogen may decrease the n^+–n^- splitting.

Steinmetz[213] has measured the microwave spectrum of CH_3NND, the deuterated species being used because of its higher stability than the hydrogen species. The deuterated species can be stored at liquid nitrogen temperature without decomposition, whereas the hydrogen species will still decompose at this temperature. To obtain a structure the HCN angle and CH bond length were assumed to be 109·5° and 1·09 Å, respectively and values of 1·24, 1·47 and 1·014 Å were taken for the NN, CN and NH bond lengths, after consideration of other similar compounds. This permitted angles CNN and NNH to be calculated as 112 and 110°, respectively. A methyl group rotational barrier of 1665 ± 40 cal/mol was also calculated.

Ackerman and coworkers[214–215] have measured the infrared spectra (4000–200 cm^{-1}) of methyldiimide and its deuterated forms, in the gas phase, condensed phase (77 K), and in nitrogen matrices (20 K), and have made the following assignments (deuterated species in brackets): N—H stretch at 3130 (2320), N=N stretch at 1575 (1550) and the N—H out-of-plane bend at 844 cm^{-1} (662). The N—H stretch agrees with that found for *trans* diimide[143]. It is interesting to note, however, that the N—H out-of-plane bends in diimide itself have been assigned at 1359 cm^{-1} (N_2H_2) and 999 cm^{-1} (N_2D_2)[144], much higher than those for the monosubstituted molecules.

Tentative assumptions[214] of geometrical parameters for methyldiimide were:

N—H	1·014 Å	∠NNH	110°
C—H	1·093 Å	∠HCH	109·5°
C—N	1·470 Å	∠HCN	109·5°
N=N	1·240 Å	∠CNN	110°

By comparing their results with those for *trans*-diazene, Ackerman and coworkers[214–215] concluded that the *trans* form can be expected to be the most stable structure of methyldiimide.

3. Theoretical studies

Very few calculations of any type have been reported in the literature for monosubstituted diimides. This is somewhat surprising since some relatively simple monosubstituted diimides, whose existence has not yet been verified experimentally, could be studied with advantage from a theoretical point of view. Of course the experimentally known monosubstituted diimides may still be too large for inexpensive theoretical work.

Ditchfield and coworkers[163], in their work discussed in an earlier section, have calculated the *n* and π^* orbital energies and singlet $n \rightarrow \pi^*$ transition energies for a number of monosubstituted diimides. Their results are summarized in Table 37. Using their standard geometry, Ditchfield and coworkers found that the *trans* isomer should be more stable than the *cis* in the ground state, with the energy difference between the two forms decreasing in the order $CH_3 > H > NH_2 > OH > F$.

TABLE 37. n, π^* Orbital energies and singlet $n \rightarrow \pi^*$ transition energies (eV) for RN=NH molecules[163]

R	ε_n	ε_{π^*}	$\Delta E(n \rightarrow \pi^*)$ Calculated	$\Delta E(n \rightarrow \pi^*)$ Observed (λ_{max})
CH_3 (*cis*)	−9·30	6·68	4·63	
NH_2 (*cis*)	−9·92	6·83	5·72	
HO (*cis*)	−10·05	6·42	5·54	
F (*cis*)	−11·14	5·67	5·75	
CH_3 (*trans*)	−8·64	6·88	3·58	3·45–3·55[212]
NH_2 (*trans*)	−9·98	6·32	4·37	
F (*trans*)	−10·05	5·87	4·22	
HO (*trans*)	−9·98	6·32	4·37	

In both the *cis* and *trans* monosubstituted diimides, the $n \rightarrow \pi^*$ transition (the lowest of two is reported) is shifted to higher energy in order $CH_3 < HO < NH_2 < F$ for the *cis*, and $CH_3 < F < HO < NH_2$ for the *trans*, although the differences for the highest three energies in the *trans* series is small. As Ditchfield and coworkers point out the changes of the *n* and π^* orbital energies resulting from σ withdrawal are more important than the π-donating effects.

Again, as with diimide itself, the existence on the azo group of two pairs of non-bonding electrons gives rise to two possible $n \rightarrow \pi^*$ transitions. However, only one low-energy u.v. band is usually observed. If the molecules have a *trans* structure, a strong interaction will exist between the lone pairs, which gives rise to a large splitting in the energies of the two *n* orbitals, and consequently two $n \rightarrow \pi^*$ transitions of very different energies. Ditchfield and collaborators find the splitting between the two *n* orbitals to be approximately 5–6 and 2·5–3·5 eV in the *trans* and *cis* isomers, respectively, thus supporting this explanation. The two $n \rightarrow \pi^*$ transitions are separated by approximately 6 and 2 eV in the *trans* and *cis* compounds. Consequently, it would be expected that the second $n \rightarrow \pi^*$ transition in the *trans* isomers will be in a much different region of the u.v. spectrum.

Merényi and coworkers[171], in their work described in a previous section, have performed *ab initio* calculations on $CH_3N{=}NH$ and its protonated form for the purpose of obtaining barriers of rotation and of inversion. Their results are reproduced in Table 38. In addition, a proton affinity of 212·5 kcal/mol and a π-orbital energy of −0·468 hartree were calculated for the *trans* form. The high values for the barrier of inversion with $CH_3N{=}NH$ are attributed to the orbital associated with the lone pair of electrons.

In this laboratory[216], we have employed the Gaussian 70 programme[29] and a minimal STO-3G basis set to calculate the total electronic energies of a number of mono- and di-substituted diimides in their *cis* and *trans* configurations. In all cases the nuclear configurations were optimized to ±0·001 Å for bond lengths and ±0·1 for bond angles. Table 39 summarizes the optimized values for the various bond

TABLE 38. Total electronic energies of $CH_3N{=}NH$ and $CH_3N{=}NH_2^+$ in various configurations[171]

Molecule	Configuration	Total energy (hartree)	Barrier (kcal/mol)
$CH_3N{=}NH$	*trans*	−148·8032	7·8
$CH_3N{=}NH$	*cis*	−148·7907	
$CH_3N{=}NH$	Invertomer (H inverts)	−148·7193	52·6 (from *trans*)
$CH_3N{=}NH$	Invertomer (CH_3 inverts)	−148·7297	46·1 (from *trans*)
$CH_3N{=}NH_2^+$		−149·1419	
$CH_3N{=}NH_2^+$	Invertomer	−149·1030	24·4
$CH_3N{=}NH_2^+$	Rotamer	−149·0371	65·8

TABLE 39. Calculated structural parameters[a] of mono- and di-substituted diimides

	Bond lengths			Bond angles		
Molecule	NN	NX	XH	NNX	NCH	HCH
HNNH (*trans*)	1·267	1·061		105·3		
HNNH (*cis*)	1·263	1·064		111·4		
HNNH (invert)	1·246	1·082		108·0		
		1·006[b]		(182·0)		
$H_3C{-}N{=}N{-}CH_3$ (*t*)	1·268	1·514	1·089	109·6	109·8	109·3
$H_3C{-}N{=}N{-}CH_3$ (*c*)	1·264	1·513	1·088	119·2	109·8	109·0
$H_3C{-}N{=}N{-}CH_3$ (i)	1·247	1·549	1·088	111·4	110·0	109·0
		1·432[b]	1·096	(182·0)	110·2	109·1
$CH_3{-}N{=}N{-}H$ (*t*)	1·268	1·060 (NH)		104·8 (NNH)		
		1·515 (NC)	1·089 (CH)	109·9 (NNC)	109·6	109·6
$CH_3{-}N{=}N{-}H$ (*c*)	1·263	1·066 (NH)		111·0 (NNH)		
		1·517 (NC)	1·089 (CH)	115·6 (NNC)	109·5	109·5
$CH_3{-}N{=}N{-}H$ (i)	1·250	1·082 (NH)	1·096 (CH)	107·6 (NNH)	109·5	109·5
on CH_3		1·436 (NC)[b]		(183·0) (NNC)		
$F{-}N{=}N{-}F$ (*t*)	1·282	1·371 (NF)		106·1 (NNF)		
$F{-}N{=}N{-}F$ (*c*)	1·277	1·373 (NF)		111·5 (NNF)		
$F{-}N{=}N{-}F$ (i)	1·250	1·398 (NF)		109·2 (NNF)		
		1·351 (NF)[b]		(182·0) (NNF)		
$NC{-}N{=}N{-}H$ (*t*)	1·277	1·062 (NH)		104·2 (NNH)		
		1·446 (NC)		109·5 (NNC)		
		1·159 ($C{\equiv}N$)		109·5 (NNC)		
$NC{-}N{=}N{-}H$ (*c*)	1·273	1·064 (NH)		111·9 (NNH)		
		1·447 (NC)		115·3 (NNC)		
		1·159 ($C{\equiv}N$)				
$F{-}N{=}N{-}H$ (*t*)	1·270	1·056 (NH)		104·0 (NNH)		
		1·370 (NF)		107·4 (NNF)		
$F{-}N{=}N{-}H$ (*c*)	1·264	1·065 (NH)		108·7 (NNH)		
		1·372 (NF)		110·6 (NNF)		
$NC{-}N{=}N{-}CN$ (*t*)	1·281	1·441 (N—C)		109·1 (NNC)		
		1·160 ($C{\equiv}N$)				
$NC{-}N{=}N{-}CN$ (*c*)	1·281	1·440 (N—C)		117·4 (NNC)		
		1·160 ($C{\equiv}N$)				

[a] Bond lengths in Å and bond angles in degrees.
[b] Bond length of inverting NX.

lengths and angles. As can be seen from the table, in the cases of diimide and dimethyldiimide calculations were also performed on the invertomers. By bending one of the NX bonds where X is either H or CH_3, the bend angle corresponding to the top of the energy barrier was located. Optimization of the nuclear geometry was then done with this bend angle (normally approximately 180°) held fixed.

The total electronic energies (including nuclear repulsion) and the transition energies for the *cis* to *trans* isomerizations are given in Table 40. It can be seen that these calculations predict that the *trans* (singlet) form will be the more stable of the two, *cis* and *trans*, for all the molecules examined except N_2F_2. In the case of N_2F_2, although other data are not entirely conclusive, nevertheless the evidence available points to the *cis* isomer as the more stable form (see Section III.C.1.a–c). However the calculated isomerization energy given in Table 40 is suspiciously small. We used the optimized N_2F_2 geometry from Table 39 and calculated, using an extended basis (6–31G), for the *cis* and *trans* forms of N_2F_2, energies of −307·441691 and −307·440781 hartree, respectively, corresponding to an isomerization energy of about 0·6 kcal/mol. This is still much smaller than the 3·0 kcal/mol value of Armstrong and Marantz[193] or the 2·1 kcal/mol obtained by Vedeneev and coworkers[208]. The calculated inversion energy of 62·1 kcal/mol is also much higher than the experimental value of 32·2 kcal/mol[206].

TABLE 40. Calculated electronic energies for mono- and di-substituted diimides

Molecule	Energy (hartree)	Transition energies (kcal/mol)
HNNH (*trans*)	−108·55696	(*trans to cis*) +7·3
HNNH (*cis*)	−108·54525	
HNNH (invert)	−108·45100	$(66·5)_{t\to i}$
CH_3NNCH_3 (*t*)	−185·72658	+6·8
CH_3NNCH_3 (*c*)	−185·71578	
CH_3NNCH_3 (i)	−185·62762	$(62·1)_{t\to i}$
CH_3—N=N—H (*t*)	−147·14214	+5·2
CH_3—N=N—H (*c*)	−147·13388	
CH_3—N=N—H (invert on CH_3)	−147·04272	$(62·4)_{t\to i}$
F—N=N—F (*t*)	−303·44088	−0·1
F—N=N—F (*c*)	−303·44102	
F—N=N—F (i)	−303·30685	$(84·2)_{c\to i}$
NC—N=N—H (*t*)	−199·09309	+6·1
NC—N=N—H (*c*)	−199·08341	
F—N=N—H (*t*)	−206·00450	+1·1
F—N=N—H (*c*)	−206·00281	
NC—N=N—CH (*t*)	−289·62259	+6·6
NC—N=N—CH (*c*)	−289·61203	

The results of our calculations for methyldiimide predict that the *trans* isomer is more stable than the *cis* by approximately 5·2 kcal/mol which agrees reasonably well with the conclusions of Merényi and coworkers although their total electronic energies reflect the higher quality of their wavefunctions. However, their CH_3 inversion energy of 46·1 kcal/mol is much lower than our 62·4 kcal/mol.

The results of very similar calculations have just been published by Howell and Kirschenbaum[217] and, as expected, our results agree quite well with the results of these authors.

IV. DIAZONIUM COMPOUNDS

A. Introduction

A number of books concerned, at least partially, with diazonium compounds have appeared in the last 25 years. Of these, two, one by Saunders[218], and the other by Zollinger[1], were published prior to 1965. More recently, Overberger and colleagues[2], have discussed organic compounds with nitrogen–nitrogen bonds and have included a section on diazonium salts. A chapter on carbonium ion formation from diazonium ions, written by Friedman[219], is contained in the series on carbonium ions by Olah and Schleyer.

The reactivity and stability of arenediazonium ions have been reviewed recently by Zollinger[220], and the diazotization of heterocyclic primary amines, has been discussed by Butler[221]. Porai-Koshits[4] summarized the current state of the problem of the structure and reactivity of aromatic diazo compounds.

Most textbooks refer to diazonium salts as ionic compounds in which the diazo group is bonded to an aromatic residue, so that the diazonium ion is the appropriate cation. It was originally believed[1] that aliphatic diazonium salts are incapable of existence. There are, however, evidences that stable non-aromatic diazonium salts can be prepared[222] and olefin diazonium compounds are also reported[223].

For the purposes of the present discussion we will consider that any cation of the form RN_2^+ may be properly considered as a diazonium ion. Consequently, the ion $N_2H_2^+$, discussed previously in section III.C, qualifies as the simplest diazonium ion. However most of the subsequent discussion will be concerned with benzenediazonium salts, and cation and monosubstituted forms, since most of the theoretical work has dealt with these compounds.

B. Crystal Structure and Spectroscopic Data

What appears to be the first crystal structure information on diazonium salts was reported in a preliminary short note by Rømming in 1959[224]. This was followed by more-complete data in 1963[225]. A single crystal of benzenediazonium chloride ($C_6H_5N_2Cl$) was examined by X-ray methods. The crystals are orthorhombic, space group C222, with unit cell dimensions: $a = 15{\cdot}152$ Å; $b = 4{\cdot}928$ Å; $c = 9{\cdot}044$ Å. The shortest Cl^- to N distance is 3·225 Å. The space group requires the $N_{(2)}—N_{(1)}—C_{(1)}\cdots C_{(4)}$ atoms to be situated on a two-fold axis of symmetry so the distances between these atoms could be found from one projection normal to this axis. Planes containing chloride ions bisect the N—N bond of the diazonium ions, and every $(N{\equiv}N—)^+$ group is surrounded by four chloride ions in a planar arrangement normal to the N—N axis, two of them are at a distance of 3·184 Å and two at a distance of 3·511 Å from this axis. The distances from the former chloride ions, the connecting line of which runs nearly normal to the plane of the benzene ring, to the $N_{(2)}$ and $N_{(1)}$ are 3·225 Å and 3·237 Å, respectively, where $N_{(1)}$ refers to the nitrogen atom attached to $C_{(1)}$. The corresponding distances from the other set of chloride ions to the $N_{(2)}$ and $N_{(1)}$ atoms are 3·548 Å and 3·559 Å. The latter chloride atoms are approximately in the plane of the benzene ring and are separated from the $H_{(2)}$ atoms by only 2·5 Å. As Rømming points out, this is half an ångström less than the sum of the van der Waals radii, so that a strong interaction is presumed to exist between these atoms.

Classical valence concepts suggest that the $N_{(1)}$ atom is equivalent to the nitrogen atom of an ammonium ion and should carry the positive charge. In the structure studied by Rømming, the distances from the $N_{(2)}$ atom to the chloride ions are nearly equal to, but slightly smaller than, those from the $N_{(1)}$ atom to the chloride ions.

Further, in the case of benzenediazonium chloride, it might be expected that some shift of electron density from $N_{(2)}$ to $N_{(1)}$ might occur. If the shift is substantial enough, the two nitrogen atoms might then share the positive charge, thereby resulting in the approximately equal separations of the two nitrogen atoms from a chloride ion.

Table 41 summarizes the internuclear distances and angles found by Rømming for the benzenediazonium ion. The NN bond length is approximately that found for gaseous nitrogen. The $N_{(1)}-C_{(1)}$ bond is 0·085 Å shorter than the aliphatic N—C bond. The carbon–carbon bonds are all found to be shorter than those in benzene (1·397 Å). The perturbation of the CCC angles is not unexpected as a consequence of the inductive effect of the N_2^+ group. Interestingly, however, the distortion in the diazonium case is more substantial than that found with benzonitrile[226], thereby demonstrating the stronger inductive effect of the N_2^+ group when compared with the nitrile group. Of course, it is well to note that the benzonitrile data to which reference is made were measured in the gas phase.

TABLE 41. Internuclear separations and angles in the benzenediazonium ion[225]

Bond	Length (Å)	Bond	Angle (degrees)
$N_{(1)}-N_{(2)}$	1·097	$N_{(2)}-N_{(1)}-C_{(1)}$	180
$N_{(1)}-C_{(1)}$	1·385	$C_{(1)}-C_{(2)}-C_{(3)}$	117·6
$C_{(1)}-C_{(2)}$	1·374	$C_{(2)}-C_{(3)}-C_{(4)}$	119·8
$C_{(2)}-C_{(3)}$	1·383	$C_{(3)}-C_{(4)}-C_{(5)}$	121·7
$C_{(3)}-C_{(4)}$	1·376	$C_{(6)}-C_{(1)}-C_{(2)}$	124·8

At about the same time, Andresen and Rømming[227] reported on the crystal structure of benzenediazonium tribromide. The compound crystallizes in the monoclinic system with space group C2/c. The tribromide ions are situated in centres of symmetry and the benzenediazonium ions on two-fold axes. The Br–Br bond length is 2·543 Å, and the N—N and N—C bond lengths in the diazonium ion are 1·11 and 1·41 Å, respectively, the latter two agreeing reasonably well with the results found for the chloride. The tribromide ion is centrosymmetric. The bromine–benzene plane separation is 3·68 Å which is approximately 0·10 Å less than the sum of the van der Waals radius for bromine and the half-thickness of the benzene molecule. The shortest distance between a central bromine and a nitrogen atom is 4·34 Å. However, the shortest distance from any bromine atom to any nitrogen atom is 3·31 Å, where the nitrogen atom is $N_{(2)}$, that is, an outer nitrogen, and the particular Br here is believed to carry the negative charge. This suggests that $N_{(2)}$ carries a substantial positive charge, again in agreement with Rømming's conclusions for benzenediazonium chloride.

Rømming and Waerstad[228] isolated the crystalline, orange-red complex of a diazonium salt and cuprous halide obtained from a Sandmeyer reaction at low temperature and in concentrated solution, and found it to consist of normal benzenediazonium ions and ($Cu_2Br_3^-$) ions. Each of the 'inner' nitrogen atoms, $N_{(1)}$, is surrounded by four bromine atoms lying in a plane approximately perpendicular to the C—N—N direction with a nitrogen to bromine distance of 3·65 Å.

Although extension of the present discussion to so-called double diazonium salts ($ArN_2X \cdot MXn$) may lie outside the intended scope of this chapter, some mention of these compounds should be made for the sake of completeness. Porai-Koshits and coworkers have published the structure of the double salt of ferric chloride and *o*-methoxybenzenediazonium chloride[229] and of *p*-*N*,*N*-dimethylaminobenzenediazonium chlorozincate[230]. In the former case the ionic structure $[o\text{-}CH_3OC_6H_4N_2]^{+}\cdot[FeCl_4]^{-}$ was shown to apply and it was suggested that the positive charge lies primarily on the terminal nitrogen atom, $N_{(2)}$. The length of the $C_{(1)}—N_{(1)}$ bond was measured as 1·48 Å, substantially larger than that found by Rømming for the chloride[225] or the bromide[227]. However the $N_{(1)}—N_{(2)}$ length of 1·11 Å was in agreement with the earlier values. The average distance between chloride ion and nitrogen atom was found to be 3·36 and 3·53 Å, for $N_{(2)}$ and $N_{(1)}$ respectively, again suggesting a concentration of positive charge on the terminal nitrogen atom, $N_{(2)}$.

In the case of *p*-*N*,*N*-dimethylaminobenzenediazonium chlorozincate[230], the structure was found to consist of planar cations $[(CH_3)_2NC_6H_4N_2]^{+}$ and tetrahedral $[ZnCl_4]^{2-}$ anions. In this case no evidence was found for the shortening of the $C_{(2)}—C_{(3)}$ or $C_{(5)}—C_{(6)}$ bonds in the benzene ring, although the $C_{(6)}—C_{(1)}—C_{(2)}$ angle is reported as 130°. Again, although a division of electron density was not possible, the results were interpreted as suggesting that $N_{(2)}$ possesses a positive charge.

C. Theoretical Studies

What appears to be the first calculations done on any diazonium ion were reported by Schuster and Polansky[231] in 1965. π-Bond orders and electron densities as calculated by the Hückel method were given for a number of diazonium ions including that of methyl and phenyl. In all cases for RN_2^+, the nitrogen atom adjacent to the R group had a calculated π density of approximately $+0{\cdot}8$ to $+0{\cdot}9$ while that on the neighbouring nitrogen atom was approximately $+0{\cdot}1$ to $+0{\cdot}2$. Klasinc and Schulte-Frohlinde[232] performed the same type of calculation on a variety of substituted phenyldiazonium ions and established correlations between the rate constants for thermal decomposition of the diazonium ions and the C—N bond orders, and a quantity labelled $(\Delta H)_n$ which is related to the difference between the π-electron energies of the diazonium and corresponding carbonium ion.

Russian workers[233, 234] were also among the first to calculate properties of diazonium ions using Hückel theory. Correlations between absorption energies and the differences in energies between the highest occupied and the lowest unoccupied orbitals were developed.

Evleth and Cox[235] measured the visible-ultraviolet absorption spectra of benzenediazonium, 2-, 3-, 4-methoxybenzenediazonium, 2,4-, 2,5-, 2,6-, 3,4-dimethoxybenzenediazonium, and 2,3,5-, 2,4,5-, 2,4,6-, 3,4,5-trimethoxybenzenediazonium cation in the 200–450 nm region. Hückel theory was employed to calculate transition energies which correlated well with those measured experimentally. The so-called Coulomb and resonance parameters were adjusted to provide the best fit with the first two electronic transitions in the benzenediazonium cation. π-Electron densities of 1·34 and 0·71 were calculated for the adjacent and terminal nitrogen atoms of this cation.

The results of experiments and calculations on the electronic absorption spectra of the benzenediazonium cation and its *p*- and *m*-substituted forms were reported by Sukigara and Kikuchi[236]. The near-ultraviolet absorption spectrum of benzenediazonium fluoroborate in ethanol solution produced two peaks at wavelengths 259 and 295 nm, and molar extinction coefficients 5640 and 1160, respectively, while in aqueous solution the peaks appear at 263 and 298 nm. From their observed fluorescence emission and excitation spectra, these authors concluded that the radiative transition occurs from the same excited state, when the system was excited to the lowest excited singlet state. No emission was observed when the diazonium salt was excited by 259 nm light. The phosphorescence emission spectrum (77 K) was observed only when the diazonium salt solution was excited by a 295 nm light. On the other hand, an e.s.r. signal (77 K, methanol solution) was obtained only when the diazonium salt was irradiated by a 259 nm light. The observed e.s.r. spectrum resembled that obtained for the phenyl σ-radical.

Sukigara and Kikuchi[236] used the earlier X-ray structural data of Rømming[225] in their Pariser and Parr[237] calculations on the benzenediazonium cations. Values of $-2{\cdot}39$ and $-2{\cdot}42$ eV were taken for β_{CC} and β_{CN}, respectively, where

$$\beta_{AB} \equiv \int X_A^*(1)\, H_{core}\, X_B(1)\, dv$$

β_{NN} and ω (the π_x electron density on the nitrogen atom attached to the carbon atom and x is the direction in the plane of the ring and perpendicular to the NN axis) were taken as adjustable parameters whose best values were $-3{\cdot}10$ eV and 1·05, respectively. Sukigara and Kikuchi ascribe the 295 nm and 259 nm absorption bands to the $^1A_1$–$^1B_1$ and $^1A_1$–$^1A_1$ transitions respectively, the calculated transition energies (experimental in brackets) being 4·18 (4·20) and 4·75 (4·79) eV, respectively. They also deduce from their results that the nitrogen atom adjacent to the ring bears almost all of the positive charge of the benzenediazonium cation and that the NN bond order is approximately three.

Sukigara and Kikuchi conclude that two processes occur from the excited $^1B_1$ state, namely, radiative transition to the ground state and intersystem crossing to a phosphorescent state. No detectable photochemical decomposition occurs after the $^1A_1$–$^1B_1$ transition. Since neither fluorescence nor phosphorescence was detected after the $^1A_1$–$^1A_1$ transition, no radiative process occurs from the excited $^1A_1$ state and no internal conversion or intersystem crossing to a radiative state occurs. From this excited state the molecule presumably decomposes rapidly to give phenyl σ-radical.

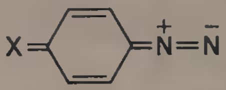
In their second paper, Sukigara and Kikuchi[236] measured the visible and near-ultraviolet absorption spectra of *p*-fluoro, *p*-chloro, *p*-bromo-, *p*-iodo, *p*-methoxy and *p*-dimethylamino-benzenediazonium cations and applied the PP method in their calculations. Table 42 summarizes their experimental results.

TABLE 42. Observed peak wavelengths and molar extinction coefficients for *para*-substituted benzenediazonium cations (aqueous solution)[236]. Reproduced by permission of the Chemical Society of Japan

Substituent	λ_{max} (nm)	log ε_{max}
F	267	4·229
Cl	281	4·195
Br	293	4·178
I	327·5	4·036
OCH_3	315	4·283
$N(CH_3)_2$	380	4·448

In their PP calculations on the *p*-substituted cations, Sukigara and Kikuchi use the electron affinity of the electron-accepting group $-C_6H_4N_2^+$ and the core resonance integrals, β_{CX}, where X = F, Cl, Br, I, O or N, as adjustable parameters. These authors conclude that the strong absorption in the visible and near-ultraviolet regions can be assigned to the $^1A_1$–$^1A_1$ transition, and that the weak absorptions of the $^1A_1$–$^1B_1$ transition are hidden in the large absorption bands of the $^1A_1$–$^1A_1$ transition. The calculations also show the large stabilizing effect that an electron-donating group at the *para* position exerts on the lowest excited $^1A_1$ electronic state. Evidence is also presented to support the contention that the strong absorption bands of the *p*-iodo-, *p*-methoxy- and *p*-dimethylamino-benzenediazonium cations have the character of intramolecular charge-transfer bands, while the strong bands of the *p*-fluoro-, *p*-chloro- and *p*-bromo-benzenediazonium cations are associated with local excitation within the benzenediazonium framework.

In addition, it was shown that the vibrational frequency of the NN group increased linearly with the N—N bond order. Further the N—N bond order decreases and the contribution of charge transfer to the ground state increases with an increase in the electron-donating capability of the substituent group. This suggests that the contribution of a resonance structure



becomes larger in the ground state as the electron-donating capability of the *para* substituent increases. This had previously been predicted by Zollinger[1].

Finally, Sukigara and Kikuchi examined the electronic structures and electronic absorption spectra of *m*-fluoro-, *m*-chloro-, *m*-bromo- and *m*-methoxy-benzenediazonium cations. A summary of their experimental results is given in Table 43.

TABLE 43. The observed peak wavelengths and molar extinction coefficients for *meta*-substituted benzenediazonium cations[236]. Reproduced by permission of the Chemical Society of Japan

Substituent	λ_{max} (nm)	log ε_{max}
F	262	4·160
	308	3·457
Cl	266	4·000
	317	3·299
Br	268·5	3·625
	323	2·972
OCH_3	273·5	3·982
	348	3·475

Treiger and coworkers[238] also applied the PP method to the benzenediazonium cation. Again β_{NN} was taken as an adjustable parameter whose best value was found to be $-4·50$ eV. The nitrogen atom adjacent to the carbon atom was calculated to possess a charge of $+0·58$, while that on the remaining nitrogen atom was $+0·27$ in semi-quantitative agreement with the results of Hückel calculations[233]. These authors note that, in the transition to the excited state with an energy of 4·04 eV ($A_1 \rightarrow B_1$), electron density is transferred from the *ortho* and the *meta* positions of the benzene ring to the diazonium group, resulting in a decrease in bond order of the N—N bond and the positive charge on the diazonium group, while in the case of the transition with an energy of 4·77 eV ($A_1 \rightarrow A_1$) the transfer occurs from the *para* position of the benzene ring.

Treiger and Bagal[239] applied the Pariser–Parr method[237] to a series of substituted benzenediazonium cations in their ground and lowest excited states. As in the work of Sukigara and Kikuchi[236], values of adjustable parameters were obtained by fitting to experimental data for the benzenediazonium cation. A linear correlation was established between the frequencies (2250–2305 cm^{-1}) of the stretching vibrations of the N—N bonds and the calculated values of the π-electronic orders of these bonds for the various substituted benzenediazonium ions. However, the largest deviation from this linear correlation was displayed by those molecules containing electron-donating substituents in the *ortho* and *para* positions, particularly in the case of the methoxy group. The authors suggest that the method of calculation employed is unsuitable when the resonance structure contributes substantially to charge transfer.

Treiger and Bagal[239] also calculated values for some of the electronic transitions and found reasonably good agreement (±0·04 eV) with the experimental values in most cases. These authors conclude that the absorption due to charge transfer in the *para* derivatives proceeds from the 4·71 eV band of the unsubstituted compound, while for the *meta* and *ortho* derivatives it can be referred to the 4·18 eV band.

Quite recently[240] low- and high-energy photoelectron spectroscopy and *ab initio* molecular orbital calculations have been applied to diazocyclopentadiene ($C_5H_4N_2$). It appears that this is the first report either of such experiments or of such calculations on any diazo compound of the form RNN where R is larger than CH_2. Single determinant, all-electron, SCFMO calculations employing a basis of gaussian functions fitted to three Slater-type orbitals were performed on diazocyclopentadiene and its singly ionized states. Bond lengths of 1·130, 1·340, 1·431 and 1·104 Å were taken for N—N, C—N, C—C and C—H, respectively.

Table 44 summarizes the calculated charge distributions of diazocyclopentadiene where $C_{(1)}$ is attached to $N_{(1)}$. The diazo group in this molecule is essentially neutral. However, the nitrogen atom attached to the carbon atom of the ring shows a net increase in its π population compared to that of the nitrogen atom in the nitrogen molecule. This increase is balanced by a decrease in 2s and 2pσ density from that found in N_2. The four remaining carbon atoms not attached to nitrogen each have approximately the same negative charge which is approximately balanced by the positive charge on the attached hydrogen atom. The carbon atom, $C_{(1)}$, attached to nitrogen, has a small net positive charge, and more π but less σ density than the

TABLE 44. Calculated charge distribution of diazocyclopentadiene[240]. Reproduced, with permission, from Aarons and coworkers, *J. Chem. Soc., Faraday Trans. II*, **6**, 1106 (1974).

	$N_{(1)}$	$N_{(2)}$	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$H_{(2)}$	$H_{(3)}$	N (in N_2)
1s	1·995	1·997	1·993	1·994	1·994	0·710	0·714	1·997
2s	1·481	1·818	1·161	1·287	1·299			1·766
2pσ	1·093	1·139	1·547	1·909	1·966			1·236
2pπ	1·192 (1·289)[a]	1·261 (0·740)	1·255	1·093	1·053			2·000
Atomic charge	−0·05	0·05	0·05	−0·28	−0·31	0·29	0·29	0

π-bond overlap populations

$N_{(1)}$–$N_{(2)}$	$C_{(1)}$–$N_{(1)}$	$C_{(1)}$–$C_{(2)}$	$C_{(2)}$–$C_{(3)}$	$C_{(3)}$–$C_{(4)}$	N–N (in N_2)
0·32	0·21	0·13	0·40	0·18	0·50[b]

[a] Values in brackets are for the nitrogen 2p orbital in the molecular plane and are not included in the π overlap populations.

[b] For one π orbital only.

other four carbon atoms. The N—N π-bond overlap population is much smaller in this diazo molecule than in N_2, and the authors interpret the C—C π-bond overlap populations as suggesting that a diene-type structure may be more appropriate than a delocalized one. Finally they regard the bonding as resulting from an initial $\sigma \rightarrow \pi_g$ electron promotion in N_2 followed by π bonding with the five-membered cyclopentadienylidene ring.

Some calculations have been performed in this laboratory[241], using the Gaussian 70 programme[29] with an STO-3G basis, to obtain more information on the diazonium cation. The calculations were done on the benzenediazonium cation and on the same cation with a fluorine substituted at the *ortho*, *meta* or *para* positions of the ring. Rømming's[225] geometry was employed in all cases. The energy decreased as the fluorine was removed from the *ortho* to the *meta* to the *para* position, although as total decrease was only 3 kcal/mol this may not be significant, given the approximate nature of the calculations. What is more interesting, however, is the observation that the charge on the nitrogen atom $N_{(1)}$ attached to the carbon atom is +0·09, while that on the remaining nitrogen atom, $N_{(2)}$, is +0·28. The carbon atom $C_{(1)}$ itself carries a charge of +0·10. No significant change in this distribution of charge is observed when fluorine is attached at any one of the *ortho*, *meta* or *para* positions. In addition, the calculations show that the σ electrons yield contributions to the total charges of $N_{(1)}$ and $N_{(2)}$ of +0·43 and +0·10, respectively while the π electrons produce −0·34 and +0·18, respectively, suggesting that $N_{(1)}$ has a deficiency of σ electrons but a surplus of π electrons. Hence in all cases greater than 50% of the positive charge is distributed around the benzene ring, most of it residing on the hydrogen atoms.

For comparison purposes similar calculations were performed on several diazo compounds, some of which may be hypothetical in the sense that they have not yet been synthesized. Atomic charges obtained are as follows:

	$N_{(1)}$	$N_{(2)}$	$C_{(1)}$
Difluorodiazomethane	−0·15	0·00	+0·36
Fluorodiazomethane	−0·10	−0·01	+0·13
Diazoacetonitrile	−0·02	+0·04	−0·02

In these cases the charge on the nitrogen atom $N_{(1)}$ attached to the carbon atom is much more dependent on the groups attached to the carbon atom.

V. ACKNOWLEDGEMENT

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CHAPTER 2

Diazonium–diazo equilibrium

VOJESLAV ŠTĚRBA

Organic Chemistry Department, Institute of Chemical Technology,
532 10 Pardubice, Czechoslovakia

I. INTRODUCTION

Diazonium ions RN_2^+ (R = substituted arene, alkene, heterocyclic compound, alkane, etc.) are strong Lewis acids. They form covalent bonds with a number of bases with formation of diazo compounds, e.g. benzenediazonium ion with OH^- gives benzenediazohydroxide $C_6H_5N{=}NOH$. Diazo compounds differ from azo compounds, such as azomethane $CH_3N{=}NCH_3$, in that the base is bound to nitrogen by an atom other than carbon (diazocyanides, $ArN{=}NCN$, are an exception). In principle there is of course no difference between the diazo compound, for example a diazohydroxide or a diazocyanide, and the azo compounds, such as azobenzene[1].

The diazonium ions which have a hydrogen atom at the α-carbon (or an acidic hydrogen at some other position, see Section IV) may also react with bases as Brönsted acids, yielding diazo compounds, e.g.

$$C_2H_5O_2CCH_2N_2^+ + B \rightleftharpoons C_2H_5O_2CCH{=}\overset{+}{N}{=}\overset{-}{N} + BH^+ \qquad (1)$$

The present chapter discusses the kinetics and mechanism of reversible formation of diazo compounds from diazonium ions and nucleophiles. The main emphasis is on the reaction of arenediazonium ions with hydroxide ions.

II. DIAZONIUM–DIAZO EQUILIBRIUM OF ALIPHATIC DIAZO COMPOUNDS

The equilibrium system diazoalkane ⇌ alkanediazonium ion ⇌ alkanediazotate (equation 2) cannot be studied, because alkanediazonium ions are not stable and usually decompose[2] immediately with formation of nitrogen and compounds derived from the cation RCH_2^+:

$$\begin{tikzcd} RCH_2N_2^+ + OH^- \arrow[r, shift left] \arrow[d, shift left, "-H^+"] & RCH_2N{=}NOH \arrow[l, shift left] \arrow[r, shift left] & RCH_2N{=}NO^- + H^+ \arrow[l, shift left] \\ RCH{=}N_2 \arrow[u, shift left] & & \end{tikzcd} \qquad (2)$$

Existence of the diazonium ion can be inferred, in some cases, from the structure of products and the presumed reaction mechanism. When R is strongly electron withdrawing, a diazo compound is formed on nitrosation of the amine under suitable conditions[2, 3]:

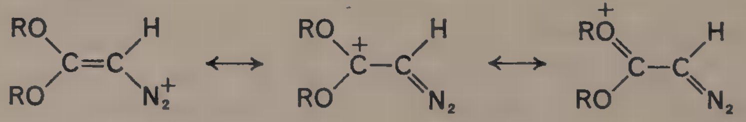
$$C_2H_5O_2CCH_2NH_2 \xrightarrow{HONO} C_2H_5O_2CCH_2N{=}NOH \xrightarrow{-OH^-}$$
$$C_2H_5O_2CCH_2N_2^+ \xrightarrow{-H^+} C_2H_5O_2CCH{=}N_2 \qquad (3)$$

In strongly basic media, the primary alkanediazotates $RCH_2N_2O^-$ are transformed into a mixture of diazoalkane and the products derived from RCH_2^+ (Reference 4). Obviously the diazoalkane is formed by action of base on $RCH_2N_2^+$ which is present in a very slight amount, according to the equilibrium shown in equation (2).

The instability of alkanediazonium ions is further demonstrated by acid-catalysed decomposition of diazoalkanes. The decomposition of diazodiphenylmethane is a general acid-catalysed reaction[5], which means that the decomposition of the diazonium ion is faster than the splitting off of the proton.

$$(C_6H_5)_2CN_2 \underset{}{\overset{H^+}{\rightleftharpoons}} (C_6H_5)_2CHN_2^+ \xrightarrow{X^-} (C_6H_5)_2CHX + N_2 \qquad (4)$$

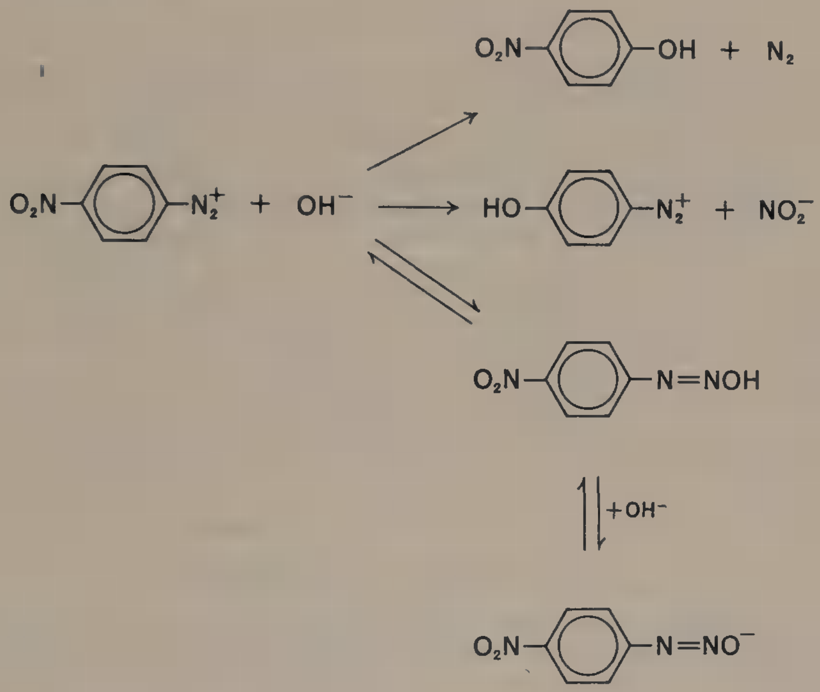
Some substituted alkenediazonium ions can exist in the form of salts with anions of strong acids as SbF_6^- (Reference 6) for example. The increased stability is due to resonance of the diazonium group with p and π electrons. Nucleophiles react with the activated double bond which results either in substitution (if halogens are present instead of RO), or in addition of H_2O or ROH giving an alkanediazonium ion which is immediately decomposed[6].



III. ARENEDIAZONIUM ION ⇌ DIAZOHYDROXIDE ⇌ DIAZOTATE EQUILIBRIA

In contrast to alkanediazonium ions, arenediazonium ions are usually quite stable in aqueous solutions in the form of salts with anions of strong acids. This stability is due to resonance interaction of the diazonium group with ring π electrons (and electrons of substituents in certain cases) and to the fact that the bond between nitrogen and a sp^2-hybridized C atom is stronger than that with the sp^3-hybridized C atom.

Substituted arenediazonium ions can react with nucleophiles in three ways[7] which are schematically represented below for the reaction of 4-nitrobenzenediazonium ion with hydroxyl ion (the first reaction proceeds by the S_N1 mechanism, and the water molecule is the real nucleophile[8]). The first and second reactions are practically irreversible, the third one is reversible and much faster except for diazonium ions having strongly activated rings such as 2,4-dinitrobenzenediazonium ion[9] or 1,4-benezenetetrazonium ion[10], $\overset{+}{N}_2C_6H_4\overset{+}{N}_2$, for which the rates of the second and third reactions are comparable.

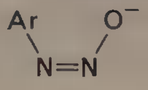


(5)

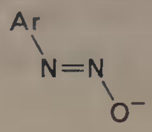
A. Development of Ideas Regarding the Reactions $ArN_2^+ + OH^-$

In 1858 Griess described the preparation of a diazonium salt by action of nitrous gases on picramide[11]. When studying the reactions of further similarly prepared diazonium salts he found[12] that benzenediazonium salt is transformed by action of potassium hydroxide into a crystalline potassium salt, the reaction being reversible. Development of azo chemistry and its application in the dyestuff industry was influenced in an important way by investigations of Schraube and Schmidt[13] published in 1894. The sodium salt prepared by action of sodium hydroxide on *p*-nitrobenzenediazonium compounds did not couple with aromatic hydroxy compounds, and on acidification it slowly gave the original diazonium salt. Similarly, while the potassium salt prepared from benzenediazonium salt coupled readily with alkaline 2-naphtholate, it rearranged on heating for several hours with concentrated potassium hydroxide into a stable, non-coupling isomer. Since the sodium salt prepared from the 4-nitrobenzenediazonium salt gave 4-nitro-*N*-methylnitrosamine by reaction with methyl iodide, the authors[13] presumed that the isomers not capable of coupling were salts of derivatives of nitrosamine, and that the reactive isomer was a diazotate. Hantzsch, who studied the stereochemistry of aromatic oximes several years earlier, came to the conclusion that on the basis of analogy between both types of compounds the matter was stereoisomerism in this case, too[14, 15]. He ascribed the *syn* structure to the reactive form and the *anti* structure to the non-reacting one.

The existence of two stereoisomers was proved later in the case of the structurally similar azobenzene[16, 17] and substituted benzenediazocyanides[18, 19]; the i.r. spectra of substituted *syn*- and *anti*-benzenediazotates were also interpreted[20] on the basis of the structures suggested by Hantzsch.



syn



anti

Two equivalents of hydroxyl ions are consumed in the transformation of a diazonium ion into the respective diazotate. Hantzsch followed this reaction conductometrically[21], and assumed that the reaction proceeds in two separate steps, as with other dibasic acids, and he even described the isolation of the presumed diazohydroxide and the measurement of its dissociation constant.

Wittwer and Zollinger[22] measured the diazonium ⇌ diazotate equilibrium with three substituted benzenediazonium salts and found that the neutralization curve showed but one step, even though two equivalents of base were consumed for one equivalent of diazonium ion. This case was similar to that described before by Schwarzenbach[23]. The diazonium ion reacts with the hydroxyl ion as a Lewis acid. The equilibrium constant K_1 of this reaction is smaller than the equilibrium constant K_2 of the reaction of the formed diazohydroxide (which is a Brönsted acid) with a further OH⁻ ion. Therefore, the diazohydroxide is transformed quickly into the diazotate ion, so that the concentration of the former is slight throughout the measurement. This result was confirmed also by spectral determination of the diazonium ion ⇌ diazotate equilibrium in a series of substituted benzenediazonium ions[24]. Only the absorption bands corresponding to the starting diazonium ion and final diazotate ion were found in the spectra. The slopes of the dependence of $\log[ArN_2^+]/[ArN_2O^-]$ (calculated from the absorbances) on pH had the value -2. This means that the diazonium ion reacts practically at once with two equivalents of OH^- ion, and the diazohydroxide concentration is negligible.

$$ArN_2^+ + OH^- \rightleftharpoons ArN_2OH \qquad K_1 \tag{6}$$

$$ArN_2OH + OH^- \rightleftharpoons ArN_2O^- + H_2O \quad K_2 \tag{7}$$

B. *Effect of Benzene Ring Substituents on the Diazonium Ion ⇌ syn-Diazotate Equilibrium*

In alkaline aqueous medium the following reversible reactions of diazonium ions take place[25, 26]:

$$ArN_2^+ + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} syn\text{-}ArN_2OH \qquad K_1 \tag{6}$$

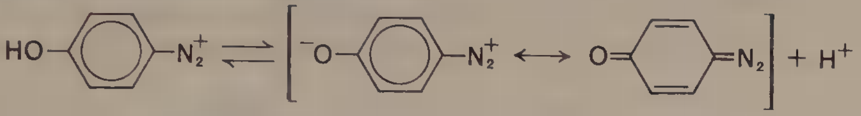
$$syn\text{-}ArN_2OH + OH^- \rightleftharpoons syn\text{-}ArN_2O^- + H_2O \quad K_2 \tag{7}$$

$$syn\text{-}ArN_2OH \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} anti\text{-}ArN_2OH \qquad K_3 \tag{8}$$

$$syn\text{-}ArN_2O^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} anti\text{-}ArN_2O^- \qquad K_4 \tag{9}$$

$$anti\text{-}ArN_2OH + OH^- \rightleftharpoons anti\text{-}ArN_2O^- + H_2O \quad K_5 \tag{10}$$

Benzenediazonium ions which have a hydroxyl group in the *ortho* or *para* position split off the proton even in mildly acidic medium; the pK_a value of 4-hydroxybenzenediazonium ion is 3·40 [27]. The diazo compounds formed are only slightly reactive and do not form diazotates even in a strongly alkaline medium.


(11)

Besides these reactions, irreversible substitutions of the nitrogen or substituents in the *ortho* or *para* positions by OH^- group (equation 5) and decomposition reactions of diazohydroxides (leading to formation of hydroxy compounds and other, often polymeric, substances) may be significant. These side-reactions make determination of equilibrium constants difficult. For example, *m*-nitrobenzenediazohydroxide decomposes so rapidly that at a pH of about 9 (the region of its maximum concentration) practically all the diazonium salt is transformed into the decomposition products within less than a minute.

With most substituted benzenediazonium ions the rate of *syn–anti* isomerization is many orders of magnitude slower than that of the reaction of the diazonium ion with OH^-, so that it does not interfere with the determination of the $ArN_2^+ \rightleftharpoons$ *syn*-ArN_2O^- equilibrium. Diazonium ions which have strong $-M$ type substituents (e.g. nitro groups) in *ortho* or *para* positions form an exception.

The transformation of diazonium ions into *syn*-diazotates can also be expressed by the following equations:

$$ArN_2^+ + H_2O \rightleftharpoons syn\text{-}ArN_2OH + H^+ \quad K_{A1} \tag{12}$$

$$syn\text{-}ArN_2OH \rightleftharpoons syn\text{-}ArN_2O^- + H^+ \quad K_{A2} \tag{13}$$

Equilibrium constants of the overall reaction of the cases described by equations (6)+(7) and (12)+(13) respectively are given by the relations:

$$K = K_1.K_2 = [ArN_2O^-]/[ArN_2^+]\,[OH^-]^2 \tag{14}$$

$$K_A = K_{A1}.K_{A2} = [ArN_2O^-]\,[H^+]^2/[ArN_2^+] = K.K_w^2 \tag{15}$$

where $K_w = [H^+]\,[OH^-]$.

As the determination of an equilibrium does not depend on the path by which it has been reached, both methods are correct. In fact practically all arenediazonium ions are transformed into diazohydroxides by reaction with hydroxyl ions. The reaction of diazonium ion with water in alkaline medium is slower by many orders of magnitude. Also diazohydroxide reacts far quicker with hydroxyl ion than with water in the pH region used for measurements of equilibrium constants of this reaction (except perhaps for the most reactive diazonium ions). On the contrary, the use of equations such as (13) and (14) is more usual and more convenient for acid–base equilibria; on introducing logarithms into equation (15) we get the relation:

$$\tfrac{1}{2}(pK_{A1}+pK_{A2})+\log\,([ArN_2O^-]/[ArN_2^+]) = pH \tag{16}$$

This means that $(pK_{A1}+pK_{A2})/2$ equals the pH of the medium in which $[ArN_2^+] = [ArN_2O^-]$ (as in the case of pK_A of the Brönsted acids). This pH was called pH_m by Lewis and Suhr[24] (Table 1).

The ratio $[ArN_2^+]/[ArN_2O^-]$ changes a hundred times on changing pH by unity, hence at $pH = (pH_m+1)$ the reaction mixture contains 1% diazonium ion and 99% diazotate ion. Concentration of diazohydroxide is negligibly low (except for very reactive diazonium salts) in the whole pH range, being maximum at pH = pH_m. The equilibrium constants K depend on ionic strength and they increase about ten times on changing the ionic strength from 1 M to 0·1 M [24].

TABLE 1. Equilibrium constants K and pH_m values of the reaction $XC_6H_4N_2^+ + 2\,OH^- \rightleftharpoons XC_6H_4N_2O^- + H_2O$

X	K^a (l^2/mol^2)	K^b (l^2/mol^2)	pH_m ^{a}
4-NO_2	$1{\cdot}3 \times 10^9$	$2{\cdot}0 \times 10^{10}$	9·44
4-CN	$2{\cdot}9 \times 10^8$	$3{\cdot}9 \times 10^9$	9·77
3-Cl	$4{\cdot}0 \times 10^6$	$1{\cdot}9 \times 10^7$	10·70
4-Cl	$3{\cdot}8 \times 10^5$	$6{\cdot}7 \times 10^5$	11·21
H	$1{\cdot}6 \times 10^4$	$2{\cdot}8 \times 10^4$	11·90
4-CH_3	$6{\cdot}6 \times 10^2$	$2{\cdot}2 \times 10^3$	12·59

[a] Reference 24: room temperature, ionic strength 1·0 M.

[b] Reference 28: 23 °C, ionic strength 0·004–0·03 M.

Dependence of log K on the Hammett σ constants is linear with the slope $\rho = 6{\cdot}3$ [24], 6·58 [28] or 6·66 [29]. The ρ values found are unusually high. One of the reasons for this is that K is a product of two equilibrium constants, so that the final value is a sum of ρ_1 and ρ_2 characterizing the formation and dissociation[24] of diazohydroxide, respectively. Similarly it is also possible to correlate pH_m with the σ constants; in this case the ρ value is negative and half that from equation (17).

$$\begin{aligned} \log(K/K_0) &= \rho\sigma = \log(K_1/K_1^0) + \log(K_2/K_2^0) \\ &= \rho_1\sigma + \rho_2\sigma = (\rho_1 + \rho_2)\sigma \qquad (17) \end{aligned}$$

It is impossible to determine the values of K_1 and K_2 or of ρ_1 and ρ_2 separately by measuring the concentrations or the pH of the equilibrium system; since $K_2 \gg K_1$ only the overall constant K is accessible. For determination of the constants of both reaction steps it is necessary to determine the rates of the reactions considered; in this case only the reaction of diazonium ion with hydroxyl ion and the reverse decomposition of diazohydroxide are suitable for measurement.

C. *Kinetics and Mechanism of the Reactions: Diazonium Ion ⇌ syn-Diazohydroxide ⇌ syn-Diazotate*

The rate of the reaction of diazohydroxide with hydroxyl ion (equation 7) is far greater than that of the decomposition of diazohydroxide into diazonium ion and hydroxyl ion (in neutral and alkaline media). Therefore, the rate-limiting step of the transformation of diazonium ion into *syn*-diazotate consists in the reaction of diazonium ion with hydroxyl ion (equation 6), whereas the rate of the reverse reaction (transformation of diazotate into diazonium ion) is limited by the splitting of the diazohydroxide.

$$\overrightarrow{v} = k_1[ArN_2^+][OH^-] \qquad (18)$$

$$\overleftarrow{v} = k_{-1}[ArN_2OH] \qquad (19)$$

At a pH comparable with pH_m or higher (the conditions suitable for determination of k_1) $[ArN_2OH] \ll [ArN_2O^-]$, and equation (20) can be written for the rate of the reverse reaction:

$$\overleftarrow{v} = k_{-1}[\mathrm{ArN_2O^-}]/K_2[\mathrm{OH^-}] = k_1[\mathrm{ArN_2O^-}]/K_1K_2[\mathrm{OH^-}] \tag{20}$$

The rate of formation of diazotate ion ($\overrightarrow{v}$) increases linearly with concentration of hydroxyl ion, and, on the contrary, the rate of the reverse reaction decreases linearly with [OH$^-$]. The observed rate constant k_{obs} is a sum of the constants in both directions (equation 21) and has its minimum at pH = pH$_\mathrm{m}$ (Figure 1, curve a)

$$k_{\mathrm{obs}} = k_1[\mathrm{OH^-}]+k_1/K_1\,K_2[\mathrm{OH^-}] = k_1([\mathrm{OH^-}]+1/K[\mathrm{OH^-}]) \tag{21}$$

when the concentrations of diazonium and diazotate ions are, after reaching the equilibrium, the same. Logarithms of the rate constants measured by spectrophotometric stopped-flow method[28, 29] correlate with σ constants (equations 22, 23).

$$\log k_1 = 2{\cdot}61\sigma + 3{\cdot}72 \qquad \text{(Reference 28)} \tag{22}$$

$$\log k_1 = 2{\cdot}06\sum\sigma + 3{\cdot}97 \qquad \text{(Reference 29)} \tag{23}$$

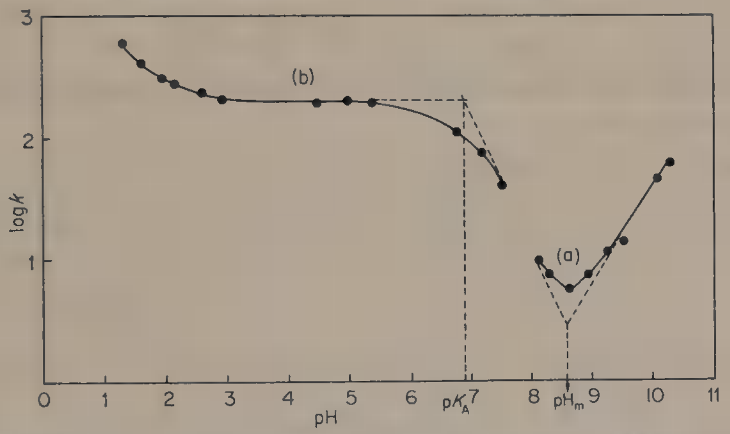


FIGURE 1. The pH dependence of log k_{obs} of the reaction 3-nitro-4-chlorobenzenediazonium ion$\rightleftharpoons$*syn*-diazohydroxide$\rightleftharpoons$*syn*-diazotate at 20 °C. (a) Transformation of diazonium ion into the diazotate; (b) transformation of diazohydroxide (in equilibrium with diazotate) into diazonium ion.

In spite of OH$^-$ ion being a much stronger base than the anions of C-acids (acetoacetanilide, acetylacetone) and naphtholate ions, the rate constants found are generally lower than those of coupling reactions with the anions mentioned by several orders of magnitude[30]. At the same time the respective ρ value (2·06) is lower than those of the coupling reactions (3–4), too. This fact is inconsistent with the rule[31] (which often is not fulfilled) that the more selective a reagent is, the more slowly it reacts. The reason is probably that the OH$^-$ ion is strongly solvated in water, and partial desolvation must take place before the N—O bond can be formed. This process necessitates considerable energy and is obviously the main cause of the relatively lower reactivity of the OH$^-$ ion. The N—O bond formation proceeds very quickly, and this step is little selective. Since the substituents in the benzene nucleus of diazonium ions have small effect on the desolvation of the OH$^-$ ion, the overall influence of substituents is relatively small which makes itself felt in the low value of the ρ constant. On the contrary, the naphtholate ions and the anions of C-acids are far less solvated, and the carbon atoms which are involved in the reaction do not form any hydrogen bonds, so that the predominant part of the activation energy is consumed in the coupling reaction (formation of C—N bond).

Under the conditions suitable for determination of k_1 it is possible to obtain only the complex constant k_{-1}/K_2 (equation 20) for the reverse reaction. The determination of k_{-1} (and K_2) necessitates starting with *syn*-diazotate and following the reaction at lower pH values when a considerable part of the diazotate is transformed into diazohydroxide in a rapid pre-equilibrium. The reaction proceeds practically only in one direction, and k_{obs} is defined by equation (24).

$$k_{\text{obs}} = k_{-1}/(1+K_2[\text{OH}^-]) = k_{-1}[\text{H}^+]/(K_{\text{A}}+[\text{H}^+]) \tag{24}$$

With increasing proton concentration log k_{obs} increases gradually more and more slowly eventually becoming pH independent (Figure 1, curve b) when almost all the diazotate has been transformed into diazohydroxide in a rapid pre-equilibrium[32].

In diluted hydrochloric acid k_{obs} again increases with increasing proton concentration, and the same is true in chloroacetate buffer for increasing concentration of chloroacetic acid; this means that the transformation of diazohydroxide into diazonium ion is a general acid-catalysed reaction[32]; the value of the Brönsted coefficient is about 0·2:

$$k_{\text{obs}} = k_{-1}+k_{\text{H}^+}[\text{H}^+]+k_{\text{HA}}[\text{HA}] \tag{25}$$

Logarithms of the rate constants k_{-1} and dissociation constants $K_{\text{A}2}$ (Table 2) correlate with σ constants:

$$\log k_{-1} = -3{\cdot}4\sum\sigma+5{\cdot}4 \tag{26}$$

$$\log K_{\text{A}2} = 1{\cdot}3\sum\sigma-8{\cdot}1 \tag{27}$$

TABLE 2. Rate and equilibrium constants of the reaction

$$\text{arenediazonium ion}+\text{OH}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \textit{syn}\text{-diazohydroxide} \overset{K_{\text{A}2}}{\rightleftharpoons} \textit{syn}\text{-diazotate}+\text{H}^+$$

at 20 °C at ionic strength 0·25 M [32]

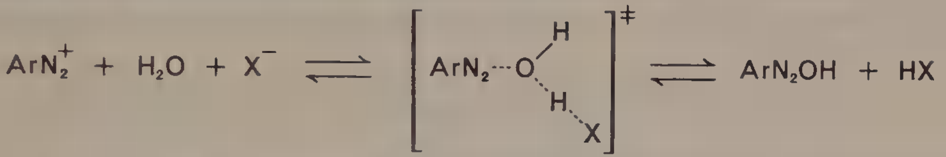
Substituents	k_1 [a] (l mol^{-1} sec^{-1})	k_{-1} (sec^{-1})	K_1	p$K_{\text{A}2}$	ArN_2OH [b] (%)
3-NO_2-4-Cl	$7{\cdot}4\times10^5$	$1{\cdot}95\times10^2$	$3{\cdot}8\times10^3$	6·90	2·05
3,5-Br_2	$3{\cdot}6\times10^5$	$4{\cdot}96\times10^2$	$7{\cdot}3\times10^2$	7·00	0·79
3,5-Cl_2	$3{\cdot}8\times10^5$	$6{\cdot}03\times10^2$	$6{\cdot}3\times10^2$	7·05	0·90
3-NO_2	$4{\cdot}5\times10^5$	$5{\cdot}34\times10^2$	$8{\cdot}4\times10^2$	7·15	1·11
3,4-Cl_2	$1{\cdot}3\times10^5$	$3{\cdot}0\times10^3$	$4{\cdot}5\times10^1$	7·30	0·28

[a] Reference 29.
[b] At pH = pH$_{\text{m}}$.

The equations (23), (26) and (27) describe quantitatively the reaction of substituted benzenediazonium ions with OH$^-$ ion and the subsequent dissociation of *syn*-diazohydroxide to *syn*-diazotate. From the values K_1 and K_2 it is also possible to calculate the maximum concentration of *syn*-diazohydroxide (at pH = pH$_{\text{m}}$). The concentrations are slight, in accordance with the predictions of Zollinger[22], and they increase with increasing value of σ constants, because K_1 increases with increasing σ value much faster than K_2 does ($\rho_1 > \rho_2$). The constant ρ_1 of the reaction (6) can be calculated either from the difference of the ρ constants derived from the equilibrium constants K and $K_{\text{A}2}$ or from the rate constants k_1 and k_{-1}. The average value of ρ_1 is 5·4.

The reaction of diazonium ion with hydroxyl ion produces first the diazohydroxide which then partially isomerizes to nitrosamine ArNHNO. The proton transfer between nitrogen and oxygen (be it inter- or intra-molecular) represents a reaction several orders of magnitude faster than the splitting off of hydroxyl ion from diazohydroxide, so that the reaction produces an equilibrium mixture of both tautomers. The extent of this isomerization is not known. The ρ constant of $\log K_A$ of substituted phenols[33] is 2·23; the inserted N=N group diminishes the ρ constant by a factor of about 0·4 so that for diazohydroxides we obtain $\rho \simeq 1$. For dissociation constants of substituted formanilides[34] (which are structurally similar to nitrosamines) the experimental ρ value was 1·53. The difference is relatively small, and the value 1·3 (equation 27) is almost in the middle, so that, from this point of view, it is impossible to decide whether the compound is a diazohydroxide, a nitrosamine or a mixture of both.

Splitting of diazohydroxides is subject to general acid catalysis, hence the reverse reaction of diazonium ion with water must be subject to general base catalysis,



$$ArN_2^+ + H_2O + X^- \rightleftharpoons \left[ArN_2\cdots O(H)\cdots H\cdots X\right]^{\ddagger} \rightleftharpoons ArN_2OH + HX \qquad (28)$$

where X stands for H_2O, RCO_2^- or even OH^-, although in the last case there is a possibility that OH^- reacts directly with the nitrogen atom of the diazonium ion.

Wittwer and Zollinger[22] found that the dependence of log k on pH for the reaction of diazotized metanilic acid with the dianion of 2-hydroxynaphthalene-6-sulphonic acid at pH > 12 is linear with a slope of −2. The rate-limiting step is the reaction of the dianion with the diazonium ion which is present in a rapid pre-equilibrium with diazotate ion. At the given pH, more than 99% of the electrophile is present in the form of ArN_2O^-, and concentration of ArN_2^+ depends linearly on $[H^+]^2$. In the case of very reactive diazonium ions and with the use of sufficient concentration of coupling component (e.g. substituted naphthol) the coupling rate becomes greater than the rate of reaction of diazonium ion with hydroxyl ion[29]. The splitting off of OH^- ion from diazohydroxide is rate limiting. The reaction rate is directly proportional to the first power of $[H^+]$ and independent of the concentration of the coupling component (naphtholate).

D. Kinetics and Mechanism of syn–anti Isomerizations

syn-Arenediazotate ions formed by reaction of diazonium ion and hydroxyl ion isomerize into *anti*-diazotate ions. Isomerization of *syn*-diazohydroxides, which in alkaline solution are present in a substantially smaller concentration, takes place to a very small extent. New equilibria are established, e.g.

$$syn\text{-}ArN_2OH \rightleftharpoons anti\text{-}ArN_2OH \qquad syn\text{-}ArN_2O^- \rightleftharpoons anti\text{-}ArN_2O^-$$

and the acid–base equilibrium

$$anti\text{-}ArN_2OH \rightleftharpoons anti\text{-}ArN_2O^- + H^+,$$

and hence also a new overall equilibrium

$$ArN_2^+ + 2\ OH^- \rightleftharpoons anti\text{-}ArN_2O + H_2O^-$$

In the case of the substituted benzenediazonium ions this equilibrium is usually established within a fraction of a second. The *syn–anti* isomerization proceeds slowly (except for diazotate ions with −M type substituents in the *para* or *ortho* position), e.g. the isomerization half-life of benzenediazotate ion is 38 min at 80 °C [24]. In all the cases known up to now the rate constant k_1 of the reaction of diazonium ion with hydroxyl ion is greater than k_4 of isomerization (equation 9) at least by several orders of magnitude, so that the two reactions can be followed separately. The effect of substituents on the isomerization rate was determined with 4- and 5-substituted 2-nitrobenzenediazotate ions[35] whose isomerizations are, due to activation by the *o*-nitro group, rapid enough even at room temperature. The respective logarithms of the constants k_4 correlate with σ and σ^- constants[35] according to equation (29)[36]. *syn*-2-Nitrobenzenediazotate ion is the basic member of the series.

$$\log k_4 = 2{\cdot}1[\sigma + 2{\cdot}4(\sigma^- - \sigma)] - 2{\cdot}83 \tag{29†}$$

In contrast to the *syn* diazotates which split off hydroxyl ion within a half-life of several msecond or less, the *anti*-diazohydroxides are much more stable. Their dissociation constants K_{A5} (equation 10 but with H_2O as the reagent) can be determined by usual methods, e.g. potentiometric titration of *anti*-diazotates with acids[26,37] or from the pH dependence of the transformation of *anti*-diazotate into diazonium ion[35, 37, 38] (Table 3).

The other rate and equilibrium constants (Tables 3 and 4) were determined by the reverse procedure[35, 37–39]: *anti*-diazotate was injected into a solution of acid or

TABLE 3. Rate constants of isomerization of substituted benzenediazotate ions (k_4) and diazohydroxides (k_{-3}) and dissociation constants of *anti*-diazohydroxides at 20 °C [35]

Substituent	k_4 (sec^{-1})	k_{-3} (sec^{-1})	pK_{A5}
H	2×10^{-6} [a]	$1{\cdot}5\times10^{-2}$ [b, c]	7·29 [b]
4-NO_2	$5{\cdot}4\times10^{-2}$ [a]	$4{\cdot}8\times10^{-3}$ [b]	6·13 [b]
2-NO_2	$1{\cdot}5\times10^{-3}$	$1{\cdot}9\times10^{-2}$	6·15
2-NO_2-5-Cl	$1{\cdot}0\times10^{-2}$	$4{\cdot}0\times10^{-2}$	5·60
2,4-diNO_2	20·9		5·0

[a] Reference 40, 25 °C.
[b] Reference 37, 25 °C.
[c] Rate constant of splitting of *anti*-diazohydroxide.

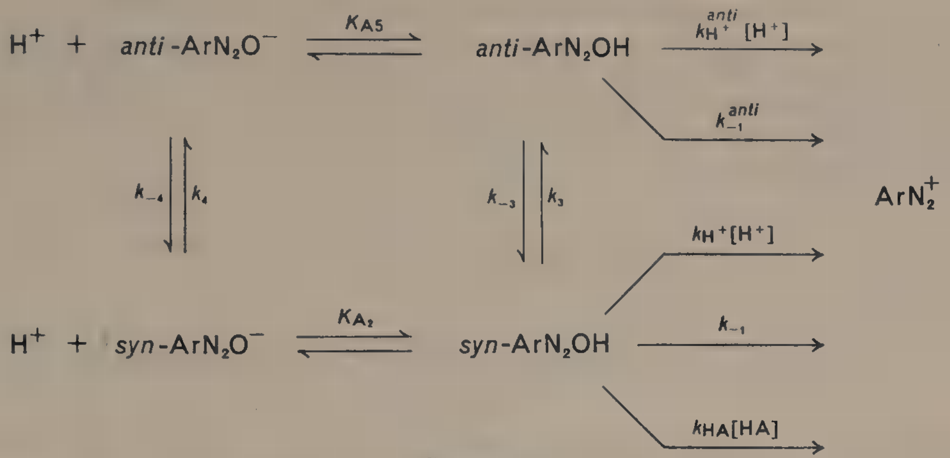
TABLE 4. Rate and equilibrium constants of *syn–anti* isomerization of substituted benzenediazotate ions at 20 °C [34]

Substituents	k_4 (sec^{-1})	k_{-4} (sec^{-1})	K_4
4-NO_2	$5{\cdot}4\times10^{-2}$ [a]		600 [b]
2-NO_2-4-CH_3	$7{\cdot}8\times10^{-4}$	$4{\cdot}2\times10^{-5}$	18·5
2-NO_2	$1{\cdot}5\times10^{-3}$	$8{\cdot}3\times10^{-5}$	18·0
2-NO_2-4-Cl	$4{\cdot}3\times10^{-3}$	$3{\cdot}7\times10^{-4}$	11·5
2-NO_2-5-Cl	$1{\cdot}0\times10^{-2}$	$8{\cdot}3\times10^{-4}$	12·0
2-Cl-4-NO_2	$3{\cdot}2\times10^{-2}$	$9{\cdot}2\times10^{-5}$	350
2,6-Cl_2-4-NO_2 [c]	$5{\cdot}5\times10^{-3}$	$1{\cdot}8\times10^{-5}$	3·0
2-NO_2-4,6-Cl_2			0·70

[a] Reference 40, 25 °C.
[b] Reference 26.
[c] Reference 38.

---

† The generalized equation is: $\log k = \rho[\sigma + r(\sigma^- - \sigma) + \log k_0$. The constants ρ, σ and σ^- have their usual meaning; the reaction constant r has been interpreted as the ratio of conjugation in a particular reaction series to that in the limiting cases requiring σ^-.



SCHEME 1

buffer containing a sufficient amount of reactive coupling component. The diazonium ion thus formed reacted rapidly with the coupling component to form the respective azo compound, so that the overall reaction was pseudo first order. The reaction course is represented in Scheme 1, and the dependence of log k_{obs} on pH is given in Figure 2 for benzenediazotate ion and its 2-nitro-4-chloro and 2,4-dinitro derivatives.

Anti-syn isomerization of benzenediazotate is very slow[24], the main reaction path being the splitting of hydroxyl ion from *anti*-diazohydroxide (Scheme 2†); from the

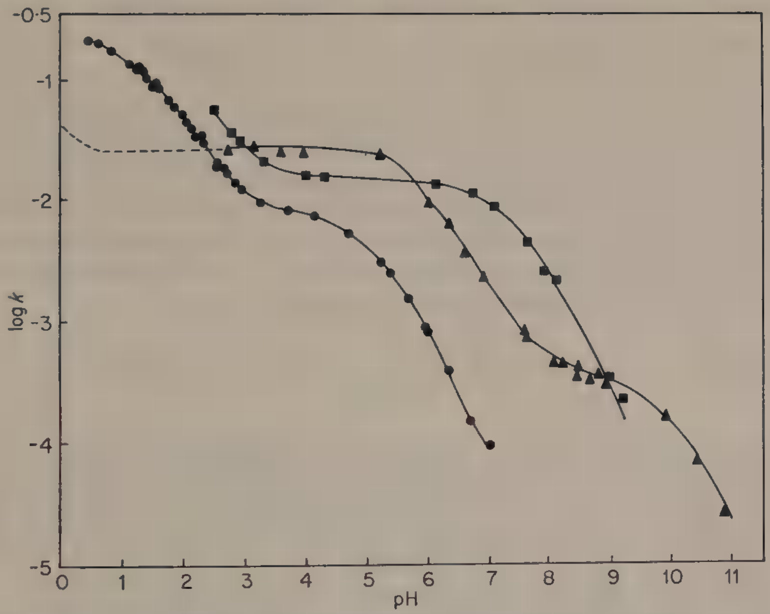


FIGURE 2. pH-Dependence of log k_{obs} of the conversion of unsubstituted (■), *anti*-2-nitro-4-chloro- (▲) and *anti*-2,4-dinitrobenzenediazotate (●) into diazonium ion.

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† As with *syn*-diazohydroxides, in this case also, two tautomeric forms are possible: diazohydroxide and nitrosamine. The diazohydroxide is, without doubt, the form which is split into diazonium ion and hydroxyl ion. Neither from the splitting rate nor from the pH dependence of log k_{obs} is it possible to determine the population of the both tautomers. The constant k_{-1}^{anti} is a product of the rate constant of the splitting of *anti*-diazohydroxide and of the molar fraction of the diazohydroxide in the mixture of the two isomers. The same is true also of the constant k_{-1} of the splitting of *syn*-diazohydroxides.

dependence of $\log k_{\text{obs}}$ on pH at pH > 6 and from the pH-independent region the constants K_{A5} and k_{-1}^{anti} (the rate constant of splitting of *anti*-diazohydroxide) were determined, respectively (Table 3). At pH < 3 the acid-catalysed splitting of *anti*-diazohydroxide begins to be significant. Logarithms of k_{-1}^{anti} of benzenediazotate ion and its 4-methyl, 4-chloro and 3-chloro derivatives correlate with the σ constants according to equation (30):

$$\log k_{-1}^{anti} = -2{\cdot}6\sigma - 1{\cdot}89 \tag{30}$$

The ρ value $-2{\cdot}6$ is comparable with that $(-3{\cdot}4)$ found for splitting of *syn*-diazohydroxides[32].

$$H^{+} + anti\text{-}C_6H_5N_2O^{-} \rightleftharpoons anti\text{-}C_6H_5N_2OH \xrightarrow{k_{-1}^{anti}} C_6H_5N_2^{+}$$

SCHEME 2

With increasing values of the substituent constant σ the splitting rate of diazohydroxides decreases and simultaneously the isomerization rate increases. With the 2-nitro-4-chloro derivative[35] the splitting of the *anti*-diazohydroxide is slower than isomerization of the diazotate and diazohydroxide, and the subsequent splitting of *syn*-diazohydroxide; these become the main reaction paths. At the highest pH values the reaction proceeds according to Scheme 3. Splitting of *syn*-diazohydroxide is the

$$anti\text{-}ArN_2O^{-} \rightleftharpoons syn\text{-}ArN_2O^{-} \overset{+H^{+}}{\rightleftharpoons} syn\text{-}ArN_2OH \xrightarrow{k_{-1}} ArN_2^{+}$$

SCHEME 3

rate-limiting step, and the dependence $\log k_{\text{obs}}$ *vs* pH has a slope of -1 (Figure 2) With increasing proton concentration the transformation of *syn*-diazotate into diazonium ion becomes more and more rapid. The *anti–syn* diazotate isomerization becomes the rate-limiting step, and the reaction rate becomes independent of pH†. Further increase in the proton concentration results in the increase of concentration of *anti*-diazohydroxide whose isomerization becomes the main reaction path and, at the same time, the rate-limiting step (Scheme 4). The reaction rate, which at first increases again, finally becomes pH independent when almost all diazotate ion has changed into *anti*-diazohydroxide. The acid-catalysed splitting of *anti*-diazohydroxide becomes significant at pH about zero.

$$H^{+} + anti\text{-}ArN_2O^{-} \rightleftharpoons anti\text{-}ArN_2OH \xrightarrow{k_{-3}} syn\text{-}ArN_2OH \longrightarrow ArN^{+}$$

SCHEME 4

Further increase in the electron-withdrawing ability of substituents results in an even greater decrease in the *syn*-diazohydroxide splitting rate and an increase in the isomerization rate. The splitting of *syn*-diazohydroxide becomes rate limiting in a broader pH range and the reverse is true of the rate-limiting transformation of *anti*- into *syn*-diazotate. In the case of the 2,4-dinitro derivative[38] (Figure 2) the non-catalysed splitting of *syn*-diazohydroxide (k_{-1}) is rate limiting up to pH about 4·5, and the reaction rate is directly proportional to the *anti*-diazohydroxide concentration. Further lowering of pH causes the proton-catalysed splitting (k_{H^+}) to become more and more significant. At pH < 1 the rate of the proton-catalysed splitting of *syn*-diazohydroxide is substantially greater than that of the reverse isomerization to *anti*-diazohydroxide. The transformation of *anti*- to *syn*-diazohydroxide becomes rate limiting, and $\log k$ is pH independent.

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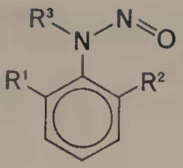
† The reaction rate does not become completely pH independent, because the individual reaction paths overlap.

E. Some Conclusions from the Results on syn–anti Isomerization

Isomerization rates of *syn*-diazotates to *anti*-diazotates depend strongly on polar effects of the substituents, especially on their $-\mathrm{M}$ effect. The value $r = 2{\cdot}4$ in equation (29), which describes the relative importance of the mesomeric effect, is probably the highest given in the literature up to now. The *anti* : *syn* diazotate concentration ratio is practically independent of the polar effects of substituents[26, 35] but it rapidly increases with increasing steric requirements of substituents in *ortho* positions[35] (Table 4). This means either that the *syn* and *anti* derivatives have (in contrast to all other published interpretations) the configuration *trans* and *cis*, respectively, or that the *trans* configuration is stabilized by substituents in *ortho* positions. A similar case is described in connection with the study of *syn–anti* configuration of substituted *N*-alkyl-*N*-nitrosoanilines[41] where the *ortho* substitution shifts the equilibrium in favour of isomer **1**:

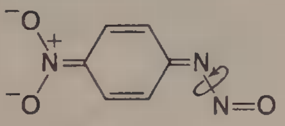


(1)

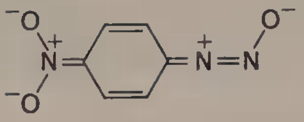
The isomerization rate of *anti*- to *syn*-diazohydroxides (Table 3) depends generally much less on polar effects and especially on the $-\mathrm{M}$ effect (equation 31) than the isomerization of diazotate ions, and it is usually far quicker. It can be presumed that

$$\log k_4 = 1{\cdot}0[\sigma + 0{\cdot}65(\sigma^- - \sigma)] - 1{\cdot}8 \tag{31}$$

the isomerization mechanism is different for the two cases. Two mechanisms can be considered for diazotate ions[26], either rotation about the N—N bond in **2** or inversion at the N atom positively charged in the transition state **3**. The rotation about the N—N bond of the nitrosamine tautomer is the most probable mechanism for diazoanhydrides.



(2)



(3)

A reaction mechanism, according to which an *anti*-diazotate would be formed directly by reaction of hydroxyl ion with the diazonium ion which is in equilibrium with *syn*-diazotate, is untenable, since in alkaline solution the isomerization rate is independent of hydroxyl ion concentration[39]. The mentioned mechanism would necessitate $v = [\mathrm{ArN}_2^+][\mathrm{OH}^-]$, and the isomerization rate would have to be inversely proportional to $[\mathrm{OH}^-]$, because $[\mathrm{ArN}_2^+]$ decreases with the square of $[\mathrm{OH}^-]$.

Substituted *anti*-benzenediazohydroxides are by about one order of magnitude stronger Brönsted acids than *syn*-diazohydroxides. Direct comparison is possible only in the case of the *m*-nitro derivatives[26, 32], but it obviously holds also for the other *meta*- and *para*-substituted diazohydroxides, because the constants of the acid–base reactions are approximately the same: 1·3 for *syn*[32] and 1·17–1·45 for *anti*[26, 37]. Hence it follows that the ratio *anti* : *syn* will be by about one order of magnitude smaller for diazohydroxides than that for diazotate ions. These conclusions do not hold for *ortho*-substituted diazohydroxides.

For the majority of substituted benzenediazonium ions it is possible to determine the equilibrium constant K of the reaction $ArN_2^+ \rightleftharpoons$ *syn*-ArN_2O^- by direct measurements on solutions in the pH range near pH_m. If the absorbances and the pH values of the reaction mixtures are measured after establishing the equilibrium of the *syn–anti* isomerization, it is possible to determine the equilibrium constant of the reaction $ArN_2^+ \rightleftharpoons$ *anti*-ArN_2O^-. As irreversible side reactions take place simultaneously, the values obtained are usually very inaccurate, or not accessible at all (e.g., with the *m*-nitro derivative). In the case of the diazonium ions having strong −M type substituents in *ortho* and *para* positions (e.g. 2,4-dinitrobenzenediazonium ion) the rate of *syn–anti* isomerization at pH close to pH_m is greater than the rate of the reverse transformation of *syn*-diazohydroxide to the diazonium ion, so that the equilibrium constant of the reaction $ArN_2^+ \rightleftharpoons$ *syn*-ArN_2O^- cannot be determined by measurements[38].

IV. DIAZONIUM–DIAZO EQUILIBRIA OF HETEROCYCLIC DIAZONIUM IONS

Diazotization of heterocyclic primary amines can be expressed by the following reaction sequence[42]:

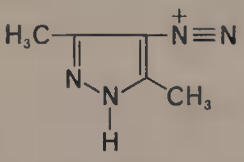
$$\mathrm{HArNH_2} \xrightarrow{\mathrm{HONO}} \mathrm{HAr\overset{+}{N}H_2NO} \overset{-\mathrm{H}^+}{\rightleftharpoons} \mathrm{HArNHNO} \rightleftharpoons \mathrm{HArN{=}NOH}$$

$$\overset{\mathrm{HX}}{\rightleftharpoons} \mathrm{HArN_2^+X^-} \overset{-\mathrm{HX}}{\rightleftharpoons} \mathrm{\overset{-}{Ar}N_2^+} \longleftrightarrow \mathrm{Ar{=}N_2}$$

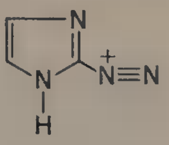
SCHEME 5

In this Scheme (contrary to general usage in this series) the symbol Ar represents a heteroaromatic ring minus *two* hydrogen atoms and the symbol HAr represents a heteroaryl group.

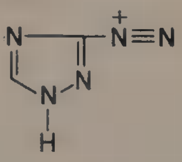
If the aromatic ring contains an acidic hydrogen atom, the diazo compounds $Ar{=}N_2$ along with the corresponding diazonium ions are usually the main reaction products. The equilibrium $HArN_2^+ \rightleftharpoons Ar{=}N_2 + H^+$ was measured[43] in a series of azols in aqueous solutions at 0 °C. The acidity of the diazonium ions increased with the number of ring N atoms. In principle, the reaction is similar to that in the aliphatic series (alkanediazonium ion $\rightleftharpoons$ diazoalkane + H^+).



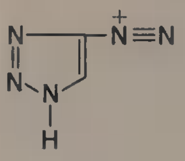
pK_A 4·95



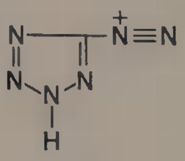
2·6



0·3



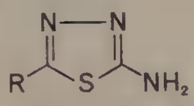
−0·4



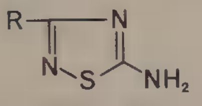
−5·2

If the five-membered ring does not contain any acidic hydrogen atom, the product of nitrosation of the amine in diluted mineral acid is usually a mixture of the nitrosamine, the diazohydroxide and the diazonium cation. The tendency to form nitrosamines and diazohydroxides usually increases with increasing number of ring heteroatoms. High yields of nitrosamines were obtained with substituted triazoles and tetrazoles[44, 45], thiadiazoles[44, 46, 47] and oxadiazoles[44]. The situation is not quite clear, e.g. substituted 5-amino-1,3,4- and -1,2,4-thiadiazoles (**4, 5**) give high yields of nitrosamines[44, 46], however, the 5-substituted-3-amino-1,2,4-thiadiazole (**6**) forms only a relatively unstable diazonium salt[48, 49] Commonly, the structure and yield of the isolated product depend on various factors such as the solubility of products, the rates of the substitution reactions with the nucleophiles present and of decomposition reactions.

From i.r. (in solid state) and n.m.r. spectra it follows[44] that the products currently denoted as nitrosamines are, in fact, mixtures of the nitrosamine and the tautomeric diazohydroxide. In alkaline medium these are transformed into *anti*-diazotates[46]. Dissociation constants were measured[44] in the case of triazole derivatives (**7**); the pK_A values were between 3·54 and 3·13 for X varying from 4-CH_3 to 4-NO_2, i.e. far lower than those of substituted benzenediazohydroxides (Tables 2 and 3).



(4)



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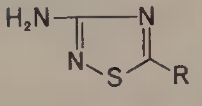

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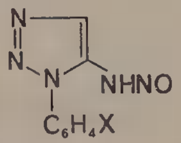
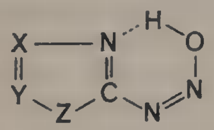


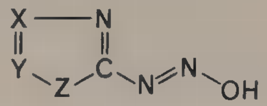
(7)

Increasing proton concentrations causes gradual transformation of the nitrosamine into the diazonium ion; the position of no such equilibrium was as yet measured. In one case the extent of transformation was followed[46] by measuring the coupling rate of the formed 3-methyl-1,2,4-thiadiazo-5-diazonium ion with 2-naphthol in dilute sulphuric acid. Under these conditions 2-naphthol reacts in its undissociated form, so that the change of the coupling rate expresses the change of the equilibrium concentration of the diazonium ion. The reaction rate increased steeply up to the highest sulphuric acid concentration used (1·65 M), which means that the nitrosamine predominated all the time in the reaction mixtures.

The extraordinary stability of five-membered heterocyclic nitrosamines (and diazohydroxides) compared with the carbocyclic aromatic diazohydroxides is due, first of all, to the strong electron-withdrawing effect of heterocyclic rings. This effect increases the reactivity of the diazonium ion and the stability of the nitrosamine in the same way as in substituted benzenediazonium ions (Table 2), but to a greater extent. 1,2,4- and 1,3,4-Thiadiazole-5-diazonium ions are far more reactive than 2,4-dinitrobenzenediazonium ion[50] (towards 2-naphthol). The isolated nitrosamines are obviously present in the form of the more stable (*anti*) isomer. Although so far no data have been published about *syn–anti* isomerization of heterocyclic nitrosamines, it can be presumed from analogy with substituted benzenediazohydroxides that the isomerization half-lives will be shorter than 1 sec in most cases. Another factor given by Butler[42] is the stabilization by intramolecular hydrogen bonding in the case of the diazohydroxide **8**. However, this form is, according to spectral analyses[44], far less populated than the nitrosamine and the isomeric diazohydroxide **9**.

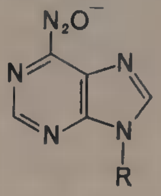


(8)

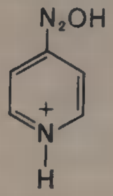


(9)

All these effects should be present in six-membered heterocyclic diazonium ions, too. However, up to now no stable nitrosamine derived from a six-membered heterocyclic amine has been isolated. By acidification of pyridine-2- and -4-diazotates[51] and 9-alkylpurine-6-diazotate[52] (**10**) solutions were prepared probably containing the respective *anti*-diazohydroxides nitrosamines. The pH dependence of log *k* of their transformation into the corresponding diazonium ion (or the products derived from the latter) has a similar character as that of the substituted benzenediazohydroxides, and the reaction is subject to general acid catalysis, too. A rather substantial difference is encountered with pyridine-4-diazohydroxide, which at pH < 4 becomes protonated to give the less reactive conjugated acid (**11**).



(10)



(11)

V. REACTIONS OF DIAZONIUM IONS WITH OTHER NUCLEOPHILES

Arenediazonium ions react with a number of nucleophiles to give diazo compounds[7, 53–55]. The free electron pair for the bond formation can be supplied by a carbon, oxygen, nitrogen, sulphur or phosphorus atom of the nucleophile. In the first case azo compounds are formed which are usually very stable, although the reaction with CN^- ions (forming arenediazocyanides) is reversible. The other adducts are called diazo compounds, however some of them (e.g. those containing N—P bonds) are denoted as azo compounds.

Some diazo compounds are very unstable, e.g. diazoethers formed by reaction of diazonium ions with substituted phenolate ions; here it is questionable whether the nucleophile and the azo group are connected by a covalent or an ionic bond. In other cases, the primarily formed diazo compound is rapidly transformed to other more stable compounds. Reaction of diazonium ions with azide ion N_3^- produces unstable diazoazides which, in a subsequent (as a rule rate-limiting) step, either decompose to give nitrogen and an aryl azide or isomerize to arylpentazoles which are also unstable[56]. Some diazo compounds are formed in other ways than from the reaction of arenediazonium ion with nucleophile.

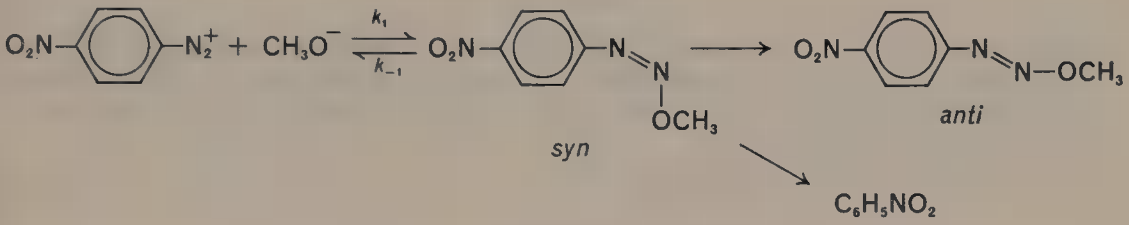
The following discussion is limited to diazo compounds for which it was possible to determine the equilibrium constant of the reaction of at least some derivative of arenediazonium ion with the nucleophile.

A. *Arenediazoethers*

Reaction of diazonium ions with alkoxide ions is analogous with the first reaction step of that with hydroxyl ion. Very reactive heterocyclic diazonium salts, e.g. 3-phenyl-1,2,4-thiadiazol-5-diazonium fluoroborate, give high yields of diazoethers even on reaction with pure methanol[57]. For preparation of substituted benzenediazoethers it is more convenient to alkylate silver diazotates with methyl iodide[58–60]; alkylation of a sodium or potassium salt produces the aryl derivative of *N*-methylnitrosamine[13].

Reaction of 4-nitrobenzenediazonium ion with methoxide ion in methanol produces, in a rapid reversible step, the diazoether probably having the *cis* configuration[61]; it is transformed to the more stable *trans* isomer and to nitrobenzene in about equal amounts[62] (Scheme 6). The isomerization rate constant is $7{\cdot}23 \times 10^{-3}$ sec^{-1} at 0 °C.

Rate constants of formation of the *syn* isomers were measured at 23 °C by the stopped-flow method[61] for 4-nitro- and 4-cyano-benzenediazonium ions ($3{\cdot}0 \times 10^8$ and $2{\cdot}0 \times 10^8$ l mol^{-1} sec^{-1}, respectively), and equilibrium constants were determined for 4-nitro- ($5{\cdot}6 \times 10^7$ l/mol), 4-cyano- ($8{\cdot}6 \times 10^6$ l/mol) and 3-chloro ($4{\cdot}2 \times 10^5$ l/mol) derivatives[61]. Both k_1 and K are by several orders of magnitude greater than the corresponding values of the reaction with hydroxyl ion in water. The half-life of the decomposition of 4-nitrobenzenediazoether to diazonium ion and methoxide ion is 130 msec, i.e. two orders of magnitude greater than that for 4-nitrobenzenediazohydroxide in water.



SCHEME 6

B. Arenediazoamino Compounds (Triazenes)

Diazonium ions give a number of compounds by reactions with nucleophiles containing an HN< group[53, 55]. The most important and most studied are arenediazoamino compounds (triazenes) which are formed by reaction of diazonium ions with primary and secondary aliphatic and aromatic (or heterocyclic) amines HNR^1R^2 (R^1 is hydrogen or alkyl, R^2 is alkyl or aryl):

$$ArN_2^+ + HNR^1R^2 \xrightleftharpoons[k_{-1}]{k_1} ArN{=}\overset{+}{N}HR^1R^2 \rightleftharpoons ArN{=}NNR^1R^2 + H^+ \qquad (32)$$

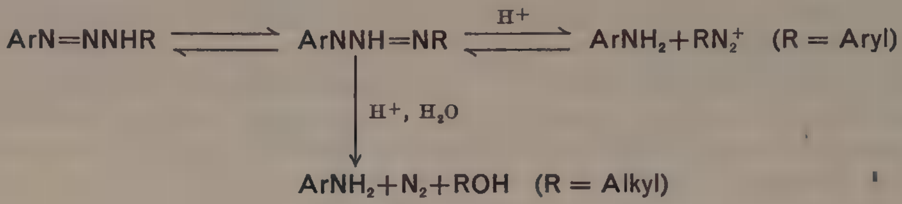
So far it has not been possible to prove *cis–trans* isomerism of these reaction products such as, for example, that of diazotates[63, 64] Measurements of dipole moments indicate[63] that the substances measured are *trans* isomers.

The reaction with aromatic amines can result either in a reversible reaction at the amino nitrogen to give a triazene or in an irreversible coupling reaction at a ring carbon atom to give an azo compound. Coupling at carbon is negligible in the case of aniline in neutral and slightly acidic media[65]; it is of minor importance with alkylanilines[66], but it represents the main reaction in the case of more reactive aromatic amines such as substituted naphthylamines. In more strongly acidic media the reverse reaction of the triazene becomes increasingly important and the content of azo compounds in reaction products increases.

The reaction with primary amines involves a further complication because two tautomeric forms are produced, the second being split into compounds other than the original diazonium salt and amine (Scheme 7). If R is aryl, the triazenes are split predominantly into the less reactive diazonium salt and less basic amine[67]. If R is alkyl, the splitting produces the aromatic amine and alcohol[68], the amount of the diazonium salt being negligible[69].

The equilibrium constant for reaction (32) has not yet been determined in any case. An attempt to determine the equilibrium concentration in the reaction with diethylamine (where the reaction is not complicated by C-coupling or by decomposition to products different from the starting substances) was made impossible by simultaneous decomposition of the diazonium salt[70].

The equilibrium constant can be calculated from the rate constant of formation of triazene and from that of the reverse reaction in those cases where two tautomeric forms of triazene are not formed.



SCHEME 7

The kinetic equations (33) and (34) are presumed for formation and decomposition of triazenes[65, 66, 71]; [R^{1}R^{2}NH] represents the concentration of the non-protonated amine. K_A is the dissociation constant of the protonated triazene; its value has not yet been determined in any case.

$$\overrightarrow{v} = k_1[\mathrm{ArN_2^+}]\,[\mathrm{R^1R^2NH}] \tag{33}$$

$$\overleftarrow{v} = k_{-1}[\mathrm{ArN{=}\overset{+}{N}HR^1R^2}] = k_{-1}[\mathrm{H^+}]/K_A[\mathrm{ArN{=}NNR^1R^2}]$$

$$= k_{\mathrm{H}^+}[\mathrm{H^+}]\,[\mathrm{ArN{=}NR^1R^2}] \tag{34}$$

$$K = [\mathrm{ArN{=}NNR^1R^2}]\,[\mathrm{H^+}]/[\mathrm{ArN_2^+}]\,[\mathrm{R^1R^2NH}] \tag{35}$$

The rate constants of formation[72] and reverse reaction[73] of triazenes were measured for the reaction of *meta-* and *para-* substituted benzenediazonium ions with dimethylamine in water at 25 and 20 °C.

The observed ρ constants of the formation and the reverse reaction of triazenes are 3·47 and $-3{\cdot}8$, respectively. The resulting $\rho = 7{\cdot}28$ for the equilibrium constant (equation 35) is only slightly higher than that for the reaction of diazonium ions with hydroxyl ion[28, 29]. The calculated rate constant k_1 of the reaction of benzenediazonium ion with dimethylamine is 450 l mol^{-1} sec^{-1}; the k_{H^+} constant of the reverse reaction can only be roughly estimated to be 10–20 l mol^{-1} sec^{-1}. The slope of the dependence of log k on pH in the measured pH range 1–3 was (instead of the expected -1, according to equation (34), provided that only minute amounts of the triazene are protonated) only about $-0{\cdot}75$. The calculated K value is about 30. For the sake of comparison with the equilibrium constant of the reaction of benzenediazonium ion with hydroxyl ion, which is equal to $2{\cdot}0 \times 10^4$ l^2/mol^2 (Reference 26) the above value must be divided by the ionic product of water K_W (which corresponds to a change of equation (32) in the sense that the protonated triazene loses its proton by reaction with hydroxyl ion). The resulting value, about 3×10^{15} l^2/mol^2 is about 11 orders of magnitude greater than that for the formation of diazotate. This difference is due, first of all, to the far greater acidity of the protonated triazene as compared with benzenediazohydroxide. Obviously here K_A is close to unity whereas it is 10^{-8} for the diazohydroxide[32].

The above-mentioned values, especially those for the reverse reaction and for the equilibrium constant, must be accepted with reserve. It cannot be excluded that isomerization† takes place side by side with the reaction and that the rate-limiting step changes with pH.

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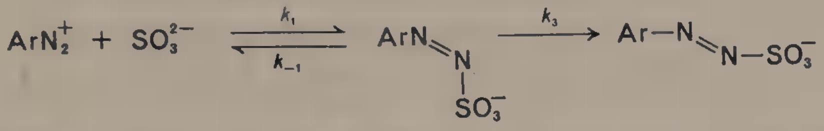
† Ritchie[70] studied the reaction kinetics of 4-chlorobenzenediazonium ion with diethylamine and observed a slower subsequent reaction independent of diethylamine concentration.

C. *Arenediazosulphonates*

The formation of diazosulphonates was described in 1869[74] and has been much studied because of its technical importance. The rate of formation of diazosulphonate is directly proportional to the concentration of arenediazonium ion and SO_3^{2-}; the diazonium ion does not react with HSO_3^- [40, 75]. In the first, very rapid, step a product is formed which was called *syn*-sulphonate by Hantzsch[76], and it is transformed slowly into the other isomer (*anti*):


(36)

The log K values of formation of *syn*-sulphonates (Table 5) correlate with the σ constants[40]; the ρ value is 5·5. The *syn*-sulphonates are very reactive and are rapidly decomposed into the starting substances. Half-life of the reverse reaction of 4-chloro derivative[70] is 15 msec. On the contrary, the *anti* isomers are extraordinarily stable. The values given for the 4-methoxy derivative are 10^7 for $K_3 = [anti]/[syn]$ and 10^{-1} sec^{-1} for the rate constant of the *anti* to *syn* transformation[77].

TABLE 5. Rate and equilibrium constants of the reaction of substituted benzenediazonium ions with sulphite ions

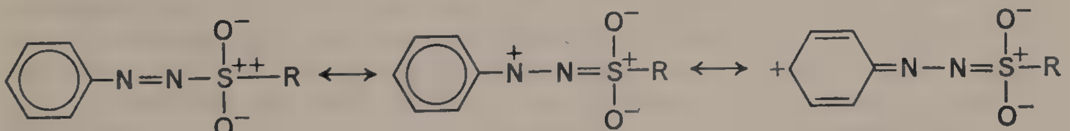
Substituent	K [a] (l/mol)	k_1 [b] (l mol^{-1} sec^{-1})	k_3 [a, c] (sec^{-1})
4-NO_2	$3{\cdot}2\times10^8$	$4{\cdot}5\times10^8$	$1{\cdot}8\times10^{-3}$
4-CN	$1{\cdot}1\times10^8$	$4{\cdot}3\times10^8$	
4-Cl	$2{\cdot}7\times10^5$	$2{\cdot}4\times10^7$	$0{\cdot}5\times10^{-3}$
H	$3{\cdot}6\times10^4$		$1{\cdot}9\times10^{-3}$

[a] Reference 40, ionic strength 1 M.
[b] Reference 70, ionic strength 10^{-3} M.
[c] At 0 °C.

D. *Arenediazosulphones*

Arenediazosulphones are formed by reaction of diazonium salts with anions of sulphinic acids[78]; usually the reaction is carried out in slightly acidic aqueous medium[79]. Only one isomer was proved in the reaction products[79, 80]. The dipole moments found[81] suggest *trans* structure of the products. The presence of the single isomer is explained[82] by lowering of the rotation barrier about the N=N bond by contribution of expanded octet structures such as **12b, c**:

$$ArN_2^+ + RSO_2^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ArN{=}NSO_2R \qquad (37)$$


(12a) **(12b)** **(12c)**

Since the water-solubility of the products is very low, the reaction kinetics of substituted benzenediazonium ions with benzenesulphinic acid were measured in methanol[82]. In contrast to the reactions of diazonium salts with most other nucleophiles, the diazosulphone is formed so slowly that the reaction can be followed by usual spectrophotometric methods. The dependence of the logarithms of the rate, and equilibrium constants on the σ constants is expressed by equations (38) to (40):

$$\log K = 3{\cdot}76\sigma + 5{\cdot}26 \tag{38}$$

$$\log k_1 = 2{\cdot}40\sigma + 2{\cdot}52 \tag{39}$$

$$\log k_{-1} = -1{\cdot}36\sigma - 2{\cdot}74 \tag{40}$$

In spite of anions of sulphinic acids being far weaker nucleophiles than the sulphite anion, the k_{-1} values are more than four orders of magnitude lower than those for the diazosulphonates. Obviously this is caused by the reverse reactions of diazosulphonates involving the more stable *trans* isomer. This fact also influences the values of the equilibrium constants. The small ρ observed for the diazosulphone equilibrium is explained[82] by the contribution of structures such as **12b** where a partial charge remains localized on the nitrogen.

E. *Arenediazothioethers*

Arenediazothioethers are formed very easily and rapidly by reaction of diazonium salts with thiols. They are very unstable and decompose, even explosively in some cases, to give nitrogen and the corresponding sulphide[83]. In contrast to aromatic hydroxy compounds the reactions with thiophenols, thionaphthols and even dithioresorcinol do not lead to coupling in the ring[84].

TABLE 6. Rate and equilibrium constants for the reaction

$$XC_6H_4N_2^+ + C_6H_5S^- \xrightleftharpoons{k_1} syn\text{-}XC_6H_4N{=}NSC_6H_5 \xrightarrow{k_3} anti\text{-}XC_6H_4N{=}NSC_6H_5$$

in methanol at 23 °C [61]

X	k_1 (l mol^{-1} sec^{-1})	K (l/mol)	k_3 (sec^{-1})
4-NO_2	$8{\cdot}7\times10^9$	$1{\cdot}9\times10^{10}$	$6{\cdot}4\times10^{-2}$
4-CN	$7{\cdot}0\times10^9$	$1{\cdot}8\times10^{10}$	$6{\cdot}6\times10^{-2}$
3-Cl	$5{\cdot}2\times10^9$		$1{\cdot}4\times10^{-1}$
4-Cl	$6{\cdot}0\times10^9$		$3{\cdot}7\times10^{-1}$
H	$1{\cdot}4\times10^9$		
4-CH_3O	$5{\cdot}7\times10^8$		

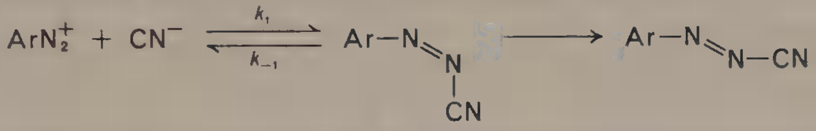
The reaction of benzenediazonium ions with thiophenoxide ion was followed by the stopped-flow method in methanolic buffers[61]. At relatively high concentrations of thiophenoxide ion the reaction of diazonium salts having a positive σ value for the substituent (4-chloro- to 4-nitro-) proceeds in two clearly separated steps. The initial rapid reaction is probably the formation of a *syn*-diazothioether, and the slower reaction is *syn–anti* isomerization. With the unsubstituted, 4-methyl and 4-methoxy derivatives the reactions followed first-order kinetics over the entire course of the reaction. The formation of *syn*-diazothioether was probably the rate-limiting step followed by a rapid *syn–anti* isomerization. Due to the isomerization, reliable values for the equilibrium constant could be obtained for the 4-nitro and 4-cyano derivatives only (Table 6):

$$ArN_2^+ + C_6H_5S^- \xrightleftharpoons[k_{-1}]{k_1} syn\text{-}ArN{=}NSC_6H_5 \xrightarrow{k_3} anti\text{-}ArN{=}NSC_6H_5 \tag{41}$$

The k_1 values approach the values for diffusion-controlled reactions; the influence of substituents is far smaller than in the other reactions studied and decreases with increasing value of σ constant. Equilibrium constants are about three orders of magnitude higher than those for reactions with CH_3O^- ion.

F. Arenediazocyanides

Substituted benzenediazonium ions react very rapidly and reversibly with cyanide ions to form *syn*-diazocyanides[85] which are slowly transformed (half-life of one to several hours at room temperature) into *anti*-diazocyanides[86]. Hantzsch[85] suggested *cis* and *trans* configuration for the *syn* and *anti* isomers, respectively, which agrees with the measured dipole moments and i.r. spectra of the two forms[18, 19]:



(42)

Equilibrium constants of formation of the *syn* isomer were measured by the use of conventional spectrophotometric methods[86] and by the stopped-flow technique[28]. The latter method affords more accurate results, because the determination of the equilibrium constant is not disturbed by slower subsequent reactions[28]. The effect of the ring substituents on the equilibrium and rate constants, determined also by the stopped-flow method, was quantitatively expressed by the Hammett equation:

$$\log K = 3{\cdot}53\sigma + 1{\cdot}82 \tag{43}$$

$$\log k_1 = 2{\cdot}31\sigma + 2{\cdot}32 \tag{44}$$

The relatively small ρ value 3·53 is (analogously to diazosulphonates) due to the partial positive charge on the nitrogen atom of the diazo group caused by the strong $-M$ effect of the CN group (mesomeric structure $Ar-\overset{+}{N}-N=C=\overline{N}$). The strong $-M$ effect of the CN group is obviously also responsible for the fact that electron-withdrawing substituents slow down the isomerization[87].

TABLE 7. Rate and equilibrium constants for the reaction of substituted benzenediazonium ions with cyanide ion in water at 23 °C [28]

Substituent	K (l/mol)	k_1 (l mol^{-1} sec^{-1})	k_{-1} (sec^{-1})
4-NO$_2$	$6{\cdot}0\times10^4$	$1{\cdot}7\times10^4$	0·28
4-CN	$1{\cdot}4\times10^4$	$7{\cdot}4\times10^3$	0·53
	$(2{\cdot}2\times10^7)$ [a]	$(2{\cdot}2\times10^6)$ [a]	(0·1) [a]
4-Br	$3{\cdot}7\times10^2$	$6{\cdot}5\times10^2$	1·75
	$(3{\cdot}2\times10^9)$ [b]	$(1{\cdot}6\times10^8)$ [b]	(0·05) [b]
4-Cl	$4{\cdot}5\times10^2$	$6{\cdot}8\times10^2$	1·5
	$(2{\cdot}5\times10^9)$ [b]	$(1{\cdot}5\times10^8)$ [b]	(0·06) [b]
4-CH$_3$	$1{\cdot}5\times10$	$9{\cdot}0\times10$	6·0
	$(1{\cdot}4\times10^8)$ [b]	$(3{\cdot}8\times10^7)$ [b]	(0·27) [b]

[a] In methanol[61].
[b] In dimethyl sulphoxide[88].

The reaction of some substituted benzenediazonium ions with cyanide ion was measured in water, in methanol[61] and dimethyl sulphoxide[88]. The equilibrium constants are three and seven orders of magnitude greater in methanol and dimethyl sulphoxide, respectively (Table 7). The influence of the medium is decisive in the case of k_1, whereas the reverse reaction showed a relatively lower decrease. A large increase in the equilibrium constant accompanying a change from a protic to polar aprotic solvent is typical for reactions with small, negatively-charged, nucleophiles[89].

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CHAPTER 3

Structural chemistry

S. SORRISO
Istituto di Chimica Fisica, Università di Perugia, 06100 *Perugia, Italy*

I. INTRODUCTION

A. General

It is normal in a chapter on structural chemistry to discuss bond distances and angles in molecules containing the characteristic group, and to explain the modifications undergone, or induced, by the latter. In the case of diazonium and diazo groups this is not sufficient because the structural data are often lacking. This makes necessary recourse to other kinds of results to discuss at least the possible configuration.

The configuration of diazo compounds has been the object of much work since their discovery about a hundred years ago[1]. Nevertheless, many problems still remain not completely solved. For example, due to the instability of the molecules examined, the type of isomerism present in some covalent diazo compounds and the reasons for its existence are still objects of discussion.

The book written by Zollinger[1] in 1961 covers the configurational aspects of the present groups. Therefore, with very few exceptions, work carried out before this year will not be covered since it has been reviewed at length in that book. A historical introduction to the configurational problems in the diazonium and diazo groups may be found in the book by Saunders[2].

Strictly structural results are relatively recent and they have not been reviewed previously. These, which have been obtained exclusively from X-ray measurements, will be treated extensively in the present chapter.

B. Usefulness and Errors in an X-Ray Examination

X-Ray data in chemistry give information on the molecular configuration and thus they are very helpful in indicating unequivocally the type of isomerism present. Besides, the refinement of the structure by means of modern computational methods often allows information to be obtained also on the hybridization of the atoms and on the bond order.

The reliability of an X-ray crystallographic determination is usually indicated by the R factor, the residual error index or discrepancy index, and by σ, the standard deviation[3, 4].

The R factor is a function of the observed (F_o) and calculated (F_c) structure factors:

$$R = \sum(|F_o| - |F_c|)/\sum|F_o|$$

R does not have a precise theoretical meaning and depends greatly on temperature factors, the complexity of the structure and the amount of data collected. The lower the value of R, the lower is the discrepancy between observed and calculated structure factors. Consequently, it is also useful to the crystallographer for following the progress of structure refinement. Initial R values of 0·50 and final ones of 0·10 are normal[3]. At present, with modern computer techniques, R values between 0·08 and 0·03 are being reported for the most reliably determined structures[4]. The R factor is a function of the intensities. Therefore, when heavy atoms are present, they may dominate the structure factor calculation. Consequently, the bond lengths involving heavy atoms will be more precisely determined than those involving light ones.

The standard deviation in bond lengths and angles is generally 0·002 Å and 0·2–1·5°, respectively, in more recent work. However for the former, given the possibility of systematic errors, it is reasonable to assign a value of 0·01 Å, even if account is taken of thermal motion (corrected value). For lighter elements, the standard deviations in bond distances are usually higher. In fact, since X-rays are diffracted by electrons, they give statistically the position of the centroid of negative charge rather than that of the nucleus. This means that while for heavy atoms the centroid of electron charge and that of the nucleus are statistically coincident, in light atoms there is a certain difference. For example, for hydrogen the difference[5] between the two is ~0·1 Å, which for lithium decreases to ~0·01 Å.

Caution is necessary in interpreting the crystallographic data in terms of the electronic structure and bond order. In fact, the standard deviation in bond length may be subject to different errors, such as the inadequacy of the atom-form factors, of the crystal model and of the temperature factors. These may become so important as sometimes to render the experimental data suspect, even if σ values are excellent.

II. DIAZONIUM SALTS

A. Outer Diazonium Salts

I. Structural data

a. *Benzenediazonium chloride*, PhN_2Cl (**1**). This molecule has been examined in two studies. In the first study[6, 7] the measurements were performed at room temperature. The compound is completely ionized; $R = 0{\cdot}06$; standard deviations 0·006–0·010 Å and 0·6–0·7°. The second study[8] was performed at −160 °C; R not specified; standard deviations 0·002 Å and 0·2°. Each diazonium group[7] is surrounded by four Cl^- ions situated in a plane perpendicular to the N—N axis. Two of the Cl^- ions lie at 3·184 and the other two at 3·511 Å to this axis. The former chlorine ions lie 3·225 and 3·237 Å away from $N_{(2)}$ and $N_{(1)}$, respectively, and the others at 3·548 and 3·559 Å. The separation between the latter and the $H_{(2)}$ atom (see Figure 1) is only 2·5 Å. Because this distance is half an ångström less than the sum of the van der Waals' radii, a strong interaction must be present between these two atoms[7].

b. *Benzenediazonium tribromide*, PhN_2Br_3[9] (**2**). Completely ionized; $R_{okl} = 0{\cdot}08$, $R_{hko} = 0{\cdot}073$ and $R_{hol} = 0{\cdot}073$ (where h, k and l are used to indicate the plane referred to); estimated standard deviations 0·04–0·05 Å and 3–4°. The spatial arrangement of tribromide ions about the diazo cation is shown in Figure 2. The $C_{(1)}$—N—N arrangement is linear. The shortest distances between the bromine atoms and $N_{(1)}$ and $N_{(2)}$ are 3·46 and 3·31 Å, respectively.

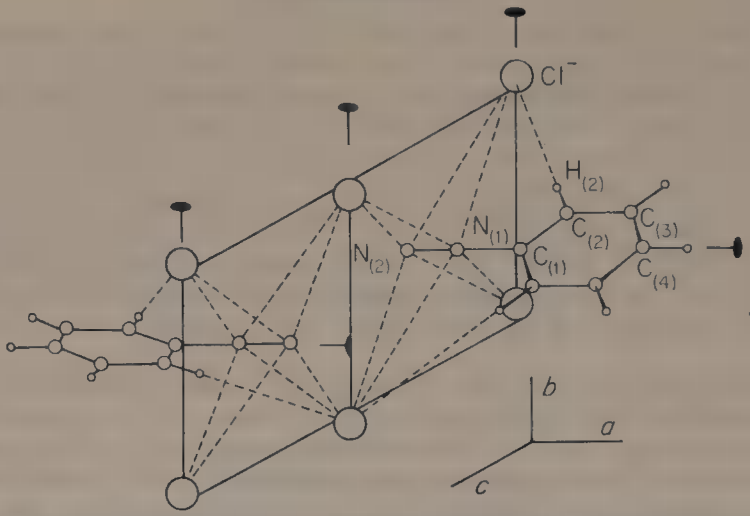


FIGURE 1. The layer of chloride and benzenediazonium ions. Reprinted, with permission, from Rømming, *Acta Chem. Scand.*, **17**, 1444 (1963).

Uncorrected bond lengths and angles

	Reference 7	Reference 8
$N_{(1)}—N_{(2)}$	1·097 Å	1·093 Å
$N_{(1)}—C_{(1)}$	1·385 Å	1·410 Å
$C_{(1)}—C_{(2)}$	1·374 Å	1·396 Å
$C_{(2)}—C_{(3)}$	1·383 Å	1·392 Å
$C_{(3)}—C_{(4)}$	1·376 Å	1·395 Å

	Reference 7	Reference 8
$C_{(1)}—N_{(1)}—N_{(2)}$	180°	—
$C_{(1)}—C_{(2)}—C_{(3)}$	117·6°	115·9°
$C_{(2)}—C_{(3)}—C_{(4)}$	119·8°	120·6°
$C_{(3)}—C_{(4)}—C_{(5)}$	121·7°	121·1°
$C_{(6)}—C_{(1)}—C_{(2)}$	124·8°	126·1°

(1)

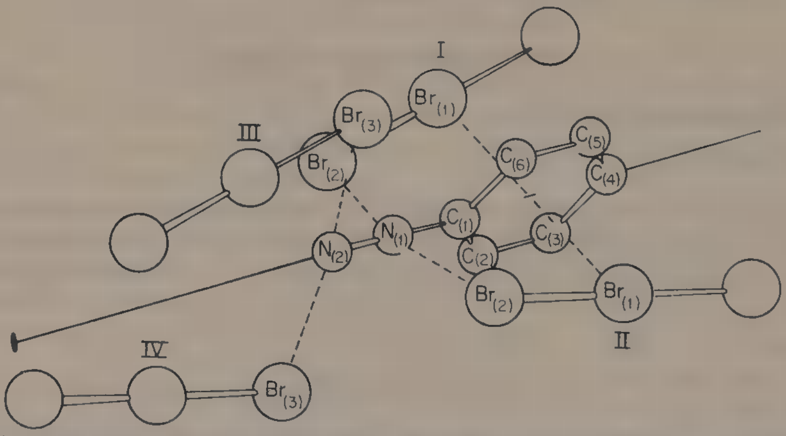


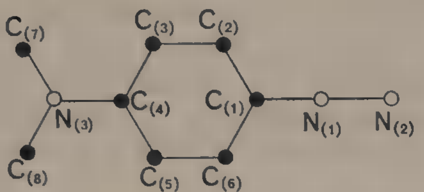
FIGURE 2. Arrangement of tribromide ions about a benzenediazonium ion. The lines $Br^{I}_{(1)}—Br^{II}_{(1)}$ and $Br^{III}_{(3)}—Br^{IV}_{(3)}$ form angles of about 85° and 35° with the plane of the benzene ring, respectively. Reprinted, with permission, from Andresen and Rømming *Acta Chem. Scand.*, **16**, 1882 (1962).

Uncorrected values

$N_{(1)}—N_{(2)}$	1·11 Å	$C_{(1)}—C_{(2)}—C_{(3)}$	114°
$C_{(1)}—N_{(1)}$	1·41 Å	$C_{(2)}—C_{(3)}—C_{(4)}$	118°
$C_{(1)}—C_{(2)}$	1·37 Å	$C_{(3)}—C_{(4)}—C_{(5)}$	125°
$C_{(2)}—C_{(3)}$	1·45 Å	$C_{(2)}—C_{(1)}—C_{(6)}$	131°
$C_{(3)}—C_{(4)}$	1·38 Å		

(2)

c. p-N,N-*Dimethylaminobenzenediazonium tetrachlorozinc*(II) $(p\text{-}Me_2NC_6H_4N_2)_2\cdot ZnCl_4$ [10,11] (3). Ionic structure; $R = 0{\cdot}141$; only the atomic coordinates have been reported; uncertainty in atomic coordinates has not been specified. From these data we have extracted the following bond distances and angles:

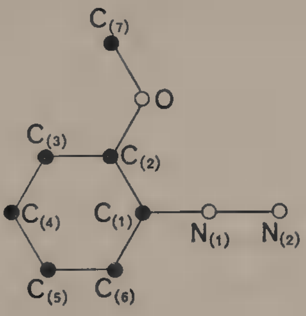


$N_{(1)}-N_{(2)}$	1·182 Å	$C_{(1)}-N_{(1)}-N_{(2)}$	169·9°
$C_{(1)}-N_{(1)}$	1·433 Å	$C_{(2)}-C_{(1)}-N_{(1)}$	110·9°
$C_{(1)}-C_{(2)}$	1·524 Å	$C_{(1)}-C_{(2)}-C_{(3)}$	108·9°
$C_{(2)}-C_{(3)}$	1·374 Å	$C_{(2)}-C_{(3)}-C_{(4)}$	128·3°
$C_{(3)}-C_{(4)}$	1·495 Å	$C_{(3)}-C_{(4)}-C_{(5)}$	116·7°
$C_{(4)}-C_{(5)}$	1·476 Å	$C_{(4)}-C_{(5)}-C_{(6)}$	118·3°
$C_{(5)}-C_{(6)}$	1·480 Å	$C_{(5)}-C_{(6)}-C_{(1)}$	117·3°
$C_{(6)}-C_{(1)}$	1·360 Å	$C_{(6)}-C_{(1)}-C_{(2)}$	129·8°
$C_{(4)}-N_{(3)}$	1·355 Å	$N_{(3)}-C_{(4)}-C_{(3)}$	122·8°
$N_{(3)}-C_{(7)}$	1·532 Å	$C_{(4)}-N_{(3)}-C_{(7)}$	119·5°
$N_{(3)}-C_{(8)}$	1·509 Å	$C_{(7)}-N_{(3)}-C_{(8)}$	120·0°

(3)

The chlorine ions form a tetrahedron about the Zn atom ($Cl-\widehat{Zn}-Cl$ 106–110° and Zn—Cl 2·28–2·35 Å). The shortest distances between $Cl_{(1)}$ and $N_{(1)}$ and $N_{(2)}$ are 3·672 and 3·435 Å, respectively, and those between $Cl_{(2)}$ and $N_{(1)}$ and $N_{(2)}$ 3·701 and 3·420 Å.

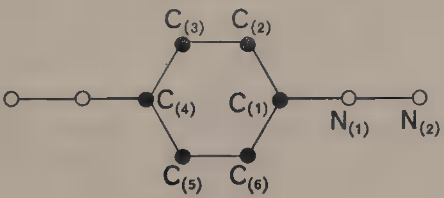
d. o-*Methoxybenzenediazonium tetrachloroiron*(III), $o\text{-}MeOC_6H_4N_2\cdot FeCl_4$ [12] (4). Ionic structure. $R = 0{\cdot}13$; standard deviation 0·01–0·02 Å. The chlorine ions form a tetrahedron around the Fe atom ($Cl-\widehat{Fe}-Cl$ 107·5–113·2° and Fe—Cl 2·165–2·230 Å). All the atoms C, N and O are coplanar. The shortest distances between the chlorine and the two nitrogen atoms are $Cl-N_{(1)}$ 3·51 and $Cl-N_{(2)}$ 3·36 Å.



Uncorrected			
$N_{(1)}-N_{(2)}$	1·11 Å	$C_{(1)}-N_{(1)}-N_{(2)}$	179°
$C_{(1)}-N_{(1)}$	1·48 Å	$C_{(2)}-C_{(1)}-N_{(1)}$	118°
$C_{(1)}-C_{(2)}$	1·38 Å	$C_{(1)}-C_{(2)}-C_{(3)}$	119°
$C_{(2)}-C_{(3)}$	1·40 Å	$C_{(2)}-C_{(3)}-C_{(4)}$	114°
$C_{(3)}-C_{(4)}$	1·41 Å	$C_{(3)}-C_{(4)}-C_{(5)}$	126°
$C_{(4)}-C_{(5)}$	1·41 Å	$C_{(4)}-C_{(5)}-C_{(6)}$	124°
$C_{(5)}-C_{(6)}$	1·49 Å	$C_{(5)}-C_{(6)}-C_{(1)}$	103°
$C_{(6)}-C_{(1)}$	1·48 Å	$C_{(6)}-C_{(1)}-C_{(2)}$	134°
$C_{(2)}-O$	1·36 Å	$C_{(1)}-C_{(2)}-O$	117°
$O-C_{(7)}$	1·45 Å	$C_{(2)}-O-C_{(7)}$	120°

(4)

e. p-*Benzenebisdiazonium tetrachlorozinc*(II), $p\text{-}N_2C_6H_4N_2\cdot ZnCl_4$ [13] (5). Ionic structure; $R = 0{\cdot}065$; standard deviations 0·012–0·017 Å and 0·8–1·2°. The

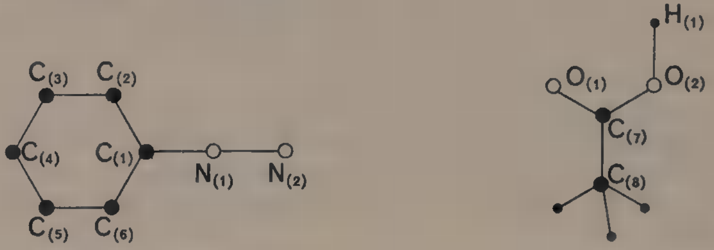


Uncorrected			
$N_{(1)}-N_{(2)}$	1·09 Å	$C_{(2)}-C_{(1)}-C_{(6)}$	128·2°
$C_{(1)}-N_{(1)}$	1·42 Å	$C_{(1)}-C_{(2)}-C_{(3)}$	115·9°
$C_{(1)}-C_{(2)}$	1·37 Å		
$C_{(2)}-C_{(3)}$	1·42 Å		
$C_{(1)}-C_{(4)}$	2·62 Å		
$C_{(2)}-C_{(5)}$	2·85 Å		

(5)

p-benzenebisdiazonium ion is, within the accuracy of the measurements, planar and the N—N—C···C—N—N arrangement is linear. The diazonium group is surrounded by four chloride ions situated in a plane perpendicular to the N—N axis. The shortest distances between the chlorine and nitrogen are Cl—$N_{(1)}$ 3·26 and Cl—$N_{(2)}$ 3·43 Å. These values are almost equal to the van der Waals' separation between these two atoms (3·3 A). Thus it is not possible to draw any conclusion as to the charge distribution in the diazonium group from the geometrical parameters†.

f. 1:1 *Complex benzenediazonium chloride–acetic acid*, $PhN_2Cl{\cdot}MeCO_2H$ [14] (6). $R = 0{\cdot}075$; standard deviations 0·006–0·016 Å and 0·5–1·2°. The crystals are built up of benzenediazonium ions, chloride ions and acetic acid molecules. The distance between the oxygen and chloride ions (3·01 Å) may indicate the presence of a hydrogen bond[14, 15], $O_{(2)}\cdots H_{(1)}\cdots Cl^-$.



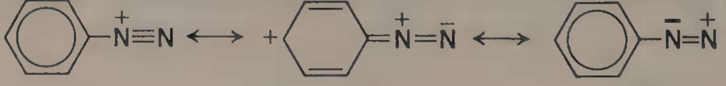
	Uncorrected	Corrected
$N_{(1)}$—$N_{(2)}$	1·093 Å	1·098 Å
$C_{(1)}$—$N_{(1)}$	1·418 Å	1·425 Å
$C_{(1)}$—$C_{(2)}$	1·384 Å	1·398 Å
$C_{(2)}$—$C_{(3)}$	1·356 Å	1·363 Å
$C_{(3)}$—$C_{(4)}$	1·396 Å	1·413 Å
$C_{(4)}$—$C_{(5)}$	1·402 Å	1·417 Å
$C_{(5)}$—$C_{(6)}$	1·360 Å	1·368 Å
$C_{(6)}$—$C_{(1)}$	1·389 Å	1·406 Å
$C_{(7)}$—$C_{(8)}$	1·470 Å	
$C_{(7)}$—$O_{(1)}$	1·216 Å	
$C_{(7)}$—$O_{(2)}$	1·326 Å	
C_{sp^2}—H	1·01–1·08 Å	
$O_{(2)}$—H	1·05 Å	

	Uncorrected	Corrected
$C_{(1)}$—$N_{(1)}$—$N_{(2)}$	177·5°	
$C_{(1)}$—$C_{(2)}$—$C_{(3)}$	118·0°	117·3°
$C_{(2)}$—$C_{(3)}$—$C_{(4)}$	121·1°	121·0°
$C_{(3)}$—$C_{(4)}$—$C_{(5)}$	119·3°	119·7°
$C_{(4)}$—$C_{(5)}$—$C_{(6)}$	120·7°	120·5°
$C_{(5)}$—$C_{(6)}$—$C_{(1)}$	117·5°	117·3°
$C_{(6)}$—$C_{(1)}$—$C_{(2)}$	123·6°	124·0°

(6)

2. Discussion

The results reported in Section II.A.1 leave no doubt as to the structure of the diazonium group. It may be seen that, with the exception of the compound **5**, in all the compounds examined the N—N distance lies in the range 1·09–1·11 Å, virtually the same as that observed in dinitrogen (1·097 Å)[16], which indicates that in the ground state the extreme form **7** clearly predominates over **8** and **9**. The presence of



(7) (8) (9)

an essentially triple N—N bond has also been arrived at from the value of the frequency of the N—N stretching vibration band (~2290 cm⁻¹)[17–21] which is between the Raman frequency of dinitrogen (2330 cm⁻¹)[22] and the stretching vibration frequency of the C≡N group (~2255 cm⁻¹ for PhCN)[23]. Also in agreement with this

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† See Note Added in Proof, p. 135.

suggestion are the theoretical calculations carried out, using different methods, by Shuster and Polansky[24] and, more extensively, by Bochvar and coworkers[25] and by Sukigara and Kikuchi[26–28].

The fact that the N—N bond is virtually a triple bond suggests that the positive charge of the benzenediazonium ion, according to the valence theory, is localized mainly on the nitrogen atom which is bonded to the phenyl ring. Several authors[11, 20] do not agree with this conclusion. They base their opinions on the fact that for most of the diazonium salts above, the shortest distance Hal—$N_{(2)}$ is always shorter than, or of the same order as, the distance Hal—$N_{(1)}$, which suggests that the positive charge of the diazo cation is slightly more localized on the terminal nitrogen or, at least, equally distributed over both nitrogen atoms. We feel that this shorter Hal—$N_{(2)}$ distance probably does not depend exclusively on the electrostatic interaction between the nitrogen and the halogen ion, but also on that between the latter and the hydrogen *ortho* to the phenyl ring[29]. This suggestion might be supported by the fact that in benzenediazonium chloride[7] (Figure 1) the distance between the $H_{(2)}$ atom and Cl^- ion is 2·5 Å, about 0·5 Å smaller than the sum of the van der Waals' radii.

X-ray data for the complexes *o*-$MeOC_6H_4N_2{\cdot}FeCl_4$ and [*p*-$Me_2NC_6H_4N_2]_2{\cdot}ZnCl_4$, together with results of MO calculations, have been used by some authors[25] to suggest the presence of a 'benzenoid zone' and of a 'quinoid' one in methoxy- and amino-diazo cations. We shall now see how far this suggestion is supported by the experimental results.

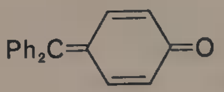
o-$MeOC_6H_4N_2{\cdot}FeCl_4$: The bond lengths in the diazonium group do not indicate the presence of conjugation with the rest of the molecule. In fact, the N—N bond (1·11 Å)[13] is virtually the same as that in benzenediazonium chloride (~1·09–1·10 Å). In addition, the $C_{(1)}$—$N_{(1)}$ bond (1·48 Å) is noticeably greater compared to the same bond in **1** (1·385–1·410 Å), whereas it should, of course, be shorter according to the canonical forms **7–9**. In agreement with these results, the methoxy group does not support the presence of conjugation with the diazonium group. In fact, the O—C_{sp^2} distance (1·36 Å) is of the same order as that in similar molecules, e.g. 1,4-dimethoxybenzene (1·36 Å)[30] and *p,p'*-dimethoxybenzophenone (1·37 Å)[31].

[*p*-$Me_2NC_6H_4N_2]_2{\cdot}ZnCl_4$: For this molecule the fact that the N—N distance is sensibly longer (1·18 Å) than in benzenediazonium chloride may be an indication that there is an increase in the contribution of the extreme forms [illegible] compared to that in the parent compound **1**, i.e. strong conjugation between the substituent and the diazonium group. In agreement with this, the $N_{(3)}$—C_{sp^2} distance (1·35 Å) is shorter than that observed in 2,5-dichloroaniline (1·40 Å)[32] and *p*-toluidine (1·43 Å)[33], and is similar to that found in *p*-nitroaniline (1·37 Å)[34] and *N,N*-dimethyl-*p*-nitroaniline (1·35 Å)[35], for which conjugation between the nitro and amino groups is accepted. These points, important for defining the structure of this compound, unfortunately are doubtful because the $C_{(1)}$—$C_{(2)}$ and $C_{(6)}$—$C_{(1)}$ distances are very different (1·53 and 1·36 Å, respectively) whereas they should be equal (within experimental error, which is less than 0·1 Å)[10, 11]. Furthermore, the present results are uncertain since the authors[10, 11] do not report the exact standard deviations in the atomic coordinates. To conclude, the above discussion on the complexes **3** and **4** shows that the present structural parameters cannot be used to prove the existence of a 'quinoid zone' about the amino group and a 'benzenoid zone' involving the diazonium group[25]. On the other hand, in this case, the theoretical calculations[25] cannot be invoked to support this suggestion since for the benzenediazonium cation they are very sensitive to the input parameters used. It seems obvious that, given the utility of X-ray measurements, amine complexes with different anions should be examined before definite conclusions can be drawn.

Further information on the electronic structure of diazo cations substituted in the phenyl ring with electron-donor groups has been obtained using other techniques.

In different solvents, good correlations have been found[17, 19, 21, 36–38] between the frequency of the stretching vibration band (ν_{NN}), its integrated band intensity, the N—N bond order and the Hammett σ_p values[39] for diazonium cations p-$XC_6H_4N_2^+$ (X = H, Me, Cl, Br, NO_2, SO_2NH_2, I, F, OMe, CO_2Et, OH, O^- or SO_3^-). For p-OH-, p-OMe- and p-Me_2N-derivatives σ^+ values have been used instead of σ_p ones. This procedure led to the result that the points for the first two derivatives were on a straight line but that for the amine compound was not[17]. This indicates further polar conjugation between the substituent and the diazonium group, which is much greater in the amine derivative.

Many workers have shown interest in the electronic structure of the latter compounds. In the spectral zone characteristic of quinones some similarity has been observed[40] between the u.v. spectra of p-amino-, p-methylamino- and p-dimethylamino-benzenediazonium cations and that of diphenylquinomethane, which has a quinoid structure **(10)**. This led to the suggestion that these molecules have an analogous structure **(11)**. There are many possible criticisms of this suggestion and it certainly appears that a completely quinoid structure for all three of the above derivatives cannot explain the other experimental results. In fact, if this were indeed the structure, there should be no appreciable variation in the electronic configuration of the diazo cation on introducing two methyl groups in place of the amine hydrogens. The opposite is the case, because on passing from the amino to the dimethylamino derivative, ν_{NN} goes from 2183 to 2166 cm^{-1} and the band at 357 goes to 382 nm[41], indicating an increase in quinoid character. Also, the N—N integrated band intensities (12·6 and 13·5 $mol^{-1}\,cm^{-2} \times 10^4$ respectively, for p-$NH_2C_6H_4N_2Cl$ and p-$Me_2NC_6H_4N_2Cl$)[18] show the same difference between these two compounds. Very probably the present amino derivatives also arise from a resonance hybrid between the canonical forms **7** and **8**. However, there is a noticeable contribution from [illegible] which, instead, in these compounds becomes **11**. This resonance form would account not only for the frequency and integrated intensity of the N—N stretching vibration band but also for the fact that for dimethylamino derivative even the σ^+ value does not lie on the ν_{NN} versus σ_p plot. Form **11**, further, would explain the much higher stability and the colour of these compounds as compared with the other diazonium salts of simple anions, the great majority of which are colourless[40].


(10)


(11)

3. Effect of the anion on the structure of diazonium cations

Much information on this matter has been obtained from infrared measurements. These have been confined to the study of the N—N stretching vibration band in complex molecules and to comparison with spectra of diazonium salts of simple anions. It is not appropriate to underline the various contributions, which are very numerous[42–59], in a chapter on structural chemistry. However, a concise discussion of the results available may be useful.

Independently of the physical state, all the diazonium salts studied to date show one absorption band in the N≡N region. Some authors[50] report two N—N bands in this region only in *p*-dialkylamino derivatives. Of these bands the more intense, at ~2170 cm^{-1}, is assigned to the N—N stretching vibration and the other, at ~2250 cm^{-1}, appears to be the first overtone of the band at ~1100 cm^{-1}, assigned to the C—N vibrations of the alkylamino groups. Instead, other authors[45–48, 56] have also observed a complex band, usually with two peaks, for many diazonium salts, independently of substitution at the phenyl ring. The reason for the appearance of a complex N—N band is not clear. In most cases it is probably due to solid-state lattice effects, since there is only a single peak on regrinding the mull[50]. To interpret the presence of complex N—N bands as caused by weak bonding between the diazonium group and the anion seems hazardous, although it cannot entirely be excluded. On the other hand, X-ray data on the complex diazonium salts examined above when compared to those for PhN_2Cl do not indicate the presence of this bond.

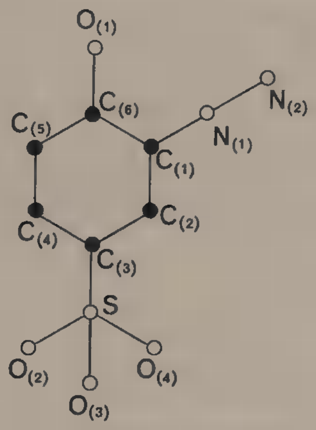
Nuttall and coworkers[50] observed that the salts of the very strong complex fluoro acids show a ν_{NN} value higher than that in other complex diazonium salts. For these authors this fact indicates that the former are completely ionic, while the latter have a weak covalent bond between the empty orbital of the diazonium group and the halogen lone pair, or between the π orbital of the diazonium group and the metal atom of the anion. The first suggestion might be preferred[50] for the following reasons. In complex diazonium salts with *p*-dimethylamino substituted cations, in which the diazonium group is less positive than in other derivatives, the ν_{NN} value does not show the clear difference between the fluoro derivatives and the others.

To conclude, the extensive spectroscopic results together with X-ray data suggest that the electronic structure of the diazo cation in diazonium salts of complex anions is substantially the same as that in the analogous simple salts.

B. *Inner Diazonium Salts*

1. 2-Diazonium-4-phenolsulphonate monohydrate

$N_2C_6H_3SO_3{\cdot}OH{\cdot}H_2O$ [60] **(12)**: $R = 0{\cdot}128$; standard deviation 0·01–0·02 Å. The compound has a zwitterionic structure; the water molecules connect these zwitterions by means of hydrogen bonding.



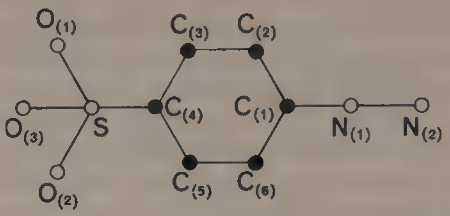
Uncorrected

$N_{(1)}—N_{(2)}$	1·08 Å	$C_{(1)}—N_{(1)}—N_{(2)}$	179°
$C_{(1)}—N_{(1)}$	1·40 Å	$N_{(1)}—C_{(1)}—C_{(2)}$	117°
$C_{(1)}—C_{(2)}$	1·42 Å	$C_{(1)}—C_{(2)}—C_{(3)}$	117°
$C_{(2)}—C_{(3)}$	1·38 Å	$C_{(2)}—C_{(3)}—C_{(4)}$	119°
$C_{(3)}—C_{(4)}$	1·43 Å	$C_{(3)}—C_{(4)}—C_{(5)}$	122°
$C_{(4)}—C_{(5)}$	1·37 Å	$C_{(4)}—C_{(5)}—C_{(6)}$	119°
$C_{(5)}—C_{(6)}$	1·38 Å	$C_{(5)}—C_{(6)}—C_{(1)}$	118°
$C_{(6)}—C_{(1)}$	1·39 Å	$C_{(6)}—C_{(1)}—C_{(2)}$	124°
$C_{(6)}—O_{(1)}$	1·35 Å	$C_{(2)}—C_{(3)}—S$	120°
$C_{(3)}—S$	1·76 Å	$C_{(3)}—S—O_{(2)}$	104°
$S—O_{(2)}$	1·46 Å	$C_{(3)}—S—O_{(3)}$	107°
$S—O_{(3)}$	1·46 Å	$C_{(3)}—S—O_{(4)}$	106°
$S—O_{(4)}$	1·44 Å	$O_{(2)}—S—O_{(3)}$	113°
		$O_{(2)}—S—O_{(4)}$	114°
		$O_{(3)}—S—O_{(4)}$	112°

(12)

2. *p*-Benzenediazonium sulphonate

$N_2C_6H_4SO_3$ (**13**): The structure of this molecule has been determined twice. In the first study[61], $R = 0{\cdot}13$, standard deviations were not reported. According to the authors, the dimensions of the phenyl ring indicate that the molecule is quinoid in character. The second study[29] has, $R = 0{\cdot}052$, standard deviations 0·002–0·004 Å and 0·1–0·3°. The C—H bond length is 0·91–0·99 Å [29].

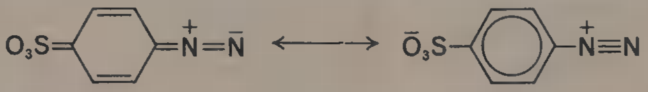


	Reference 61	Reference 29	
	Un-corrected	Un-corrected	Corrected
$N_{(1)}-N_{(2)}$	1·14 Å	1·091 Å	1·091 Å
$C_{(1)}-N_{(1)}$	1·39 Å	1·410 Å	1·412 Å
$C_{(1)}-C_{(2)}$	1·45 Å	1·390 Å	1·398 Å
$C_{(2)}-C_{(3)}$	1·38 Å	1·371 Å	1·374 Å
$C_{(3)}-C_{(4)}$	1·41 Å	1·392 Å	1·399 Å
$C_{(4)}-C_{(5)}$	1·44 Å	1·376 Å	1·384 Å
$C_{(5)}-C_{(6)}$	1·37 Å	1·380 Å	1·382 Å
$C_{(6)}-C_{(1)}$	1·45 Å	1·377 Å	1·384 Å
$S-C_{(4)}$	1·75 Å	1·798 Å	1·801 Å
$S-O_{(1)}$	1·47 Å	1·449 Å	1·457 Å
$S-O_{(2)}$	1·48 Å	1·438 Å	1·451 Å
$S-O_{(3)}$	1·42 Å	1·450 Å	1·459 Å

	Uncorrected	
	Reference 61	Reference 29
$C_{(1)}-N_{(1)}-N_{(2)}$	178°	179·6°
$N_{(1)}-C_{(1)}-C_{(2)}$	117°	116·2°
$C_{(1)}-C_{(2)}-C_{(3)}$	114°	116·3°
$C_{(2)}-C_{(3)}-C_{(4)}$	125°	120·4°
$C_{(3)}-C_{(4)}-C_{(5)}$	119°	121·0°
$C_{(4)}-C_{(5)}-C_{(6)}$	121°	120·7°
$C_{(5)}-C_{(6)}-C_{(1)}$	118°	116·1°
$C_{(6)}-C_{(1)}-C_{(2)}$	124°	125·4°
$C_{(3)}-C_{(4)}-S$	121°	118·7°
$C_{(4)}-S-O_{(1)}$	107°	105·4°
$C_{(4)}-S-O_{(2)}$	106°	105·9°
$C_{(4)}-S-O_{(3)}$	106°	104·7°
$O_{(1)}-S-O_{(2)}$	112°	113·9°
$O_{(1)}-S-O_{(3)}$	112°	112·2°
$O_{(2)}-S-O_{(3)}$	114°	113·7°

(13)

There has been discussion as to whether *p*-benzenediazonium sulphonate has a quinoid structure (**14**) or a benzenoid one, of the predominant extreme form (**15**).



(14) **(15)**

The data available suggest that this molecule, and also **12**, has a zwitterionic structure although, according to some authors[41], a small contribution from canonical form **14** cannot be entirely excluded from the spectroscopic results. In fact, the N—N stretching band frequency lies at 2296 cm^{-1} (in petroleum ether)[20] in benzenediazonium chloride and at 2284 cm^{-1} in *p*-benzenediazonium sulphonate. Instead, in *p*-diazo oxide, $OC_6H_4N_2$, for which a prevalent quinoid structure is now believed to exist, ν_{NN} (in $CHCl_3$) lies at 2088 cm^{-1}. On the other hand, the structural data do not appear useful in this case since a small participation of canonical form **14** could cause a variation in the bond lengths of the same order as that of the experimental errors.

In agreement with a zwitterionic structure, the $N_{(1)}—N_{(2)}$ distance (1·08 and 1·09 Å, respectively, in 2-diazonium-4-phenolsulphonate monohydrate and in *p*-benzenediazonium sulphonate[29]) is of the same order as that found in most diazonium salts (1·10–1·11 Å)[7–9, 11]. In turn, the $C_{(1)}—N_{(1)}$ bond length is 1·40–1·41 Å and compares very favourably with the values observed for unsubstituted diazonium salts (1·39–1·42 Å). Finally, these results are confirmed by the value of the C—S bond length, which is very near to that found in similar molecules[62, 63].

III. DIAZOTATES

A. Isomerism

Addition of a strong base to an aqueous solution of a diazonium salt leads to rather complex transpositions, which have been of interest for a long time[1]. The reaction scheme which is presently agreed on[1, 64–72] is the following:

$$\mathrm{ArN_2^+ + OH^-} \xrightleftharpoons{\text{slow}} syn\text{-}\mathrm{ArN_2OH} \qquad (1)$$

$$syn\text{-}\mathrm{ArN_2OH + OH^-} \xrightleftharpoons{\text{fast}} syn\text{-}\mathrm{ArN_2O^- + H_2O} \qquad (2)$$

$$syn\text{-}\mathrm{ArN_2O^-} \xrightleftharpoons{\text{slow}} anti\text{-}\mathrm{ArN_2O^-} \qquad (3)$$

$$\mathrm{ArN_2^+ + OH^-} \rightleftharpoons anti\text{-}\mathrm{ArN_2OH} \qquad (4)$$

$$anti\text{-}\mathrm{ArN_2OH} \rightleftharpoons anti\text{-}\mathrm{ArN_2O^- + H^+} \qquad (5)$$

There is kinetic evidence only for the participation of *syn*-diazohydroxide in the reaction[1, 64, 71], while *anti*-diazohydroxide has been identified spectroscopically but not isolated in the pure state[1, 64].

The existence of two diazotate ions in aqueous solution at appropriate pH, which is now accepted by most workers[1], was in doubt until very recently[72, 73]. Their existence now seems definitely established even for the *syn*-isomer of *p*-nitrophenyldiazotate, which could not be detected previously because of its high lability[74].

The problem of the type of isomerism present in diazotate ions has been widely studied[1]. However, since the techniques available were unsuitable, the results obtained were never conclusive. Most workers[1, 20] agreed that the isomerism present in diazotates is geometrical isomerism (equation 6). However, the evidence put forward to support this claim was essentially based on the analogy with similar compounds or on kinetic results. Direct confirmation has been obtained only recently, via the three-dimensional X-ray structural analysis of potassium-*syn*-methyl-diazotate[75]. The results obtained, which are reported in Section III.B, may be extended, so far as this type of isomerism is concerned, to the corresponding phenyl derivative (PhN_2OK), since Müller and coworkers[76] found that both compounds are prepared in the same way and have similar properties.

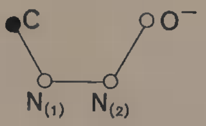
(6)

cis (*syn*) *trans* (*anti*)

The problem of the configuration of the *syn* and *anti* isomers is now largely clarified and will not, therefore, be treated at length.

B. Structure of Potassium-syn-methyl-diazotate

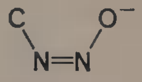
$MeN_2O—K$ (**16**): This is the only diazotate for which structural parameters are available; $R = 0{\cdot}084$; standard deviations 0·008–0·01 Å and 0·5°. The C—N and N—N bond lengths in **16**, (1·477 and 1·246 Å, respectively) are of the same order as those observed in azomethane (1·474 and 1·244 Å, respectively)[77]. By contrast, the N—O distance (1·306 Å) is shorter than that observed usually (1·39–1·41)[75].

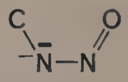


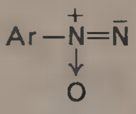
Uncorrected			
$N_{(1)}—N_{(2)}$	1·246 Å	$C—N_{(1)}—N_{(2)}$	116·2°
$C—N_{(1)}$	1·477 Å	$N_{(1)}—N_{(2)}—O$	119·8°
$N_{(2)}—O$	1·306 Å		
$N_{(1)}$ O	2·208 Å	K O	2·650–2·785 Å
K $N_{(2)}$	2·900 Å	K $N_{(1)}$	2·914–2·957 Å

(16)

These results may be explained by invoking the participation of the extreme forms **17a** and **17b** to the resonance hybrid, with the predominance of the former. The data reported for **16** exclude the alternative theory on the configuration of diazotates[1, 78–81], according to which the stable isomer (*anti*) has the same configuration as that put forward by Hantzsch, whilst the labile one (*syn*) has the structure **18**.


(17a)


(17b)

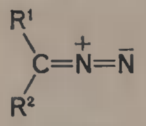

(18)

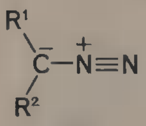
IV. DIAZOALKANES

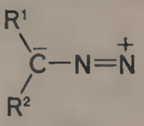
A. General

The structures of only a few diazoalkanes not containing other characteristic groups (diazomethane, 2-bromodiazofluorene and phenyl(triphenylsilyl)diazomethane) have been determined. The structural parameters for diazomethane have been reviewed previously[1, 82, 83] and will not be reported here.

In the diazoalkanes examined to date, the C—N bond length (1·28–1·32 Å) is greater than that observed for a C_{sp^2}=N bond (1·23–1·26 Å)[84]. At the same time, the N—N distance (1·12–1·13 Å) is greater than that found for dinitrogen and for benzenediazonium chloride (1·09)[8, 16]. In agreement with most workers[85–92], this evidence suggests that the $=CN_2$ group is a resonance hybrid between the canonical forms **19** and **21**. Form **21** is commonly not reported since its contribution is very small compared to that of **19** and **20**, as it possesses fewer covalent bonds and there is a larger charge separation.


(19)


(20)


(21)

The participation of the two extreme forms **19** and **20** to the resonance hybrid is confirmed by the infrared spectra. In fact, the frequency of the N—N stretching vibration band (2088 cm^{-1} in ether and in CCl_4 for the molecule CH_2N_2)[88, 93] is smaller than that observed for the *p*-dimethylaminobenzenediazonium cation (2166 cm^{-1}, in petroleum ether)[20], for which a relevant contribution of a quinoid form is now proved.

There has been some work on the relative contributions of forms **19** and **20** by means of n.m.r. and electric dipole moment measurements.

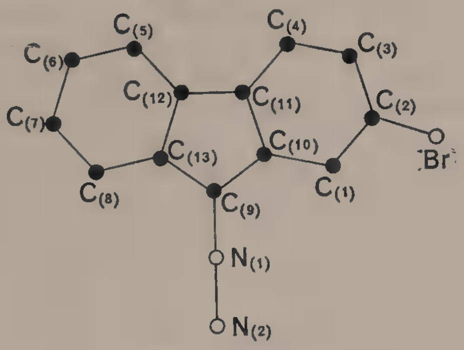
Interpretation of the n.m.r. spectra was based on the observation that in form **19** the electron density on the carbon atoms α and β to the diazo group is different from that in **20**. Consequently, the chemical shift of the protons bonded to these carbon atoms should give some indication as to the participation of the two canonical forms[94, 95]. To this purpose, Ledwith and Friedrich[89] determined the nuclear magnetic resonance shielding parameters for the following compounds: H_2CN_2, $MeCHN_2$, CH_2CHCHN_2, $EtOCOCHN_2$, $MeOCOCHN_2$, $PhCHN_2$, Ph_2CN_2, $(p\text{-}MeOC_6H_4)_2CN_2$, diazocyclopentadiene and 9-diazofluorene. For these molecules a greater shielding than that for similar compounds[96, 97] was found. According to the authors[89] this may be due to a considerable participation of form **20** and/or to the presence of diamagnetic anisotropy in the diazo group analogous to that observed for acetylenes and nitriles[98, 99].

It now appears that the high shielding found in n.m.r. spectra is due in the main to the presence of diamagnetic anisotropy. In fact, from the observed moments for the molecules Ph_2CN_2 (1·27–1·42 D)[100, 101], $(p\text{-}ClC_6H_4)_2CN_2$ (0·65 D)[100, 101] and using $\mu(\overrightarrow{C_{sp^2}\text{—}Cl}) = 1{\cdot}59$ D [102], a value of $\mu(\overrightarrow{CN_2})$ of *c.* 1·0 D, having the direction indicated[103], is obtained. Taking into consideration the fact that the theoretical moment of form **19** is smaller than that of **20** (5·46 and 6·24 D, respectively, for diazomethane)[90], we deduce that the first predominates over the second. In this context it is worthy of note that for diazomethane **19** and **20** are present in the ratio 66/34 [90], in agreement with an independent estimate of 70/30 obtained from microwave quadrupole measurements[104].

B. X-Ray Data

1. 2-Bromodiazofluorene

$C_{13}H_7N_2Br$ [105] (**22**): $R = 0{\cdot}09$; standard deviations 0·031–0·040 Å and 1·8–2·8°. All the atoms lie in the same plane apart from Br, $C_{(7)}$ and $N_{(2)}$, which are slightly shifted from this plane.



Uncorrected

$C_{(1)}—C_{(2)}$	1·452 Å	$C_{(7)}—C_{(8)}$	1·407 Å
$C_{(2)}—C_{(3)}$	1·385 Å	$C_{(8)}—C_{(13)}$	1·429 Å
$C_{(3)}—C_{(4)}$	1·339 Å	$C_{(13)}—C_{(12)}$	1·404 Å
$C_{(4)}—C_{(11)}$	1·431 Å	$C_{(13)}—C_{(9)}$	1·429 Å

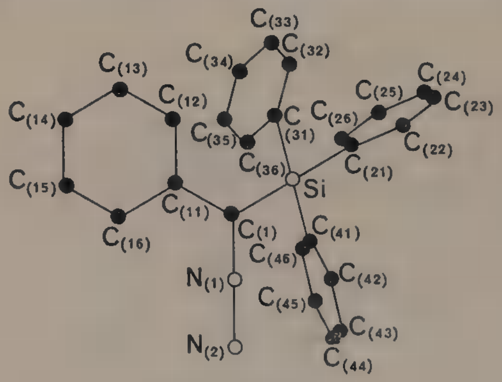
Uncorrected

$C_{(11)}-C_{(12)}$	1·501 Å	$C_{(9)}-C_{(10)}$	1·456 Å
$C_{(12)}-C_{(5)}$	1·384 Å	$C_{(10)}-C_{(11)}$	1·393 Å
$C_{(5)}-C_{(6)}$	1·349 Å	$C_{(10)}-C_{(1)}$	1·362 Å
$C_{(6)}-C_{(7)}$	1·404 Å	$C_{(2)}-Br$	1·876 Å
$N_{(1)}-N_{(2)}$	1·124 Å	$C_{(9)}-N_{(1)}$	1·323 Å
$C_{(1)}-C_{(2)}-C_{(3)}$	121·1°	$C_{(12)}-C_{(5)}-C_{(6)}$	120·8°
$C_{(2)}-C_{(3)}-C_{(4)}$	121·7°	$C_{(5)}-C_{(6)}-C_{(7)}$	127·5°
$C_{(3)}-C_{(4)}-C_{(11)}$	118·6°	$C_{(6)}-C_{(7)}-C_{(8)}$	109·9°
$C_{(4)}-C_{(11)}-C_{(10)}$	119·6°	$C_{(7)}-C_{(8)}-C_{(13)}$	125·9°
$C_{(11)}-C_{(10)}-C_{(1)}$	122·7°	$C_{(8)}-C_{(13)}-C_{(12)}$	117·9°
$C_{(10)}-C_{(1)}-C_{(2)}$	115·9°	$C_{(11)}-C_{(12)}-C_{(5)}$	117·8°
$C_{(11)}-C_{(12)}-C_{(13)}$	108·7°	$C_{(13)}-C_{(9)}-N_{(1)}$	126·2°
$C_{(12)}-C_{(13)}-C_{(9)}$	104·8°	$C_{(10)}-C_{(9)}-N_{(1)}$	102·5°
$C_{(13)}-C_{(9)}-C_{(10)}$	112·9°	$C_{(9)}-N_{(1)}-N_{(2)}$	178·2°
$C_{(9)}-C_{(10)}-C_{(11)}$	104·4°	$C_{(1)}-C_{(2)}-Br$	118·5°
$C_{(10)}-C_{(11)}-C_{(12)}$	109·0°	$C_{(3)}-C_{(2)}-Br$	120·3°
$C_{(4)}-C_{(11)}-C_{(12)}$	133·4°	$C_{(5)}-C_{(12)}-C_{(11)}$	131·2°

(22)

2. Phenyl(triphenylsilyl) diazomethane

$Ph(Ph_3Si)CN_2$ [106] (23): $R = 0{\cdot}117$; standard deviations 0·016–0·020 Å and 0·5–1·4°. The C—H bond length is 1·05–1·08 Å. The molecule is monomeric. The structural parameters of the CN_2 group are very close to those found for diazomethane[1, 82, 83]. The Si—C bond distance (1·865 Å) is similar to that observed for tetraphenylsilane (1·872 Å)[107]. The present data do not suggest the participation of a form $\equiv\overset{-}{\mathrm{Si}}=\mathrm{C}-\overset{+}{\mathrm{N}}\equiv\mathrm{N}$, involving 3d orbitals, to the resonance hybrid.



Uncorrected

$Si-C_{(1)}$	1·882 Å	$C_{(1)}-C_{(11)}$	1·468 Å
$Si-C_{(21)}$	1·863 Å	$C_{(1)}-N_{(1)}$	1·280 Å
$Si-C_{(31)}$	1·871 Å	$N_{(1)}-N_{(2)}$	1·130 Å
$Si-C_{(41)}$	1·846 Å		
$C_{(11)}-C_{(12)}$	1·366 Å	$C_{(31)}-C_{(32)}$	1·380 Å
$C_{(12)}-C_{(13)}$	1·375 Å	$C_{(32)}-C_{(33)}$	1·372 Å
$C_{(13)}-C_{(14)}$	1·347 Å	$C_{(33)}-C_{(34)}$	1·353 Å
$C_{(14)}-C_{(15)}$	1·358 Å	$C_{(34)}-C_{(35)}$	1·380 Å
$C_{(15)}-C_{(16)}$	1·364 Å	$C_{(35)}-C_{(36)}$	1·392 Å
$C_{(16)}-C_{(11)}$	1·413 Å	$C_{(36)}-C_{(31)}$	1·391 Å

Uncorrected

$C_{(21)}-C_{(22)}$	1·383 Å	$C_{(41)}-C_{(42)}$	1·359 Å
$C_{(22)}-C_{(23)}$	1·386 Å	$C_{(42)}-C_{(43)}$	1·374 Å
$C_{(23)}-C_{(24)}$	1·360 Å	$C_{(43)}-C_{(44)}$	1·342 Å
$C_{(24)}-C_{(25)}$	1·369 Å	$C_{(44)}-C_{(45)}$	1·353 Å
$C_{(25)}-C_{(26)}$	1·381 Å	$C_{(45)}-C_{(46)}$	1·415 Å
$C_{(26)}-C_{(21)}$	1·357 Å	$C_{(26)}-C_{(41)}$	1·393 Å
$C_{(1)}-Si-C_{(21)}$	108·3°	$C_{(31)}-Si-C_{(41)}$	110·7°
$C_{(1)}-Si-C_{(31)}$	109·2°	$Si-C_{(1)}-C_{(11)}$	125·7°
$C_{(1)}-Si-C_{(41)}$	107·1°	$Si-C_{(1)}-N_{(1)}$	115·3°
$C_{(21)}-Si-C_{(31)}$	112·1°	$C_{(11)}-C_{(1)}-N_{(1)}$	118·8°
$C_{(21)}-Si-C_{(41)}$	109·2°	$C_{(1)}-N_{(1)}-N_{(2)}$	178·1°
$C_{(1)}-C_{(11)}-C_{(12)}$	120·6°	$Si-C_{(31)}-C_{(32)}$	124·5°
$C_{(11)}-C_{(12)}-C_{(13)}$	122·3°	$C_{(31)}-C_{(32)}-C_{(33)}$	122·0°
$C_{(12)}-C_{(13)}-C_{(14)}$	119·0°	$C_{(32)}-C_{(33)}-C_{(34)}$	119·9°
$C_{(13)}-C_{(14)}-C_{(15)}$	120·4°	$C_{(33)}-C_{(34)}-C_{(35)}$	119·9°
$C_{(14)}-C_{(15)}-C_{(16)}$	122·0°	$C_{(34)}-C_{(35)}-C_{(36)}$	120·6°
$C_{(15)}-C_{(16)}-C_{(11)}$	118·6°	$C_{(35)}-C_{(36)}-C_{(31)}$	119·3°
$C_{(16)}-C_{(11)}-C_{(12)}$	117·7°	$C_{(36)}-C_{(31)}-C_{(32)}$	118·2°
$C_{(16)}-C_{(11)}-C_{(1)}$	121·8°	$C_{(36)}-C_{(31)}-Si$	117·0°
$Si-C_{(21)}-C_{(22)}$	119·6°	$Si-C_{(41)}-C_{(42)}$	121·9°
$C_{(21)}-C_{(22)}-C_{(23)}$	122·8°	$C_{(41)}-C_{(42)}-C_{(43)}$	124·7°
$C_{(22)}-C_{(23)}-C_{(24)}$	118·1°	$C_{(42)}-C_{(43)}-C_{(44)}$	118·3°
$C_{(23)}-C_{(24)}-C_{(25)}$	121·0°	$C_{(43)}-C_{(44)}-C_{(45)}$	120·2°
$C_{(24)}-C_{(25)}-C_{(26)}$	119·0°	$C_{(44)}-C_{(45)}-C_{(46)}$	121·8°
$C_{(25)}-C_{(26)}-C_{(21)}$	122·7°	$C_{(45)}-C_{(46)}-C_{(41)}$	118·0°
$C_{(26)}-C_{(21)}-C_{(22)}$	116·4°	$C_{(46)}-C_{(41)}-C_{(42)}$	116·8°
$C_{(26)}-C_{(21)}-Si$	123·9°	$C_{(46)}-C_{(41)}-Si$	121·0°

(23)

V. AROMATIC DIAZOCYANIDES

A. Synthesis

The following isomers of these compounds have been isolated: the addition product $PhN_2CN{\cdot}HCN$ and the two isomeric forms, *syn* and *anti*, of the diazocyanide. The former is labile and the latter stable. The addition product is prepared in acid medium and in excess of cyanide[108–111]. The other two compounds are also prepared in acid medium, but the cyanide is added slowly and is always in less than molar ratio with respect to the diazonium salt and the acid[112–115]. If the reaction is carried out at −5 °C and in sufficiently concentrated solution, the labile form precipitates as a crystalline compound. At room temperature, the labile isomer slowly isomerizes to the stable one. Finally, if the reaction is carried out by adding a neutral solution of the diazonium salt to a concentrated solution of potassium cyanide in a water–alcohol mixture at −20 °C, the compound obtained is completely different from those mentioned above[108, 116]. On X-ray evidence[116] this compound has been assigned the formula $ArN_2C(NH)CN$.

B. Structures

The structural parameters of the stable isomer of the diazocyanides have been determined in three works. Unfortunately, because of their low stability, no structural study has been carried out on the labile *syn* isomers. Even qualitative data on the latter would have allowed definite conclusions to be arrived at regarding the type of isomerism present in diazocyanides. This has been much discussed (see Section V.C).

The bond distances in the *anti*-diazocyanides fall in the following ranges: C_{sp^2}—N, 1·29–1·42 Å; N—N, 1·25–1·32 Å; N—C_{sp}, 1·36–1·41 Å and C≡N 1·14–1·15 Å. Comparison of these distances with those for *trans*-azobenzene and its symmetrical derivatives gives useful information on the electronic structures of diazocyanides. In *trans*-azobenzene[117], *trans*-4,4′-dichloroazobenzene[118], *trans*-4,4′-azodiphenetole[119], *trans*-4-phenylazobenzene[120] the bond distances are: C_{sp^2}—N, 1·43–1·46 Å, and N—N, 1·23–1·25 Å. The presence of some delocalization in the azobenzenes (bond order 1·9 for N—N and 1·1 for C_{sp^2}—N)[84] has been suggested by comparison with the aliphatic analogues. For the diazocyanides, which have no symmetry elements, this delocalization increases since the C_{sp^2}—N bond length is shorter, and the N—N greater, than those of *trans*-azobenzenes.

1. *p*-Chlorobenzene-*anti*-diazocyanide

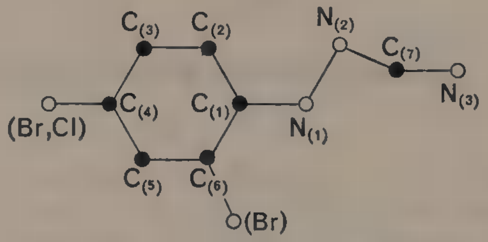
$ClC_6H_4N_2CN$ [121] (24): $R = 0{\cdot}082$; standard deviations 0·007–0·030 Å and 0·7–1·9°. The molecule is planar.

2. *o*-Bromobenzene-*anti*-diazocyanide

$BrC_6H_4N_2CN$ [122] (25): $R = 0{\cdot}059$; the standard deviations are 0·006–0·011 Å and 0·7°. The molecule is almost planar.

3. *o,p*-Dibromobenzene-*anti*-diazocyanide

$Br_2C_6H_3N_2CN$ [123] (26): $R = 0{\cdot}168$; almost planar.

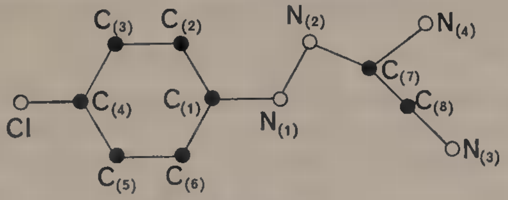


	(24)	(25)		(26)
	Uncorrected	Uncorrected	Corrected	Uncorrected
$N_{(3)}-C_{(7)}$	1·152 Å	1·140 Å	1·142 Å	1·153 Å
$N_{(2)}-C_{(7)}$	1·389 Å	1·362 Å	1·364 Å	1·414 Å
$N_{(1)}-N_{(2)}$	1·249 Å	1·269 Å	1·276 Å	1·322 Å
$C_{(1)}-N_{(1)}$	1·426 Å	1·400 Å	1·403 Å	1·288 Å
$C_{(1)}-C_{(2)}$	1·439 Å	1·380 Å	1·383 Å	1·406 Å
$C_{(2)}-C_{(3)}$	1·371 Å	1·352 Å	1·355 Å	1·366 Å
$C_{(3)}-C_{(4)}$	1·404 Å	1·383 Å	1·389 Å	1·322 Å
$C_{(4)}-C_{(5)}$	1·390 Å	1·366 Å	1·371 Å	1·469 Å
$C_{(5)}-C_{(6)}$	1·379 Å	1·384 Å	1·388 Å	1·337 Å
$C_{(6)}-C_{(1)}$	1·387 Å	1·388 Å	1·396 Å	1·511 Å
$C_{(4)}-Cl$	1·736 Å			
$C_{(6)}-Br$		1·906 Å	1·914 Å	1·850 Å
$C_{(4)}-Br$				1·928 Å

	Uncorrected	Uncorrected	Corrected	Uncorrected
$N_{(2)}-C_{(7)}-N_{(3)}$	174·2°	172·5°		170·5°
$N_{(1)}-N_{(2)}-C_{(7)}$	108·0°	113·0°		113·9°
$C_{(1)}-N_{(1)}-N_{(2)}$	116·6°	113·6°		113·2°
$C_{(2)}-C_{(1)}-N_{(1)}$	120·9°	125·7°		128·3°
$C_{(2)}-C_{(1)}-C_{(6)}$	122·1°	117·6°		115·8°
$C_{(3)}-C_{(2)}-C_{(1)}$	118·9°	122·0°		125·6°
$C_{(4)}-C_{(3)}-C_{(2)}$	118·1°	119·0°		112·2°
$C_{(5)}-C_{(4)}-C_{(3)}$	122·6°	119·9°		124·6°
$C_{(6)}-C_{(5)}-C_{(4)}$	120·2°	119·7°		122·4°
$C_{(1)}-C_{(6)}-C_{(5)}$	117·9°	120·8°		117·9°
$C_{(3)}-C_{(4)}-Cl$	122·0°			
$C_{(1)}-C_{(6)}-Br$	121·4°			122·0°
$C_{(3)}-C_{(4)}-Br$				112·3°

4. *p*-Chlorobenzene-*anti*-diazoimidoglyoxynitrile

$ClC_6H_4N_2C(NH)CN$[116] (27): $R = 0{\cdot}09$; standard deviations 0·007–0·014 Å and 0·5–0·8°. Other bond lengths: C—H, 0·90–1·05 Å (±0·1), and N—H, 1·05 (±0·11). The molecule is essentially planar. The structure of the $C_6H_4N_2$ group is very similar to that observed in the other *anti*-diazocyanides.



Uncorrected

$Cl-C_{(4)}$	1·735 Å	$Cl-C_{(4)}-C_{(3)}$	119·1°
$C_{(1)}-C_{(2)}$	1·381 Å	$Cl-C_{(4)}-C_{(5)}$	119·3°
$C_{(2)}-C_{(3)}$	1·368 Å	$C_{(1)}-C_{(2)}-C_{(3)}$	119·5°
$C_{(3)}-C_{(4)}$	1·391 Å	$C_{(2)}-C_{(3)}-C_{(4)}$	119·6°
$C_{(4)}-C_{(5)}$	1·374 Å	$C_{(3)}-C_{(4)}-C_{(5)}$	121·6°
$C_{(5)}-C_{(6)}$	1·395 Å	$C_{(4)}-C_{(5)}-C_{(6)}$	119·4°
$C_{(1)}-C_{(6)}$	1·400 Å	$C_{(5)}-C_{(6)}-C_{(1)}$	118·3°
$C_{(1)}-N_{(1)}$	1·447 Å	$C_{(6)}-C_{(1)}-C_{(2)}$	121·7°
$N_{(1)}-N_{(2)}$	1·264 Å	$N_{(1)}-C_{(1)}-C_{(2)}$	124·4°
$N_{(2)}-C_{(7)}$	1·441 Å	$N_{(1)}-C_{(1)}-C_{(6)}$	113·9°
$C_{(7)}-C_{(8)}$	1·432 Å	$C_{(1)}-N_{(1)}-N_{(2)}$	112·9°
$C_{(8)}-N_{(3)}$	1·136 Å	$N_{(1)}-N_{(2)}-C_{(7)}$	111·2°
$C_{(7)}-N_{(4)}$	1·273 Å	$N_{(2)}-C_{(7)}-N_{(4)}$	114·5°
		$N_{(2)}-C_{(7)}-C_{(8)}$	119·1°
		$N_{(4)}-C_{(7)}-C_{(8)}$	126·6°
		$C_{(7)}-C_{(8)}-N_{(3)}$	177·2°

(27)

C. *Isomerism*

Since there are no literature data on the structure of the *syn* isomers of diazocyanides, it may be useful to comment on the type of isomerism present in these compounds.

On the basis of the structural results obtained for the benzene-*anti*-diazocyanides seen above there are two possibilities for the isomerism of diazocyanides:

$$\mathrm{ArN{=}NNC} \rightleftarrows \mathrm{ArN{=}NCN} \qquad (7)$$


(8)

syn (*cis*) *anti* (*trans*)

The disagreement as to the significance of the chemical evidence, which has occupied several workers[124–130], shows that it cannot constitute conclusive proof for either of the possibilities (7) and (8). The only physical results currently available have been obtained from dipole moment and infrared spectra measurements.

The electric dipole moments of some diazocyanides[114], measured in benzene, are shown in Table 1. What conclusions can be drawn from these data? Since the group moments for nitrile and *iso*-nitrile are very similar[131], information on the configuration may be obtained[132] from an examination of several members of the series rather than by treating each singly. The situation (7) leads virtually to the same difference in observed dipole moments in each pair of *syn*/*anti* isomers. Since, as seen from Table 1, this is not the case, this possibility may be excluded. The possibility remains of a geometrical isomerism (8). We can try to verify this as follows. The group moment $\mu(2,4,6\text{-}Br_2C_6H_2N)$ may be assumed equal, to a good approximation, to $\mu(\overrightarrow{PhN})$, which is *c.* 2·0 D [114]. Using this value, from the moment observed for 2,4,6-tribromobenzene-*anti*-diazocyanide, $\mu(\overrightarrow{N{-}C{\equiv}N})$ is estimated to be *c.* 2·0 D [114]. With this value and the usual bond and group moments[102], the following theoretical moments (μ_{calc}) for the *anti* isomers of $XC_6H_4N_2CN$ molecules are then deduced (X, μ_{calc}, μ_{obs}): 4-Cl, 2·4, 2·73; 4-Br, 2·4, 3·78; 4-NO_2, 2·0, 1·47. The discrepancy between observed and calculated moments do not allow conclusions to be drawn as to the presence of geometrical isomerism.

TABLE 1. Observed dipole moments (D) for some aromatic diazocyanides[114]

Compound	μ_{syn}	μ_{anti}	$\mu_{syn}-\mu_{anti}$
p-$ClC_6H_4N_2CN$	2·93	3·73	−0·80
p-$BrC_6H_4N_2CN$	2·91	3·78	−0·87
o-$BrC_6H_4N_2CN$	3·79	5·32	−1·53
p-$NO_2C_6H_4N_2CN$	2·04	1·47	+0·57
o,*m*,*p*-$Br_3C_6H_2N_2CN$	2·5	4·0	+1·5

Interpretation of the i.r. spectra is based on the assumption that two geometrical isomers should have C≡N stretching bands very close to one another in frequency (ν_{CN})[115, 133]. This is observed, for example, in 1-cyano-1-propene[134], which gives ν_{CN} at 2221 cm^{-1} for the *cis* isomer and at 2223 for the *trans* isomer. By contrast, the difference between the ν_{CN} values for a pair of structural isomers is of the order of 100 cm^{-1} [115, 135, 136]. Several authors have used these observations to obtain information on the type of isomerism present in diazocyanides. The results obtained are shown in Table 2. The data in this table reveal some disagreement among the various workers. A difference in the ν_{CN} values between the labile and the stable isomers has been found only by some authors[115]. It seems hazardous to use this evidence alone as sufficient to indicate the presence of structural isomerism. In fact, the integrated intensity of the C≡N stretching vibration is greater in the stable isomer (nitrilic) than in the labile one (isonitrilic) while an isonitrile usually shows a more intense C≡N band than the corresponding nitrile[115, 135, 136]. In addition, the difference in the ν_{CN} values is much smaller in a pair of diazocyanides than between nitrile–isonitrile pairs. Some workers explain this fact[115] by invoking a strong

$\mathrm{Ar{-}N{=}}\underset{\curvearrowleft}{\mathrm{N{-}}}\overset{\curvearrowright}{\mathrm{C{\equiv}N}}$ conjugation, which would not only lower the frequency for this isomer but would also lead to an almost linear —NNCN group. This explanation is discounted by the X-ray structural parameters obtained for the benzene-*anti*-diazocyanides (see Section V.B). In fact, these molecules have a non-linear structure with a C≡N bond equal to 1·14 Å, which is of the same order, if not lower, as that found in most nitriles studied to date[137].

Table 2. Frequency (ν_{CN}) and intensity of absorption (A) of the C≡N stretching vibration band for some aromatic diazocyanides

Compound	Isomer	ν (cm^{-1})	$A \times 10^{-4}$ (cm^{-2} mol^{-1} l)
p-$MeOC_6H_4N_2CN$	*syn*	2150[a]	0·11
	anti	2190	0·47
p-$ClC_6H_4N_2CN$	*syn*	2187[b]	
	anti	2187	
p-$BrC_6H_4N_2CN$	*syn*	2154[a] 2187[b] 2185[c]	0·026
	anti	2192[a] 2187[b] 2185[c]	0·17
p-$NO_2C_6H_4N_2CN$	*syn*	2162[a] 2187[b]	0·037
	anti	2193[a] 2187[b]	0·064
o,m,p-$Br_3C_6H_2N_2CN$	*syn*	2187[c]	
	anti	2185	

[a] In CCl_4 [115].
[b] In CCl_4 [132].
[c] The tribromo compounds were examined in $CHCl_3$ and CS_2 solutions and the monobromo one in nujol mull[133].

To conclude, the results of Kazitsyna and coworkers[115] also do not constitute proof that situation (7) is present. On the basis of indirect evidence, i.e. by analogy with similar compounds, we tend, like most workers[1], toward isomerism of geometrical type (8).

VI. DIAZOKETONES

A. Isomerism

1. General

Different diazoketones may be obtained, depending on the position of the carbonyl group with respect to the diazo group. Most work has been centred on the α-derivatives because they are the easiest to prepare and have also numerous applications in organic syntheses[1, 138–141].

The configurations adopted by α-diazoketones depend on the conjugation between the diazo group, which in this case acts with a +M effect, and the carbonyl group, which exerts a −M effect. The atomic orbital scheme involved in this delocalization is shown in Figure 3. For the only molecular structure of α-diazoketones solved to date, 1,4-bisdiazo-2,3-butanedione[142], the following values were obtained: $\widehat{\mathrm{CNN}}$ 176·8°, $\widehat{\mathrm{CCN}}$ 116·5°. These results indicate that in the α-diazoketones the carbon atom $C_{(2)}$ (Figure 3) is essentially sp^2 hybridized and both nitrogen atoms have sp hybridization. The π_y orbitals are localized on the latter two atoms, which each furnish an electron to the bond formed between them. Instead, the π_x orbitals are delocalized over several atoms (e.g. five in the case of diazoacetone, $MeCOCHN_2$) to different extents depending on the nature of the substituents R^1 and R^2. The nitrogen atom $N_{(1)}$ donates two electrons to this molecular orbital and all the other atoms donate one each. The delocalization of the π_x electrons on the atoms of the molecular skeleton causes the central $C_{(1)}—C_{(2)}$ bond to become partially double bonded. It follows that two rotational isomers may exist, each having the $COCN_2$ group more or less planar (Figure 3) depending on the electronic, steric and electrostatic effects exerted by R^1 and R^2.

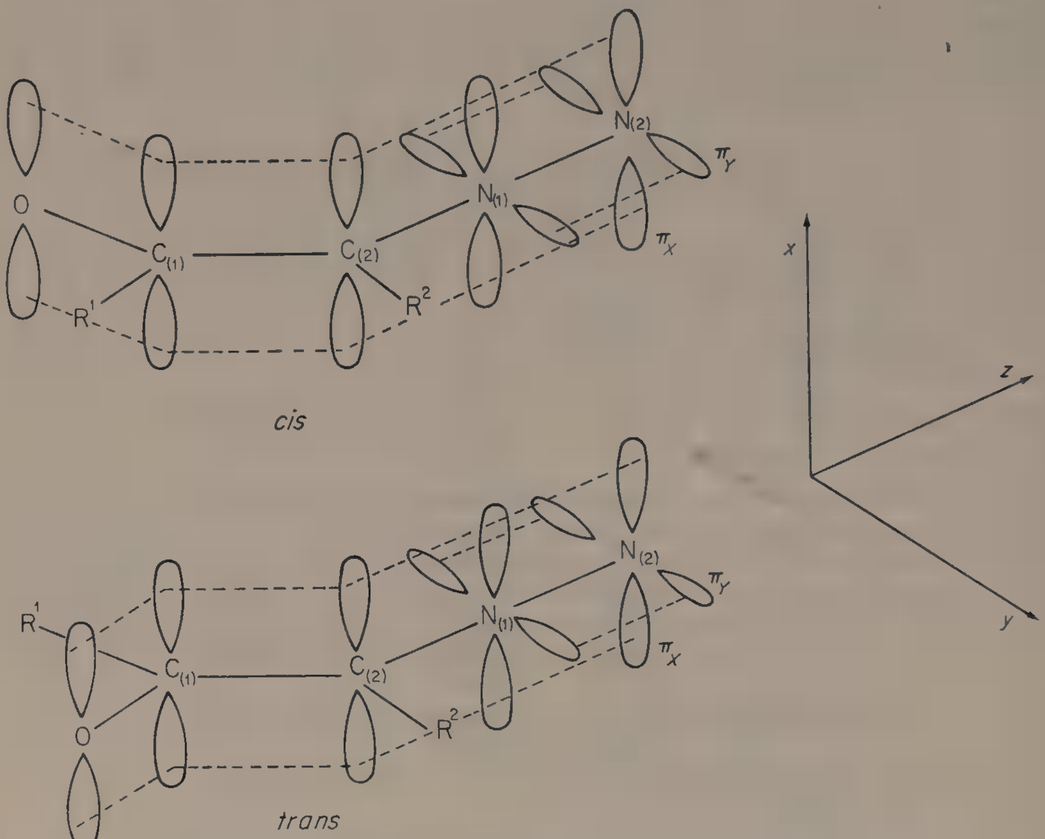


FIGURE 3. Atomic orbital scheme involved in conjugation between diazo and carbonyl groups.

Apart from this geometrical isomerism, α-diazoketones may also, in theory, show structural isomerism due to the transposition of the hydrogen atoms α to the carbonyl group. Depending on whether the hydrogen migrates to the carbonyl oxygen or to the terminal nitrogen there will be keto–enol or diazo–isodiazo isomerism, respectively.

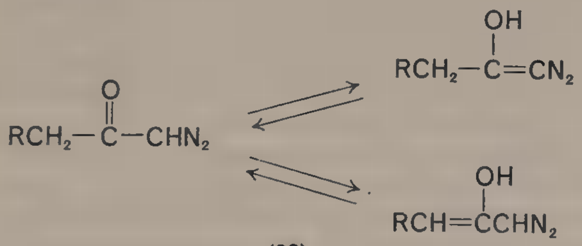
Identification of the type of isomerism present becomes more difficult since diazoketones may form an intermolecular hydrogen bond with another diazoketone molecule or with a hydroxylic compound[143–145]. This explains why early results, although experimentally valid, often led to incorrect conclusions.

We now examine the theoretical and experimental evidence for the type of isomerism present in α-diazoketones in different media.

2. Ultraviolet/visible and infrared spectra

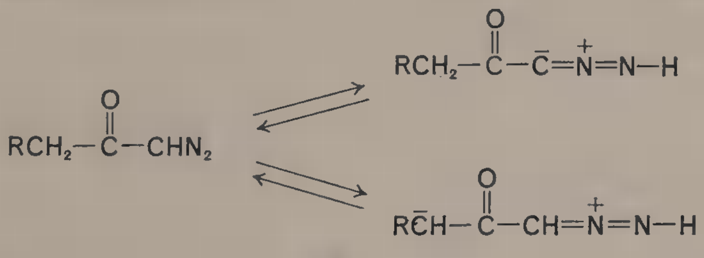
The ultraviolet/visible spectra of α-diazoketones in mixtures of non-polar and hydroxylic solvents show a characteristic behaviour. The $-COCN_2$ group has an intense band at *c.* 245–250 nm, which becomes weaker with increase in the hydroxylic/non-polar solvent ratio, and another band at 270–290 nm which at the same time increases in intensity[146–150]. There are no shifts in the bands on going from one solvent to the other. In almost all the cases studied to date the curves show an isosbestic point which seems less clear the lower is the availability of the carbonyl oxygen lone pair, i.e. the higher is the frequency of the C=O stretching mode[148]. The presence of an isosbestic point suggests that two species exist in solution in equilibrium with one another[151]. There are four possibilities for our molecules:

the keto–enol equilibrium



(28)

the diazo–isodiazo equilibrium



(29)

the conformational equilibrium

$$\textit{cis} \rightleftharpoons \textit{trans}$$

(30)

and, finally, the presence of a hydrogen bond (31).

The existence of an isosbestic point does not necessarily mean that situations **28** or **29** are present since it is also observed for molecules which do not contain transposable hydrogen atoms[148, 149]. The same may be said of the conformational equilibrium, **30**, since a similar dependence on solvent and an isosbestic point are also found in the spectra of compounds for which this isomerism is not possible, e.g. 2-diazocyclohexanone[152], 3-diazonorcamphor and 3-diazocamphor[153].

For a variety of reasons, we favour the possibility (**31**). In agreement with Fahr[148] it is our opinion that in mixed solvents there is formation of a hydrogen bond between the diazo compound and the hydroxylic solvent. The evidence for this conclusion is derived from the fact that the isosbestic point becomes more evident the greater is the availability of the oxygen lone pair to form this type of bond. The presence of the latter is proved by the behaviour of the O—H stretching vibration band of phenol in the presence of various α-diazoketones[149]. This interpretation explains why the same behaviour in mixed solvents is observed for molecules for which two conformers are possible and those for which they are not[149, 152, 153]. In agreement with this, for diazoacetone, $MeCOCHN_2$, and diazoacetophenone, $PhCOCHN_2$, it was observed that the band due to the $\pi \rightarrow \pi^*$ transition in the *cis* isomer overlaps that in the *trans* isomer.[153]

As to the infrared spectra of α-diazoketones in mixed solvents, Foffani and coworkers[149] observed that integrated intensities and frequencies of the N—N stretching vibration band are almost invariant for diazoacetone, diazoacetophenone and benzoyl(diazo)phenylmethane on varying the ratio between non-polar and hydroxylic solvents. Moreover the C=O stretching band at 1662 cm^{-1} in diazoacetone decreases in intensity, in C_2Cl_4 as solvent, with increasing quantity of phenol. At the same time the peaks at 1643 and 1633 cm^{-1}, which are very weak in intensity in non-polar solvents, became more intense with increasing phenol concentration. These phenomena may be due to the presence of hydrogen bonding between the carbonylic compound and the hydroxylic solvent, which stabilizes one conformer more than the other. According to this, for molecules having two conformers, one peak in the N—N stretching band disappears in the presence of hydroxylic solvents[154]. This interpretation, which reconciles the u.v. and i.r. results, appears plausible but requires further experimental justification.

The atoms involved in the hydrogen bond may, in theory, be the terminal nitrogen, the carbon of the diazo group and the carbonyl oxygen. Involvement of the nitrogen or of the carbon atom may be excluded since the i.r. spectra of phenol in the presence of diphenyldiazomethane (0·004 M) in CCl_4 show no evidence for its presence[145]. The only atom available is thus the carbonyl oxygen.

The formation of an intermolecular hydrogen bond between two diazoketone molecules has recently been established[144, 145] for $RCOCHN_2$ compounds. N.m.r. measurements were carried out in weakly accepting solvents such as CCl_4 and d_6-benzene at a temperature at which interconversion between possible rotamers is very fast and it was found that the chemical shift varies regularly with the concentration of the diazo compound[145].

The possibility that two rotamers exist in equilibrium in apolar solvents, foreseen by Foffani and coworkers[149], has recently been established by Sorriso and coworkers[155, 156] by examining the N—N stretching vibration band in CCl_4. This band is suitable for our purpose because it falls in a frequency range in which other groups present in the molecule do not absorb. The molecules $CH_2ClCOCHN_2$, $CHCl_2COCHN_2$, t-BuCOCt-BuN_2, $PhCOCHN_2$ and $PhCOCMeN_2$ show a single N—N stretching band, while $MeCOCHN_2$, $MeCOCMeN_2$ and $PhCOCPhN_2$ give split N—N bands (Figure 4). Since rotamers stabilized by a sufficiently high-energy barrier to interconversion have different i.r. spectra, the splitting of the diazo band indicates the presence of two conformers.

Insight into the reasons for the existence of two rotamers in α-diazoketones comes also from an examination of the frequencies of the carbonyl and diazo stretching vibrations, which fall around 1650 and 2080 cm^{-1}, respectively[88, 93, 155–158]. These frequencies are clearly shifted compared to those in the corresponding ketones[23] and diazohydrocarbons[88, 93]; ν_{CO} moves to lower frequency and ν_{NN} to higher frequency. This indicates that in these molecules the carbonyl group has less double-bond character than it does in ketones, while the N—N bond is of higher order than in diazohydrocarbons of the same order of substitution. In other words, a third limiting form, **34**, which occurs at the expense of form **33**, is in addition to the canonical forms **32** and **33** also present in diazohydrocarbons. The participation of the form **34** gives the central C—C bond a partial double bond character. The contribution of forms of type **33** and **34** is higher the higher the frequency of the diazo band and the lower its intensity. The opposite holds for contribution of forms of the type **32** [93, 159, 160].

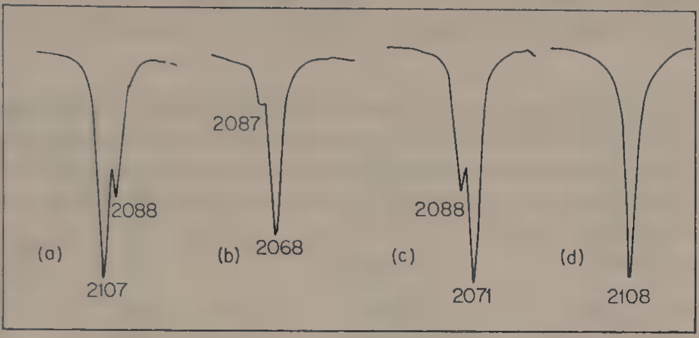
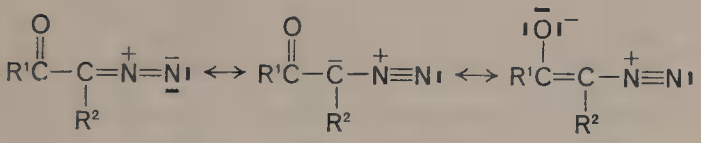
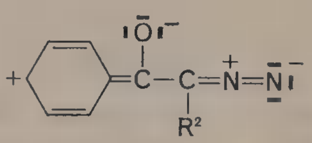


FIGURE 4. Profile of N—N stretching vibration band observed in CCl_4 for: (a) diazoacetone $MeCOCHN_2$; (b) 1-acetyl-1-diazoethane, $MeCOCMeN_2$; (c) benzoyl(diazo)phenylmethane, $PhCOCPhN_2$; (d) diazoacetophenone, $PhCOCHN_2$.



$$R^1\overset{O}{\overset{\|}{C}}-\underset{R^2}{\underset{|}{C}}=\overset{+}{N}=\overset{-}{\underline{N}}| \longleftrightarrow R^1\overset{O}{\overset{\|}{C}}-\underset{R^2}{\underset{|}{\overset{-}{C}}}-\overset{+}{N}\equiv N| \longleftrightarrow R^1\overset{|\overline{O}|^-}{\overset{|}{C}}=\underset{R^2}{\underset{|}{C}}-\overset{+}{N}\equiv N|$$

(32) **(33)** **(34)**



(35)

When R^1 is a phenyl group, forms of the type **35** may also contribute[88, 149].

3. Nuclear magnetic resonance

One of the most important applications of n.m.r. spectroscopy is in structural studies by means of the chemical shift (δ) and coupling constant (J) parameters[96, 97, 161, 162]. The chemical shift and coupling constant, which give complementary structural information, are directly connected to the electron distribution about the nucleus and to the type of bond between the nuclei, respectively. Both parameters change with change in the molecular environment. Thus, the use of the technique in studies of the type of isomerism present and determination of thermodynamic parameters for isomer equilibrium is understandable.

α-Diazoketones of general formula $RCOCHN_2$ have been widely studied using p.m.r.[144]. Some results of this study are shown in Table 3. Temperature-dependent p.m.r. spectra have been observed for the molecules $HCOCHN_2$, $MeCOCHN_2$, $EtCOCHN_2$, $PhCH_2COCHN_2$, $MeOCOCHN_2$ and $EtOCOCHN_2$. At room temperature there is a single sharp peak which broadens and splits into a doublet on lowering the temperature (Figure 5). Only a single peak is observed in the *t*-butyl derivative (*t*-$BuCOCHN_2$) and in aryldiazoketones ($PhCOCHN_2$, *p*-$NO_2C_6H_4COCHN_2$ and *p*-$MeOC_6H_4COCHN_2$) the intensity of which remains constant at different temperatures. As for analogous cases[163–165] this indicates that two forms are present in equilibrium in the first six compounds, whilst the aryldiazoketones give only a single peak and thus only a single species, or else two in rapid interconversion or coincidentally having the same chemical shift. Given the steric effects present, the *t*-butyl derivative almost certainly exists in a single, very distorted, form.

TABLE 3. Fractional populations (*P*), equilibrium constants (K_{eq}) and standard free-energy differences (ΔF) of the *cis* and *trans* forms of diazoketones ($RCOCHN_2$), 40% w/w solution in deuteriochloroform. Reprinted with permission from Kaplan and Meloy, *J. Amer. Chem. Soc.*, **88**, 950 (1966). Copyright by the American Chemical Society

R	P_{cis}	P_{trans}	K_{eq} (*T*, °C)	ΔF (kcal/mol) (*T*, °C)
H[a]	0·69 ±0·02[c]	0·31 ±0·02	0·449 (−20)	0·40 (−20)
Me	0·924±0·008	0·076±0·008	0·082 (−40)	1·16 (−40)
Me[b]	0·903±0·002	0·097±0·002	0·180 (−40)	0·79 (−40)
t-C_4H_9	>0·99	<0·01[d]		
$PhCH_2$	0·962±0·002	0·038±0·002	0·040 (−40)	1·49 (−40)
MeO	0·538±0·004	0·462±0·004	0·859 (−50)	0·07 (−50)
EtO	0·54 ±0·01	0·46 ±0·01	0·840 (−50)	0·08 (−50)

Values of energy of activation (E_a), frequency factor (*A*), free energy of activation ($\Delta F'$) and temperature of coalescence (T_c) for hindered internal rotation about the C—C central bond in diazoketones ($RCOCHN_2$), 40% w/w solution in deuteriochloroform

	cis → *trans*			*trans* → *cis*			
R	E_a (kcal/mol)	log *A*	$\Delta F'_{298\ K}$ (kcal/mol)	E_a (kcal/mol)	log *A*	$\Delta F'_{298\ K}$ (kcal/mol)	T_c (°C)
Me	15·5±0·9[e]	12·8	15·4	15·5±0·9[e]	13·9	13·9	12·8
Me[e]	15·9±0·6	15·0	15·4	15·9±0·6	16·1	14·1	13·5
Et	16·1±0·6	13·6	15·3	16·2±0·6	14·8	13·5	6·5
$PhCH_2$	18·2±0·6	14·9	15·3	18·2±0·6	16·3	13·4	1·0
MeO	12·5±0·9	12·6	12·8	12·5±0·9	12·7	12·7	−25·0
Eto	9·0±0·8	9·7	13·3	9·0±0·8	9·8	13·2	−32·5

[a] Concentration unknown.
[b] 20% w/w solution in deuteriochloroform.
[c] Average deviation involving at least two separate samples.
[d] The *trans* resonance line was not observed.
[e] Errors represent the precision of the Arrhenius plots. The free energies of activation were calculated from the relationship $\Delta F'_T = 2{\cdot}303\ RT \log (\tau_x KkT/h)$. The transmission coefficients, *K*, are assumed to be unity.

For the compounds which give doubling of the methine proton peak at low temperatures, attempts have been made to assign structures. Kaplan and Meloy[144] considered the possibilities: keto–enol (**28**) and diazo–isodiazo (**29**) structural isomerisms; geometrical isomerism (**30**) (Figure 3). Tautomeric equilibria (**28**) and (**29**) may be excluded since the $^{13}C—H$ coupling constant for high-temperature time-average species is the same as that of the species predominant at low temperature (*J* = 199 c.p.s.) for $MeCOCHN_2$, $EtCOCHN_2$ and $EtOCOCHN_2$. If structural isomers had been present, the time-averaged species at high temperature would have been expected to show coupling constants different from those of the species predominant at low temperature, since the two species have different C—H environments.

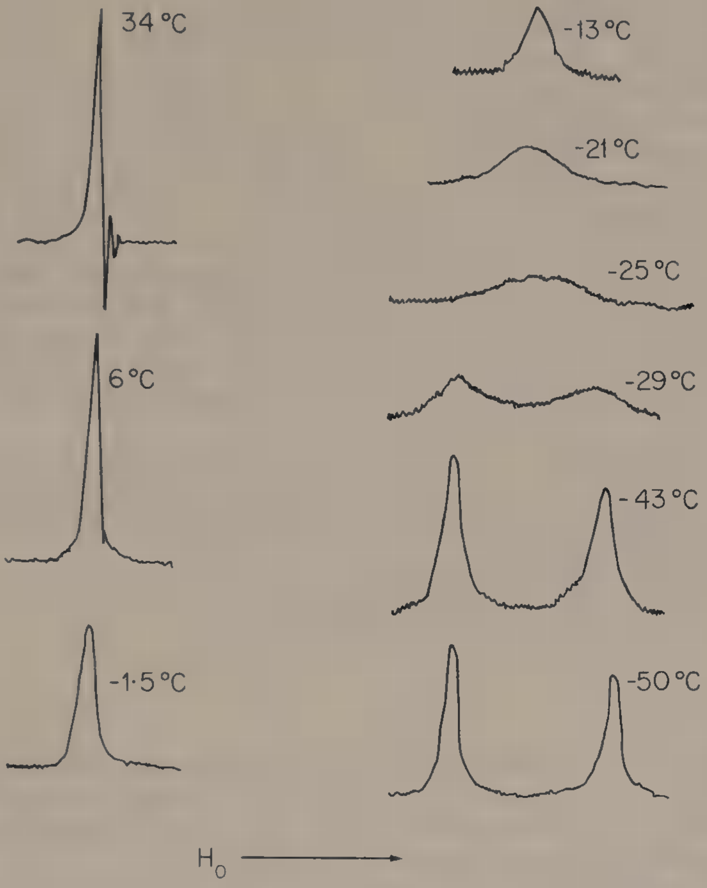


FIGURE 5. Temperature dependence of the n.m.r. spectrum of the methine proton of methyl diazoacetate ($MeOCOCHN_2$). Reprinted, with permission, from Kaplan and Meloy, *J. Amer. Chem. Soc.*, **88**, 950 (1966). Copyright by the American Chemical Society.

Having assigned the two peaks to the two conformers[166–169], the thermodynamic parameters for the *cis* $\rightleftarrows$ *trans* equilibrium have been calculated by integrating the peaks (Table 3). The values listed in this table show that the ratio of the two conformers does not depend only on steric factors.

The energy barriers to interconversion between the two rotamers fall in the range 9–18 kcal/mol. The lower values are obtained for diazo esters, in which diazo–carbonyl conjugation is lower and hence the double-bond character of the C—C central bond is lower.

The $^{13}C—H$ coupling constant ($J = 199$ c.p.s.) indicates[144] that the C—H bond has high s character (41%), which suggests that the methine hydrogen may participate in hydrogen bonding.

The p.m.r. evidence leaves little doubt that the isomerism present in α-diazoketones is geometrical isomerism. Further conformational studies are thus aimed more at obtaining insight into the effect of the R^1 and R^2 groups on the *cis*/*trans* ratio and into the theoretical aspects of this isomerism rather than proving its existence.

4. Electric dipole moments

The usefulness of electric dipole moments in conformational studies has been known for some time[102, 170–172]. For α-diazoketones this technique has been used to determine the relative contribution of the two rotamers and to study the effect of the R^1 and R^2 groups. The observed dipole moments, in benzene, at 25 °C and assuming $P_a = 0$, are (compound, dipole moment in debye): $MeCOCHN_2$, 3·37; $CH_2ClCOCHN_2$, 2·80; $CHCl_2COCHN_2$, 2·65; CCl_3COCHN_2, 2·46[103]; $PhCOCHN_2$, 3·66; p-$MeC_6H_4COCHN_2$, 4·01; p-$ClC_6H_4COCHN_2$, 3·08; p-$BrC_6H_4COCHN_2$, 3·11; p-$MeOC_6H_4COCHN_2$, 3·73; $PhCH_2COCHN_2$, 3·31; $Ph(CH_2)_2COCHN_2$, 3·39[173]; $BzCPhN_2$, 2·77; m-$ClC_6H_4COCHN_2$, 3·34; o-$ClC_6H_4COCHN_2$, 3·56[101]; $MeCOCMeN_2$, 2·45; t-BuCOCt-BuN_2, 1·98; $PhCOCMeN_2$, 2·75; p-$ClC_6H_4COCMeN_2$, 2·05; o-$ClC_6H_4COCMeN_2$, 3·18[174].

The observed moments indicate that whilst $MeCOCHN_2$, $PhCH_2COCHN_2$, $Ph(CH_2)_2COCHN_2$, $BzCPhN_2$, o-$ClC_6H_4COCHN_2$, $MeCOCMeN_2$, p-$ClC_6H_4COCMeN_2$, $PhCOCMeN_2$ and o-$ClC_6H_4COCMeN_2$ may be two rotamers, only one species, the *cis* one, is present in halogen derivatives of diazoacetone. Presumably there is a strong electrostatic effect by the halogen atom on the diazo group.

The aryldiazoketones are almost entirely present as the *cis* conformer. This result agrees with the X-ray data[175] and with the fact that only a single sharp peak for the methine proton is observed in the n.m.r.[144] and the N—N stretching vibration band is single in CCl_4 [155].

Finally, the *t*-butyl derivative gives only a single rather distorted structure with an angle of *c.* 140° between the CCO and CCN planes.

5. MO calculations

MO calculations on α-diazoketones have essentially two aims: to see if there is theoretical justification for the rotational isomerism found experimentally, and to obtain information on the molecular conformation of rather complicated compounds, information not obtainable by other means.

Csizmadia and coworkers[153] have performed MO calculations on diazoacetone and diazoacetophenone using Hoffmann's extended Hückel method. The scheme used and the results obtained are shown in Figures 6 and 7. From Figure 6 it may be seen that two conformers, *cis* and *trans*, both with almost the same energy and the $COCHN_2$ group planar, are possible for diazoacetone. The energy barrier height to interconversion between the two species (~14 kcal/mol) is of the same order as that determined experimentally from n.m.r. spectra in $CDCl_3$ (~16 kcal/mol)[144]. As expected, variation in the angle ϕ has an almost negligible effect on the relative energies of the two rotamers and on the barrier height.

By contrast, the effect on changes in angle ϕ in diazoacetophenone is considerable (Figure 7). At $\gamma = 120°$ and $\phi = 0°$ there is only a single isomer, the *cis* form. Instead on varying the angle ϕ, i.e. on rotating the phenyl group out of the molecular plane, diazoacetophenone gives two conformers having similar energies and a barrier height of the order of 14 kcal/mol. This result is not in agreement with the i.r. and n.m.r. spectra and the dipole moments, which suggest only one isomer, the *cis* one. The discrepancy between theoretical and experimental evidence may be due to solvation and/or to entropic factors[153].

Sorriso and coworkers have studied the molecules $CH_2ClCOCHN_2$, $MeCOCMeN_2$[176], $PhCOCPhN_2$ and $PhCOCMeN_2$[177] by the CNDO/2 method using the structural parameters of Figures 6 and 7. The calculated energies suggest

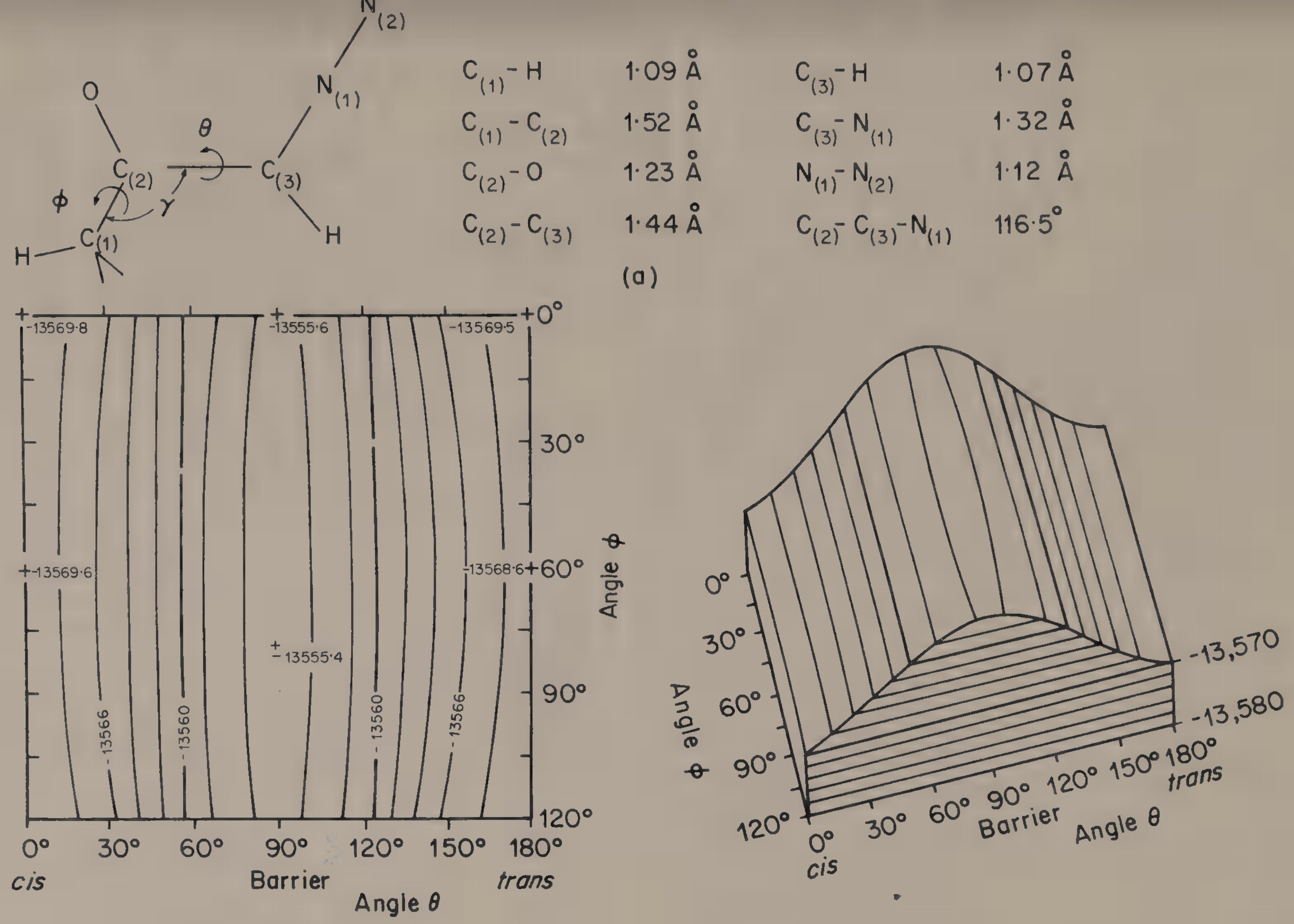
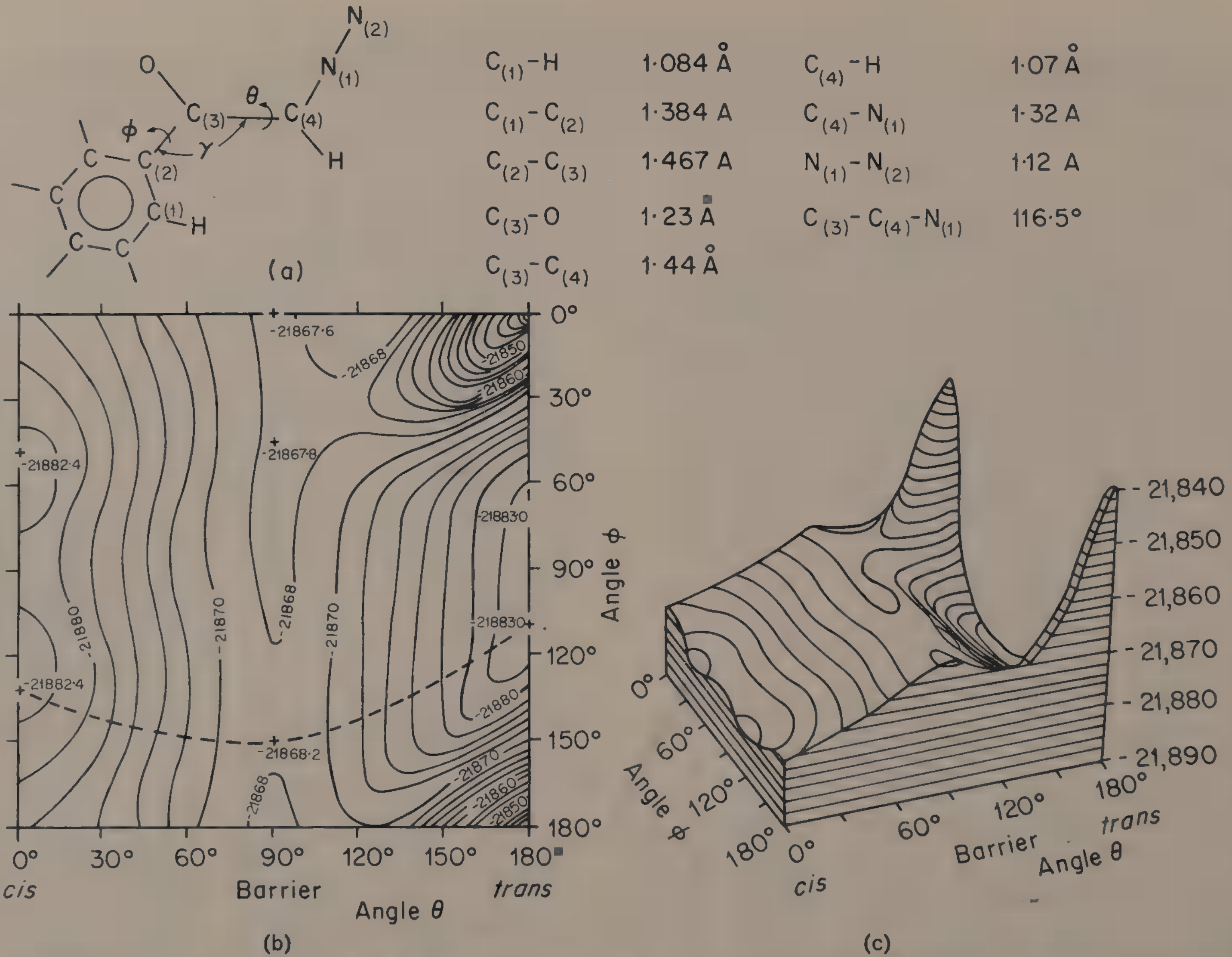


FIGURE 6. Geometrical parameters (a) and energy surface for diazoacetone, MeCOCHN$_2$ ($\gamma = 120°$). Numbers on surface refer to energy in kcal/mol; (b) contour diagram, (c) perspective view. Reprinted, with permission, from Csizmadia, Houlden, Meresz and Yates, *Tetrahedron*, **25**, 2121 (1969).



$C_{(1)}-H$	1·084 Å	$C_{(4)}-H$	1·07 Å
$C_{(1)}-C_{(2)}$	1·384 A	$C_{(4)}-N_{(1)}$	1·32 A
$C_{(2)}-C_{(3)}$	1·467 A	$N_{(1)}-N_{(2)}$	1·12 A
$C_{(3)}-O$	1·23 Å	$C_{(3)}-C_{(4)}-N_{(1)}$	116·5°
$C_{(3)}-C_{(4)}$	1·44 Å		

FIGURE 7. Geometrical parameters (a) and energy surface for diazoacetophenone, $PhCOCHN_2$ ($\gamma = 120°$). Numbers on surface refer to energy in kcal/mol; (b) contour diagram, (c) perspective view. Reprinted, with permission, from Csizmadia, Houlden, Meresz and Yates, *Tetrahedron*, **25**, 2121 (1969).

that two conformers were present in equilibrium in $MeCOCMeN_2$ and $PhCOCPhN_2$ and only one, the *cis*, in the chloro derivative. Finally, two forms in rapid interconversion exist for $PhCOCMeN_2$.

For $PhCOCMeN_2$ and $PhCOCPhN_2$, as for the diazoacetophenone, there is concerted rotation of the phenyl and the methyl groups about the bond with the molecular skeleton during the interconversion between the two rotamers.

The phenyl group bonded to the carbonyl conjugates with it, in agreement with experimental results[88, 149]. In addition, in $PhCOCPhN_2$ the phenyl bonded to the diazo group conjugates with it. Despite this, diazo–carbonyl conjugation predominates over the others.

6. Conclusions

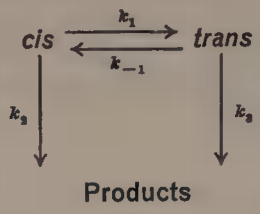
The results obtained to date show that the isomerism present in α-diazoketones is geometrical isomerism. As mentioned in Section VI.A.1, this arises because of conjugation between diazo and carbonyl groups, which makes the central C—C bond partially double-bonded. This suggestion is supported by the frequency of the N—N and C—O stretching vibrations compared with those in diazohydrocarbons and ketones. The presence of two conformers is confirmed by the low-temperature doubling of the methine proton in n.m.r. spectra of several diazoketones of the type $RCOCHN_2$ and the doubling of the N—N stretching vibration band. MO calculations using two different methods also show that, if hindrance of all kinds is absent, the configuration preferred by the $COCN_2$ group is a planar one.

Two factors seem to control the *cis* $\rightleftarrows$ *trans* equilibrium in α-diazoketones $R^1COCR^2N_2$. The first is diazo–carbonyl conjugation, which is responsible for the energy barrier height to interconversion between the two conformers. The latter increases if R^1 is electron attracting and decreases if it is an electron donor. By contrast, it is lowered if R^2 is electron attracting since such a group involves the π system of the diazo group, lowering the conjugation of the latter with the carbonyl. The second factor is the influence of steric and electrostatic effects exerted between R^1, R^2, the carbonyl group and the diazo group. This factor causes variations in both the height and relative energy of the two conformers and therefore in their population.

Finally, for most of the molecules of general formula $RCOCHN_2$, the *cis* conformer is preferred to the *trans* one. This may be due to two reasons. The first is the fact that the diazo group is larger than the hydrogen and therefore repulsion between it and R is greater than that between the hydrogen and R. The second is the through-space interaction between the carbonyl and the diazo group. The latter may be related to the presence of a fraction of negative charge on the carbonyl oxygen and of one of positive charge on $N_{(1)}$ which would attract one another, or to an interaction between the π systems of the diazo and the carbonyl groups. That a certain stabilizing action is present in the *cis* form is shown by the clear predominance of the *cis* species over the *trans* one in diazoacetaldehyde, $HCOCHN_2$. N.m.r. measurements lead to a *cis*/*trans* ratio of 7/3 for this molecule[144]. In the absence of the stabilizing effect, the *trans* form would have been favoured, as shown by models constructed using van der Waals' radii.

B. Configuration and Wolff Rearrangement

Knowledge of the configuration of α-diazoketones allows suggestions to be made regarding the mechanism of their decomposition[144]. However, in order that the products obtained may be correlated with the structures of the starting molecules, it is necessary that the rate of interconversion between the two rotamers be lower than their rate of decomposition (36). This is not the case for diazoacetone[144], for which a first-order rate constant of $1{\cdot}68 \times 10^{-4}$ sec^{-1} has been calculated for the decomposition in *t*-butanol at 80 °C, and the *cis* → *trans* interconversion has a rate constant of 10^3 sec^{-1}.

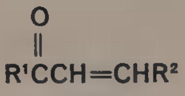


(36)

It is known that the decomposition of α-diazoketones (37) under appropriate conditions, leads to α,β-unsaturated ketones (38) and ketenes (39). The photolytic and silver-oxide catalysed decomposition of α-diazoketones at room temperatures gives mainly **38** and at high temperature **39**. For $PhCOCMeN_2$ and $(Me_3C)COC(CMe_3)N_2$, the dipole moment data allow a semiquantitative analysis of the results.

$R^1C(=O)C(CH_2R^2)N_2$

(37)



$R^1C(=O)CH{=}CHR^2$

(38)

$R^1R^2CH_2C{=}C{=}O$

(39)

If two conformers with $COCN_2$ group planar are present for these molecules, the following *cis*/*trans* ratio would be expected: $PhCOCMeN_2$, 44/56 and $(Me_3C)COC(CMe_3)N_2$, 7/93. These values are of the same order as the ketene/unsaturated ketone ratios obtained experimentally. In fact, for the unsaturated ketone, for decomposition of $PhCOCMeN_2$ catalysed by Ag_2O[178] we obtain a ratio of 72%, and for decomposition of $(Me_3C)COC(CMe_3)N_2$ (pyrolysis, irradiation or acid-catalysed rearrangement)[179] we obtain 80–90%. This evidence suggests that there is some dependence of the mechanism of decomposition on the conformation of α-diazoketones. This would mean that the decomposition occurs not through an intermediate carbene radical but, rather, via a concerted migration process of an alkyl or aryl group and loss of a nitrogen molecule[144]. The *cis* form presents the more suitable situation for this mechanism, which would also explain the effect of temperature on the nature of the decomposition products. In fact, increase in temperature favours the higher energy rotamers (for the two molecules concerned, the *cis* form) and with this the formation of the ketene, exactly as observed experimentally.

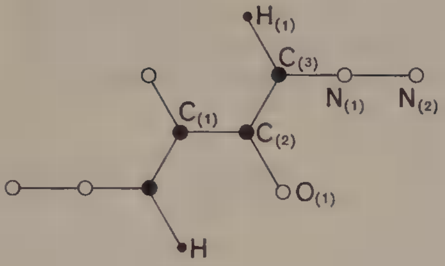
Finally, the fact that the two molecules $PhCOCMeN_2$ and $(Me_3C)COC(Me_3C)N_2$ are not planar means that the mechanism describing the Wolff rearrangement is most facilitated in the *cis* conformer and impeded in the *trans* one and that there are intermediate situations between these two extremes.

C. *Structures*

The molecules of α-diazoketones for which X-ray crystal structures have been reported are not, unfortunately, the more representative ones. It is, therefore, not possible to deduce general conclusions for this class of compounds nor to describe their electronic configuration from the present structural results.

1. 1,4-Bisdiazo-2,3-butanedione

$C_4H_2N_4O_2$ [142] (**40**): $R = 0{\cdot}029$, standard deviation = 0·001 Å. The molecule is planar with a centre of symmetry and has a *cis* conformation for both $COCN_2$ groups. As pointed out by the authors[142], these results appear to be contradictory. In fact, the C—O distance, of the same order as that commonly observed for ketones[137], and the N—N bond, virtually the same as that for diazonium salts (see Section II.A.1), suggest a structure of the 'diazo oxide' type **32** and **33**, in which the triple-bonded N—N type **33** predominates, as in unsubstituted diazonium salts. In contrast, the values above indicate a significant double-bond character in the bonds C—N and $CO—CN_2$ which may be rationalized by invoking a sensible contribution by the canonical forms **32** and **34**, respectively, to the resonance hybrid.



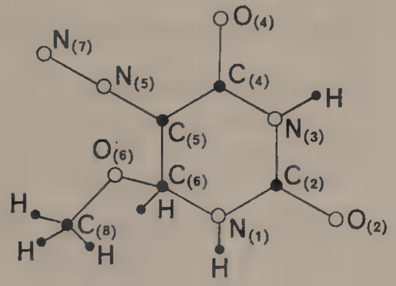
Uncorrected			
$N_{(1)}—N_{(2)}$	1·114 Å	$C_{(3)}—N_{(1)}—N_{(2)}$	176·8°
$C_{(3)}—N_{(1)}$	1·313 Å	$N_{(1)}—C_{(3)}—C_{(2)}$	116·5°
$C_{(2)}—C_{(3)}$	1·418 Å	$N_{(1)}—C_{(3)}—H_{(1)}$	116·3°
$C_{(1)}—C_{(2)}$	1·531 Å	$C_{(3)}—C_{(2)}—O_{(1)}$	125·2°
$C_{(2)}—O_{(1)}$	1·222 Å	$C_{(3)}—C_{(2)}—C_{(1)}$	114·0°
$C_{(3)}—H_{(1)}$	0·92 Å		

(**40**)

As mentioned previously (Section VI.A.2), the formation of an intramolecular hydrogen bond between the methine hydrogen and the oxygen of the carbonyl group in solution has been reported by several workers. For the molecule treated here, there seems to be little evidence for such a bond in the solid state as the minimum O···H distance (2·66 Å), even considering the usual X-ray displacement of the hydrogen atom, is slightly higher than the commonly observed value of 2·52 Å [142].

2. 5-Diazo-6-methoxy-6-hydrouracil

$C_5H_6N_4O_3$ [180] (**41**): $R = 0{\cdot}056$; standard deviation ≤0·007 Å. Only the bond distances have been reported.

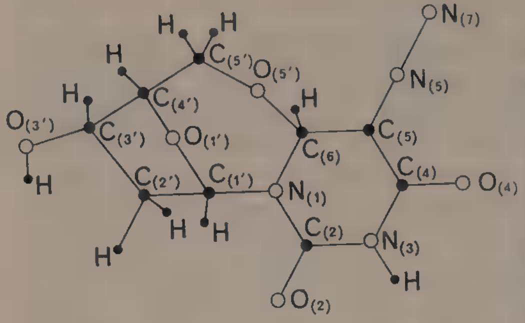


Uncorrected			
$N_{(5)}—N_{(7)}$	1.113 Å	$C_{(2)}—O_{(2)}$	1·241 Å
$C_{(5)}—N_{(5)}$	1·332 Å	$C_{(2)}—N_{(1)}$	1·337 Å
$C_{(5)}—C_{(4)}$	1·436 Å	$C_{(6)}—N_{(1)}$	1·440 Å
$C_{(4)}—O_{(4)}$	1·218 Å	$C_{(5)}—C_{(6)}$	1·472 Å
$C_{(4)}—N_{(3)}$	1·381 Å	$C_{(6)}—O_{(6)}$	1·421 Å
$C_{(2)}—N_{(3)}$	1·370 Å	$C_{(8)}—O_{(6)}$	1·436 Å

(**41**)

3. 2′-Deoxy-5-diazo-6-hydro-O⁶,5′-cyclouridine

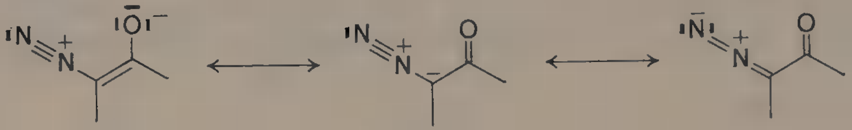
$C_9H_{10}N_4O_5$ [180] (**42**): $R = 0{\cdot}052$; standard deviation ≤0·007 Å. Only the bond distances have been reported.



Uncorrected			
$N_{(5)}-N_{(7)}$	1·120 Å	$C_{(6)}-O_{(5\ )}$	1·415 Å
$C_{(5)}-N_{(5)}$	1·308 Å	$O_{(5')}-C_{(5')}$	1·433 Å
$C_{(5)}-C_{(4)}$	1·431 Å	$C_{(5')}-C_{(4')}$	1·519 Å
$C_{(4)}-O_{(4)}$	1·234 Å	$C_{(4')}-O_{(1')}$	1·449 Å
$C_{(4)}-N_{(3)}$	1·361 Å	$C_{(1')}-O_{(1')}$	1·404 Å
$N_{(3)}-C_{(2)}$	1·381 Å	$C_{(1')}-N_{(1)}$	1·486 Å
$C_{(2)}-O_{(2)}$	1·219 Å	$C_{(1')}-C_{(2')}$	1·529 Å
$N_{(1)}-C_{(2)}$	1·349 Å	$C_{(2')}-C_{(3')}$	1·519 Å
$C_{(6)}-N_{(1)}$	1·457 Å	$C_{(3')}-O_{(3')}$	1·431 Å
$C_{(5)}-C_{(6)}$	1·484 Å	$C_{(3')}-C_{(4')}$	1·522 Å

(42)

The bond distances observed for **41** and **42** suggest that as for the other diazoketones, the $COCN_2$ group in these molecules is a resonance hybrid between the canonical forms **43–45**. The other parts of the molecule do not conjugate with $COCN_2$ group.



(43) **(44)** **(45)**

VII. DIAZO OXIDES

A. General

When alkali is added to *ortho*- and *para*-hydroxy-substituted diazonium salts and the mixture heated, compounds of the type **46** are obtained:

(46)

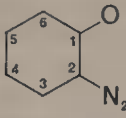
The nature of the bonding present and the character of the six-membered ring are the subject of this section.

These substances are of some interest as they are used as intermediates in the laboratory and in industry and because they can be viewed, theoretically, as representing a situation intermediate between the diazonium salts and the diazoalkanes.

Various names have been suggested for these compounds: diazoquinones, diazoanhydrides, diazo oxides and quinone diazides. For the derivatives of benzene and naphthalene, the names diazophenols and diazonaphthols, respectively, have also been used. In the present chapter for most cases we will adopt the name diazo oxides.

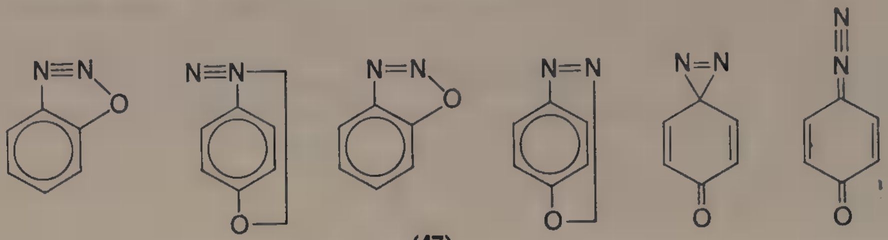
Several suggestions have been put forward as to the structure of diazo oxides[181–189], **47** and **48**. Some of these are now unacceptable on the basis of modern electronic theory. Others, such as the cyclic structures, may be excluded on the basis of the X-ray data (Section VII.C) and of the frequencies of the N—N and C—O stretching vibration bands, some of which are shown in Table 4. As can be seen from this table, these frequencies are found in regions characteristic of absorptions by a N—N bond intermediate between a double and a triple bond and by a C—O bond slightly lower than a double bond.

TABLE 4. Values of the stretching vibration frequencies ν_{NN} and ν_{CO} for some diazo oxides

Substituent	Solvent or physical state	ν_{NN} (cm^{-1})		ν_{CO} (cm^{-1})		Reference
Diazophenols: *ortho* derivatives						
Unsubstituted	KBr	2175	2140	1620		190
5-Me	KBr	2175	2130	1613		190
4,5-Me_2	KBr	2170	2120	1625		190
4,5-Me_2	$CHCl_3$	2150	2100	1625		191
5-Bu-*t*	$CHCl_3$	2182	2160	1618		190
3,5-(Bu-*t*)$_2$	$CHCl_3$	2135	2124	1625		190
5-MeO	$CHCl_3$	2128		1620		190
3,6-MeO	$CHCl_3$	2135	2087	1613		190
5-$PhCH_2O$	$CHCl_3$	2150		1620		190
5-Cl	$CHCl_3$	2205	2158	1613		190
6-Cl	$CHCl_3$	2195	2158	1610		190
4,5-Cl_2	$CHCl_3$	2160		1613		190
3,5-Br_2	Paraffin mulls	2110		1582		192
4-NO_2	Paraffin mulls	2157		1562		192
4-NO_2	Paraffin mulls	2183	2150			41
4,6-$(NO_2)_2$	KBr	2225				193
4-COOH	KBr	2215				193
Diazophenols: *para* derivatives						
Unsubstituted	$CHCl_3$	2080				191
Unsubstituted	Paraffin mulls	2109				41
2,6-Me_2	$CHCl_3$	2090		1615		191
2,6-Me_2	Dioxane	2060		1600		194
2,5-Me_2	$CHCl_3$	2070				191
2,6-Cl_2	KBr	2140				193
2-Me, 6-COOH	KBr	2225				193
2-CCOH, 6-NO_2	KBr	2225				193
Diazonaphthols						
1,2-Naphthaquinone-1-diazide	$CHCl_3$	2132	2096	1621		195
4-Nitro-1,2-naphthaquinone-1-diazide	Paraffin mulls	2015		1642		192
1,2-Naphthaquinone-2-diazide	$CHCl_3$	2155	2114	1621		195
1,2-Naphthaquinone-2-diazide	Paraffin mulls	2148		1610	1618	192
1,4-Naphthaquinonediazide	Paraffin mulls	2014		1618		192

For the values of the stretching vibration frequencies reported for other diazo oxides see Reference 196.

The problem of the electronic structure of diazo oxides may at present be put in these terms: should these compounds be considered quinoid (**48a**) or benzenoid (**48b**) in character, or a resonance hybrid between both extreme forms **48**? We will attempt a reply to this question in Section VII.B.



(47)

(48a) **(48b)**

B. Electronic Structure

Some time ago, Sidgwick and coworkers[197] suggested that the diazo oxides could better be represented by a resonance hybrid between the two forms **48**. This idea was later accepted by other authors[198, 199]. Anderson and Roedel[189] found that the visible and ultraviolet spectra of some diazophenols and diazonaphthols were very similar to those of the corresponding quinones and inferred that the former must have a quinoid structure. Le Fèvre and coworkers[192, 200], from dipole moment measurements and i.r. and u.v. spectra, concluded that the diazo oxides are a resonance hybrid between the canonical forms **48**, the quinoid form clearly predominating. The electric dipole moments, determined in non-polar solvent, are reported in Table 5. Vector analysis of the moments of this table may give the following qualitative information. As the moment observed for phenanthraquinone is 3·0 D and $\mu(\overrightarrow{C{=}\overset{+}{N}{=}\overset{-}{N}})$ is *c.* 5·4 D [200], theoretical moments of *c.* 2·4 D are obtained[200] for the quinoid form **48a** of 1,4-naphthaquinonediazide and 1,4-benzoquinonediazide, which are much lower than the values observed for these compounds (4·2 and 5·0 D, respectively)[200]. The calculated moments become equal to the observed ones if it is assumed that the diazo oxides are a resonance hybrid between the two forms **48**, in which, however, the contribution of the zwitterionic form must be very small as it has a rather high theoretical moment (27·4 D [200].

TABLE 5. Electric dipole moments observed for some quinone diazides[a]

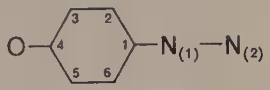
Compound	μ (D)
3,5-Dibromo-1,2-benzoquinone-2-diazide	2·9
1,2,-Naphthaquinone-1-diazide	4·0
1,2-Naphthaquinone-2-diazide	3·5
4-Nitro-1,2-naphthaquinone-1-diazide	4·6
1,4-Naphthaquinonediazide	4·2
p-Benzoquinonediazide	5·0

[a] In benzene, at 25 °C. $P_a = 0$.

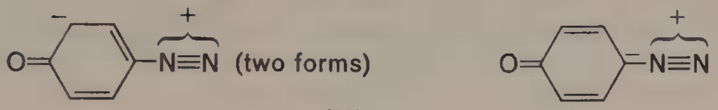
The dipole moment evidence is supported by i.r. measurements. In fact, Le Fèvre and coworkers observed that the frequency of the C—O stretching vibration band, which is much lower than in the quinone analogues, indicates that in the diazo oxides an extreme form is present in which the C—O bond is a single bond[192]. Results in agreement with these have also been obtained by Whetsel and coworkers[41].

The presence of a structure intermediate between the benzenoid and quinoid types was also suggested by Vaughan and Phillips[201] from thermal stability measurements.

Unusual results on the electronic structure of diazo oxides have been obtained by Kazitsyna and coworkers[25, 202]. These authors performed MO calculations, using the Hückel approximation, on *o*- and *p*-diazo oxides having different substituent groups. It was found that the C—O bond order is slightly lower than double and the negative charge on the oxygen atom is slightly higher than that usually calculated for a carbonyl oxygen. In the molecule **49** the bond order for the bonds $C_{(4)}—C_{(3)}$ and $C_{(4)}—C_{(5)}$ is very close to that for a quinoid structure. However, on going from the atoms $C_{(2)}$ and $C_{(6)}$ towards the diazo group the situation changes. In fact, the bond order of $C_{(1)}—C_{(2)}$ and $C_{(6)}—C_{(1)}$ is noticeably higher than that for a quinoid structure and the C—N and N—N bonds are almost entirely single and triple bonds, respectively. In addition, the fraction of positive charge is localized on the two nitrogen atoms, which rationalizes the tendency of diazo oxides to undergo diazo coupling reactions. According to Kazitsyna and coworkers, the electronic structure of the present compounds is better described if the forms **50** are present, in addition to **48**. The participation of these canonical forms to the mesomerism of diazo oxides might account for the above-mentioned C—O, C—N and N—N bond orders and also for the fact that the negative charge is greater on the oxygen atom and on the atoms $C_{(1)}$, $C_{(3)}$ and $C_{(5)}$. Finally, it was found that the distribution of electrons on the molecule is very sensitive to the parameters used. Although this result is further evidence that the electronic system of the diazo group is very mobile it also induces caution in the interpretation of results from such calculations.



(49)



(50)

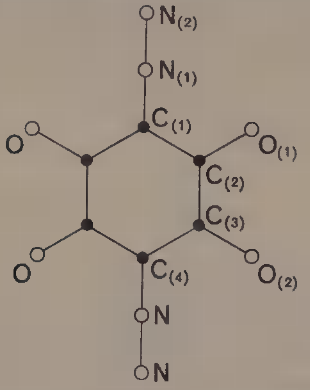
We cannot conclude this examination of the literature data without underlining the similarity in i.r. behaviour between the diazo oxides and the α-diazoketones. In both types of compounds the ν_{NN} and ν_{CO} values are noticeably shifted compared to those in the corresponding diazohydrocarbons and ketones: ν_{NN} to higher frequency and ν_{CO} to lower frequency. From the evidence discussed above we come to the conclusion that this behaviour has a single cause: conjugation between the π system of the diazo group and the π electrons of the C—O bond. Consequently, at the present stage of work on these compounds, the most likely situation seems that of a resonance hybrid having the main extreme forms **48**, with the quinoid form being predominant.

C. X-Ray Data

The two diazo oxide structures determined to date are not representative of this class of compounds, and the data reported here cannot give insight on the electronic structure of these molecules.

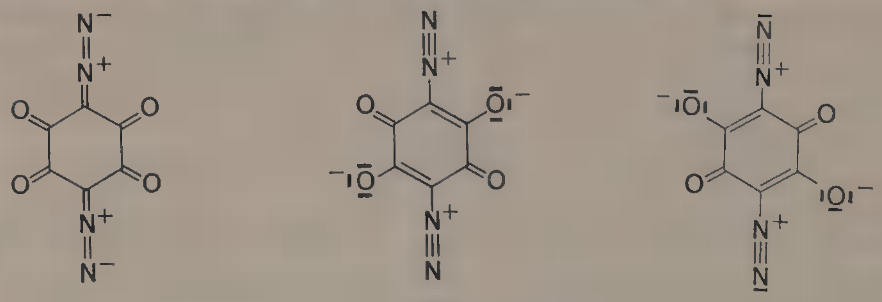
1. 3,6-Bisdiazocyclohexanetetraone

$C_6N_4O_4$ [203] (**51**): $R = 0{\cdot}079$; standard deviations 0·010 Å and 0·7–0·9°. The molecule is planar. The N—N bond length (1·10 Å) is of the same order as that of diazonium salts (see Section II.A.1), while it is slightly shorter than that found in diazoalkanes (1·12–1·13 Å). This would indicate that the form having a triple N—N bond is predominant, as in diazonium salts which are not substituted in the benzene ring. Instead, the fact that the C—O bond length (1·21 Å) is practically the same as that found in 1,4-benzoquinone (1·22 Å) [204, 205] may in part be explained by remembering that the two diazo groups conjugate with four CO groups, which decreases the conjugation effect in the CO's. Finally, the CO—CO bond length is 1·54 Å, indicating the presence of a single bond, while the CO–CN_2 bond (1·43 Å) is slightly longer than for an aromatic bond (1·39 Å). The above evidence is sufficient to allow the conclusion that the electronic structure of this molecule may be described by a resonance hybrid between several extreme forms, the most important of which are those of **52**. The distance between molecular planes in the crystal (not <2·90 Å) indicates that there are no intermolecular contacts.



Uncorrected			
$N_{(1)}$—$N_{(2)}$	1·107 Å	$C_{(1)}$—$N_{(1)}$—$N_{(2)}$	177·9°
$C_{(1)}$—$N_{(1)}$	1·357 Å	$C_{(2)}$—$C_{(1)}$—$N_{(1)}$	114·4°
$C_{(1)}$—$C_{(2)}$	1·433 Å	$C_{(6)}$—$C_{(1)}$—$C_{(2)}$	129·1°
$C_{(2)}$—$C_{(3)}$	1·541 Å	$C_{(1)}$—$C_{(2)}$—$O_{(1)}$	123·8°
$C_{(3)}$—$C_{(4)}$	1·437 Å	$C_{(1)}$—$C_{(2)}$—$C_{(3)}$	114·9°
$C_{(2)}$—$O_{(1)}$	1·214 Å	$C_{(2)}$—$C_{(3)}$—$O_{(2)}$	119·2°
$C_{(3)}$—$O_{(2)}$	1·208 Å	$C_{(2)}$—$C_{(3)}$—$C_{(4)}$	115·9°

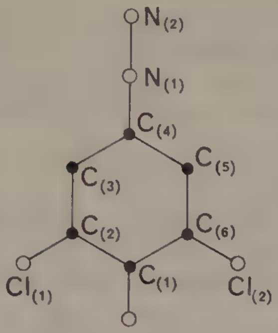
(51)



(52)

2. 2,6-Dichloro-4-diazo-2,5-cyclohexadien-1-one

$C_6H_2Cl_2N_2O$ [206] (**53**): $R = 0{\cdot}105$; standard deviations 0·013–0·018 Å and 0·10–0·14°.



Mean uncorrected values			
$N_{(1)}-N_{(2)}$	1·099 Å	$C_{(4)}-N_{(1)}-N_{(2)}$	178·7°
$C_{(4)}-N_{(1)}$	1·368 Å	$C_{(6)}-C_{(5)}-C_{(4)}$	115·1°
$C_{(5)}-C_{(4)}$	1·441 Å	$C_{(1)}-C_{(6)}-C_{(5)}$	125·9°
$C_{(6)}-C_{(5)}$	1·360 Å	$Cl_{(2)}-C_{(6)}-C_{(5)}$	117·6°
$C_{(6)}-Cl_{(2)}-$	1·752 Å	$O-C_{(1)}-C_{(6)}$	124·2°
$C_{(1)}-C_{(6)}-$	1·434 Å	$C_{(2)}-C_{(1)}-C_{(6)}$	114·0°
$C_{(1)}-O$	1·221 Å	$Cl_{(1)}-C_{(2)}-C_{(1)}$	117·0°
$C_{(1)}-C_{(2)}$	1·461 Å	$C_{(3)}-C_{(2)}-C_{(1)}$	123·0°
$C_{(2)}-Cl_{(1)}$	1·708 Å	$C_{(4)}-C_{(3)}-C_{(2)}$	117·9°
$C_{(2)}-C_{(3)}$	1·368 Å	$C_{(5)}-C_{(4)}-C_{(3)}$	123·9°
$C_{(3)}-C_{(4)}$	1·393 Å		

(53)

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Note Added in Proof

The zinc atom is nearly tetrahedrally surrounded by chlorine atoms, with the Cl—$\widehat{\text{Zn}}$—Cl angles of 105·8° and 117·0°, both with an estimated standard deviation of 0·2°. The Zn—Cl distance is 2·238 Å (e.s.d. 0·002 Å), in agreement with the results obtained by Nesterova and coworkers[11] for *p*-*N*,*N*-dimethylaminobenzenediazonium tetrachlorozinc(II) (**3**).

In the present molecule you can observe a more accentuated shortening of the distance $C_{(1)}$—$C_{(4)}$ found in benzenediazonium chloride (**1**) and in *o*-methoxybenzenediazonium tetrachloroiron (**4**). This effect, qualitatively explanable by a diminution in the p character of orbitals $C_{(1)}$ in the links $C_{(1)}$—$C_{(2)}$ and $C_{(1)}$—$C_{(6)}$ and by an increase in the character p along $C_{(1)}$—$N_{(2)}$, has been attributed to the presence of the diazonium group[13].

CHAPTER 4

Thermochemistry of diazo compounds and organic azides[†]

ROBERT SHAW

1162 Quince Avenue,
Sunnyvale, California 94087, *USA*

I. INTRODUCTION

A search of the literature has revealed no information on diazonium compounds and very little in the way of experimental data on diazo compounds and azides, so the emphasis of this chapter is on estimation. The literature searched included *Chemical Abstracts*, IUPAC's *Bulletin of Thermochemistry and Thermodynamics*, and the two classic monographs[1, 2], Stull, Westrum and Sinke's *The Chemical Thermodynamics of Organic Compounds* and Cox and Pilcher's *Thermochemistry of Organic and Organometallic Compounds*.

The methods of estimation are based on additivity techniques developed by Benson and his coworkers[3–5]. It would not be appropriate to give a detailed discussion of additivity principles here because they have been adequately covered previously, in earlier volumes in this series[6, 7]. Nor would it be appropriate in a review article of this size to estimate the thermodynamic properties of all possible

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[†] Since the volume *The Chemistry of the Azido Group* (1971) did not contain a chapter on thermochemistry, it was decided to annex the material available on the azido group to this chapter.

compounds of interest. The main emphasis here is on the methyl, ethyl, vinyl, and phenyl derivatives in the hope that they will form a basis for further work. A few other compounds are included.

The thermochemical properties discussed here are the heat of formation, the entropy and the heat capacity for the ideal gas state at a temperature of 298·15 K (25 °C). For the sake of brevity, the terms molar, gas and 298·15 K will be omitted from the thermochemical symbols. Otherwise, the nomenclature will be that recommended by IUPAC[8]. For example, the symbol for the heat of formation of methyl azide in the ideal gas state at 298·15 K is denoted here by $\Delta_f H^\theta(CH_3N_3)$. Since the unit of energy recommended by IUPAC is the joule, all heats of formation will be in units of kJ/mol, followed by a value in the previously accepted unit, kcal/mol. The conversion factor is cal = 4·18 J. The symbol for the standard molar entropy is S^θ (chemical compound) and that for the standard molar heat capacity is c_p^θ (chemical compound). The units for all entropies and heat capacities will be J/(mol K). As with the heats of formation, the value of the entropy and heat capacity in the previously accepted unit cal/(mol K) will also be given.

Most of the measurements reported in this review are good to ± 10 kJ/mol, 2 kcal/mol, for the heat of formation and ± 5 J/(mol K), 1 cal/(mol K), for the entropy and heat capacity. Most of the estimates are good to ± 20 kJ/mol, 5 kcal/mol, for the heat of formation and ± 10 J/(mol K), 2 cal/(mol K), for the entropy and heat capacity.

II. DIAZO COMPOUNDS

A. Diazomethane

Diazomethane is the only diazo compound for which experimental results have been reported. Langer, Hipple and Stevenson[9] obtained a value of 195 ± 25 kJ/mol, 46 ± 6 kcal/mol, for the heat of formation of diazomethane from the appearance potential of CH_2^+ in the mass spectrum of diazomethane. Moore and Pimentel[10] calculated the entropy to be 242·4 J/(mol K), 58·0 cal/(mol K), and the heat capacity to be 52·7 J/(mol K), 12·6 cal/(mol K), from statistical mechanics and the infrared spectrum of diazomethane.

B. Diazoethane

No measured thermochemical data have been reported for diazoethane. The heat of formation, entropy and heat capacity of diazoethane may be estimated by assuming that the difference between diazoethane and diazomethane is the same as the difference between ethylacetylene and methylacetylene, equation (1).

$$CH_3(CHN_2) - H(CHN_2) = CH_3(CH_2C{\equiv}CH) - H(CH_2C{\equiv}CH) \qquad (1)$$

From equation (1), it follows that

$$CH_3(CHN_2) = H(CHN_2) + CH_3(CH_2C{\equiv}CH) - H(CH_2C{\equiv}CH) \qquad (2)$$

By using equation (2), inserting values for diazomethane from the previous section and values for ethyl- and methyl-acetylene from Stull, Westrum and Sinke[1], I estimated the heat of formation of diazoethane to be 172 kJ/mol, 41·2 kcal/mol, the entropy as 285 J/(mol K), 68·2 cal/(mol K), and the heat capacity as 73·5 J/(mol K), 17·6 cal/(mol K). The results are summarized in Table 1.

TABLE 1. Estimation of the standard molar heat of formation, entropy and heat capacity of diazoethane, diazopropylene and diazotoluene in the ideal gas state at 298·15 K (25 °C)

Compound	$\Delta_f H^\theta$		S^θ		c_p^θ		Method of estimation
	kJ/mol	kcal/mol	J/(mol K)	cal/(mol K)	J/(mol K)	cal/(mol K)	
Diazoethane	172·2	41·2	285·1	68·2	73·5	17·6	$CH_3(CHN_2) - H(CHN_2) =$ $CH_3(CH_2C{\equiv}CH) - H(CH_2C{\equiv}CH)$
Diazopropylene	277·1	66·3	309·9	73·9	93·6	22·4	$CH_2{=}CH(CHN_2) - H(CHN_2) =$ $CH_2{=}CH(CH_2CH{=}CH_2) - H(CH_2CH{=}CH_2)$
Diazotoluene	284·2	68·0	408·0	97·6	115·0	27·5	$Ph(CHN_2) - H(CHN_2) =$ $Ph(CH_2CH{=}CH_2) - H(CH_2CH{=}CH_2)$

C. Diazopropylene

No experiments have been reported on the thermochemical properties of diazopropylene. Values may be estimated by assuming that the difference between diazopropylene and diazomethane is the same as the difference between 3-vinyl-1-propyne and propyne, equation (3).

$$CH_2{=}CH(CHN_2) - H(CHN_2) = CH_2{=}CH(CH_2C{\equiv}CH) - H(CH_2C{\equiv}CH) \qquad (3)$$

From equation (3), it follows that

$$CH_2{=}CH(CHN_2) = H(CHN_2) + CH_2{=}CH(CH_2C{\equiv}CH) - H(CH_2C{\equiv}CH) \qquad (4)$$

Unfortunately, neither Stull, Westrum and Sinke[1] nor Cox and Pilcher[2] list thermochemical properties of 3-vinyl-1-propyne. Furthermore, it is not possible to estimate values using group additivity because one of the groups, namely the $(C{-}C_d,C_t,H_2)$† group, has not been evaluated[4].

Another solution is to assume that the difference between diazopropylene and diazomethane is the same as the difference between 1,4-pentadiene and propylene, equation (5).

$$CH_2{=}CH(CHN_2) - H(CHN_2) = CH_2{=}CH(CH_2CH{=}CH_2) - H(CH_2CH{=}CH_2) \qquad (5)$$

From equation (5), it follows that

$$CH_2{=}CH(CHN_2) = H(CHN_2) + CH_2{=}CH(CH_2CH{=}CH_2) - H(CH_2CH{=}CH_2) \qquad (6)$$

By using equation (6), inserting values for diazomethane from the previous section and values for 1,4-pentadiene and propylene from Stull, Westrum and Sinke[1], I estimated the thermochemical properties of diazopropylene. The results are given in Table 1.

D. Diazotoluene

No experimental values have been reported for the thermochemical properties of diazotoluene. Values may be estimated by assuming that the difference between diazotoluene and diazomethane is the same as the difference between 3-phenylpropyne and propyne, equation (7).

$$Ph(CHN_2) - H(CHN_2) = Ph(CH_2C{\equiv}CH) - H(CH_2C{\equiv}CH) \qquad (7)$$

From equation (7), it follows that

$$Ph(CHN_2) = H(CHN_2) + Ph(CH_2C{\equiv}CH) - H(CH_2C{\equiv}CH) \qquad (8)$$

Unfortunately, neither Stull, Westrum and Sinke[1] nor Cox and Pilcher[2] list the thermochemical properties of 3-phenylpropyne. Furthermore, it is not possible to estimate values using group additivity because one of the groups, namely, the $(C{-}C_B,C_t,H_2)$‡ group, has not been evaluated[4].

Another solution is to assume that the difference between diazotoluene and diazomethane is the same as the difference between 3-phenylpropylene and propylene, equation (9).

$$Ph(CHN_2) - H(CHN_2) = Ph(CH_2CH{=}CH_2) - H(CH_2CH{=}CH_2) \qquad (9)$$

† Where C_d is a double-bonded carbon atom and C_t is a triple-bonded carbon atom.
‡ Where C_B is a benzenoid carbon atom.

From equation (9), it follows that

$$Ph(CHN_2) = H(CHN_2) + Ph(CH_2CH{=}CH_2) - H(CH_2CH{=}CH_2) \tag{10}$$

Although no values for 3-phenylpropylene are known[1,2], it is possible to estimate its thermochemical properties using group additivity because all the groups are available[4]. (While it is not noted in the text of Reference 4, it is probable that the values for the group ($C-C_B,C_d,H_2$) are assigned, that is, estimated by analogy with a similar group.) The results are given in Table 1.

III. ORGANIC AZIDES

A. Hydrogen Azide

The thermochemical properties of hydrogen azide have been measured experimentally[11-15]. They are listed in Table 2 along with similar data for organic azides[16-19].

Experimental work on the heat of formation of hydrogen azide has been reviewed by Evans, Yoffe and Gray[13]. (The reference for the heat of formation of hydrogen azide in another review[4] is wrong.) Dows and Pimentel[15] used statistical mechanics to calculate the entropy and heat capacity of hydrogen azide from its infrared spectrum.

B. Methyl, Ethyl, Vinyl and Phenyl Azides

No thermochemical properties have been measured for methyl, ethyl, vinyl and phenyl azides, but they can be estimated with reasonable accuracy using additivity techniques[3-5], as follows.

The heats of formation of cyclopentyl azide, cyclohexyl azide and 2-hydroxyethyl azide have all been measured in the liquid state (see Table 2). Fagley and Myers[19] measured the surface tension of cyclopentyl and cyclohexyl azides and, from an empirical correlation of surface tension with heat of vaporization, estimated the heat of vaporization of cyclopentyl azide to be 41·8 kJ/mol, 10 kcal/mol, and that of cyclohexyl azide to be 46·0 kJ/mol, 11 kcal/mol. Thus the heat of formation in the ideal gas state of cyclopentyl azide is 220·7 kJ/mol, 52·8 kcal/mol, and that of cyclohexyl azide is 154·2 kJ/mol, 36·9 kcal/mol.

Fagley, Klein and Albrecht[16] measured the heat of formation of 2-hydroxyethyl azide in the liquid state (see Table 2). The heat of vaporization of ethyl azidoacetate may be estimated as follows. The boiling point of ethanol[1] is 352 K and that of cyclohexane[1] is very similar at 354 K. Therefore it may be assumed that the heat of vaporization of 2-hydroxyethyl azide is the same as that for cyclohexyl azide, namely, 46·0 kJ/mol, 11 kcal/mol. Thus the heat of formation of 2-hydroxyethyl azide in the ideal gas state is 140·0 kJ/mol, 33·5 kcal/mol.

All three compounds, namely cyclopentyl, cyclohexyl and 2-hydroxyethyl azides, contain the group ($C-C,H_2,N_3$). Furthermore, for all three compounds, values are known[4] for all the additional groups that make up each molecule. For example, 2-hydroxyethyl azide is made up of the groups ($O-C,H$), ($C-C,H_2,O$) and ($C-C,H_2,N_3$). Thus from the known value of the heat of formation of 2-hydroxyethyl azide and from the known values of the ($O-C,H$) and ($C-C,H_2,O$) groups, a value is obtained for the ($C-C,H_2,N_3$) group. Similarly, values for the ($C-C,H_2,N_3$) group may be obtained from cyclopentyl and cyclohexyl azides. The results are given in Table 3. The results show that there is reasonable agreement between the two values from the cycloalkyl compounds, but that there is poor agreement with

TABLE 2. The standard molar heat of formation, entropy and heat capacity of azides that have been determined experimentally at 298·15 K (25 °C)

		$\Delta_f H^\theta$			S^θ			c_p^θ		
Compound	State	kJ/mol	kcal/mol	Reference	J/(mol K)	cal/(mol K)	Reference	J/(mol K)	cal/(mol K)	Reference
HN_3	l	269·1	64·37	11–13						
	g	299·5	71·66	11–13	238·6	57·08	15	43·6	10·44	15
	g	293·8	70·3	14						
	g	296·8	71·0		238·7	57·1		43·5	10·4	Selected value
$HOCH_2CH_2N_3$	l	94·0	22·5	16						
$C_3H_3(N_3)_3$	s	915·4	219	13, 17						
$N_3CH_2COOC_2H_5$	l	139·2	33·3	13, 18						
cyclo-$C_5H_9N_3$	l	178·9	42·8	2, 13, 19						
PhN_3	l	344·0	82·3	13, 18						
cyclo-$C_6H_{11}N_3$	l	108·3	25·9	2, 13, 19						

the value derived from 2-hydroxyethyl azide. In selecting the group value to be used in further calculations, I ignored the value from 2-hydroxyethyl azide and obtained an average value from the other two compounds.

TABLE 3. Heat of formation in the ideal gas state at 298·15 K (25 °C) for the (C—C,H_2,N_3) group, determined from values for the heats of formation of 2-hydroxyethyl, cyclopentyl and cyclohexyl azides, and from other known[4] group values

Compound	$\Delta_f H^\theta$(C—C,H_2,N_3) kJ/mol	kcal/mol
$HOCH_2CH_2N_3$	332·3	79·5
cyclo-$C_5H_{10}N_3$	277·1	66·3
cyclo-$C_6H_{11}N_3$	257·5	61·6
Selected value	267·5	64·0

Ethyl azide is made up of two groups, namely, the (C—C,H_3) group and the (C—C,H_2,N_3) group. The value of the heat of formation of the (C—C,H_3) group is known[4] to be −42·2 kJ/mol, −10·1 kcal/mol, giving the heat of formation of ethyl azide as 225·3 kJ/mol, 53·9 kcal/mol, as shown in Table 4.

The heat of formation of phenyl azide has been measured in the liquid state (see Table 2). The heat of vaporization may be estimated as follows. The boiling point of benzene[1] is 353 K and that of cyclohexane is 354 K. Therefore it may be assumed that the heat of vaporization of phenyl azide is the same as that of cyclohexyl azide, namely, 46·0 kJ/mol, 11·0 kcal/mol, giving the heat of formation of phenyl azide in the ideal gas state as 385·8 kJ/mol, 92·3 kcal/mol, as shown in Table 4.

No experimental results have been reported for the heat of formation of methyl azide. However, it may be estimated as follows. From the above discussion on ethyl and phenyl azides, the difference in the heats of formation of ethyl and phenyl azide is −160·5 kJ/mol, −38·4 kcal/mol. From the literature[4], the difference between the heats of formation of ethyl and phenyl chlorides is −159·7 kJ/mol, −38·2 kcal/mol. It is therefore a good approximation to say that

$$\Delta_f H^\theta(\mathrm{EtN_3}) - \Delta_f H^\theta(\mathrm{PhN_3}) = \Delta_f H^\theta(\mathrm{EtCl}) - \Delta_f H^\theta(\mathrm{PhCl}) \qquad (11)$$

It may be assumed then that

$$\Delta_f H^\theta(\mathrm{MeN_3}) - \Delta_f H^\theta(\mathrm{EtN_3}) = \Delta_f H^\theta(\mathrm{MeCl}) - \Delta_f H^\theta(\mathrm{EtCl}) \qquad (12)$$

It follows from equation (12) that

$$\Delta_f H^\theta(\mathrm{MeN_3}) = \Delta_f H^\theta(\mathrm{EtN_3}) + \Delta_f H^\theta(\mathrm{MeCl}) - \Delta_f H^\theta(\mathrm{EtCl}) \qquad (13)$$

From equation (13) and known values for the heats of formation of ethyl azide (Table 4) and methyl and ethyl chlorides[1], the heat of formation of methyl azide is 246·6 kJ/mol, 59·0 kcal/mol. This value is in very good agreement with an earlier estimate of 238·3 kJ/mol, 57·0 kcal/mol, by Evans, Yoffe and Gray[13].

Similarly, the heat of formation of vinyl azide was estimated from equation (14)

$$\Delta_f H^\theta(\mathrm{CH_2{=}CHN_3}) = \Delta_f H^\theta(\mathrm{EtN_3}) + \Delta_f H^\theta(\mathrm{CH_2{=}CHCl}) - \Delta_f H^\theta(\mathrm{EtCl}) \qquad (14)$$

TABLE 4. Estimation of the standard molar heat of formation, entropy and heat capacity of methyl, ethyl, vinyl and phenyl azides in the ideal gas state at 298·15 K (25 °C)

	$\Delta_f H^\theta$		S^θ		c_p^θ		
Compound	kJ/mol	kcal/mol	J/(mol K)	cal/(mol K)	J/(mol K)	cal/(mol K)	Method of estimation
Methyl azide	238·3	57·0					From cycloalkyl azides[13]
	246·6	59·0					$MeN_3 - EtN_3 = MeCl - EtCl$
			283·0	67·7	67·7	16·2	$MeN_3 = MeNCO$
	242·4	58·0	283·0	67·7	67·7	16·2	Selected value
Ethyl azide	225·3	53·9					Group additivity, see text
			322·3	77·1	90·5	21·6	$EtN_3 = EtCl$
Vinyl azide	366·6	87·7					$CH_2{=}CHN_3 - EtN_3 = CH_2{=}CHCl - EtCl$
			295·5	70·7	75·7	18·1	$CH_2{=}CHN_3 = CH_2{=}CHCl$
Phenyl azide	385·8	92·3					$PhN_3 - EtN_3 = PhCl - EtCl$
			357·0	85·4	102·4	24·5	$PhN_3 = PhNCO$

No measurements have been reported for the entropies or heat capacities of methyl, ethyl, vinyl or phenyl azides. However comparison of the values for hydrogen azide, HN_3, with those for hydrogen isocyanate, HNCO (see Table 5), suggest that it would be a good approximation to assume that the entropy and heat capacity of methyl azide is equal to those for methyl isocyanate, equations (15) and (16).

$$S^{\theta}(MeN_3) = S^{\theta}(MeNCO) \tag{15}$$

$$c_p^{\theta}(MeN_3) = c_p^{\theta}(MeNCO) \tag{16}$$

Values for the entropies and heat capacities of ethyl, vinyl and phenyl azides were estimated similarly to those for methyl azide.

TABLE 5. Comparison of the standard molar entropy and heat capacity of hydrogen azide, hydrogen cyanate and hydrogen isocyanate in the ideal gas state at 298·15 K (25 °C)

	S^{θ}			c_p^{θ}		
Compound	J/(mol K)	cal/(mol K)	Reference	J/(mol K)	cal/(mol K)	Reference
HN_3	238·7	57·1	15	43·5	10·4	15
HOCN	230·3	55·1	20	44·3	10·6	20
HNCO	237·8	56·9	20	45·1	10·8	20

IV. SUMMARY OF THERMOCHEMICAL PROPERTIES OF DIAZO COMPOUNDS AND ORGANIC AZIDES

For convenience, the measured and estimated heats of formation, entropies and heat capacities discussed in the previous sections have been collected in Table 6.

TABLE 6. Measured and estimated standard molar heats of formation, entropies and heat capacities of diazo-methane, -ethane, -propylene and -toluene, and of hydrogen, methyl, ethyl, vinyl and phenyl azides in the ideal gas state at 298·15 K (25 °C)

	$\Delta_f H^{\theta}$		S^{θ}		c_p^{θ}		
Compound	kJ/ mol	kcal/ mol	J/ (mol K)	cal/ (mol K)	J/ (mol K)	cal/ (mol K)	Table
Diazo-							
-methane	195	46	242·4	58·0	52·7	12·6	Text
-ethane	172·2	41·2	285·1	68·2	73·5	17·6	1
-propylene	277·1	66·3	308·9	73·9	93·6	22·4	1
-toluene	284·2	68·0	408·0	97·6	115·0	27·5	1
Azides							
hydrogen	296·8	71·0	238·7	57·1	43·5	10·4	2
methyl	242·4	58·0	283·0	67·7	67·7	16·2	4
ethyl	225·3	53·9	322·3	77·1	90·5	21·6	4
vinyl	366·6	87·7	295·5	70·7	75·7	18·1	4
phenyl	385·8	92·3	357·0	85·4	102·4	24·5	4

V. VALUES FOR ESTIMATING THERMOCHEMICAL PROPERTIES BY GROUP ADDITIVITY

The principles and use of group additivity have been described in considerable detail elsewhere[3-7, 21]. A simple example was given earlier in the discussion of ethyl azide.

Values of the thermochemical properties of the groups are summarized in Table 7.

TABLE 7. Group values for estimating the thermochemical properties of diazoalkanes and organic azides

Group	Source molecule	$\Delta_f H^\theta$		S^θ		C_p^θ	
		kJ/mol	kcal/mol	kJ/mol	kcal/mol	kJ/mol	kcal/mol
$C_d—C,H,N_2$	CH_3CHN_2	214·4	51·3	158·0	37·8	47·6	11·4
$C_d—C_d,H,N_2$	$CH_2{=}CHCHN_2$	222·4	53·2	166·8	39·9	53·5	12·8
$C_d—C_B,H,N_2$	$PhCHN_2$	191·4	45·8	199·8	47·8	62·3	14·9
$C—C,H_2N_3$	EtN_3	267·5	64·0	195·2	46·7	64·4	15·4
$C_d—H,N_3$	$CH_2{=}CHN_3$	340·2	81·4	180·2	43·1	54·3	13·0
$C_B—N_3$	PhN_3	316·8	75·8	116·2	27·8	34·7	8·3

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CHAPTER 5

Detection and determination of diazo and diazonium groups

DAVID A. BEN-EFRAIM

The Weizmann Institute of Science, Rehovot, Israel

This chapter covers diazoalkanes, diazoketones, diazoesters, diazonium salts and diazoamino compounds (triazenes, tetrazenes), as well as related compounds of the general formula RN=NX, such as diazotates, diazocyanides, diazosulphonates, etc.; azo compounds, however, are excluded. The arenediazonium salts and the aromatic diazoamino compounds play a major role in the manufacture of azo dyes. Diazoalkanes and diazoketones are also important reagents and intermediates, respectively, in organic synthesis. Many of these compounds are rather unstable, and are conveniently handled in solution. Consequently spectroscopic methods as well as effective chemical methods of analysis are of great significance in the elucidation of their structures and in their detection and determination.

I. DETECTION BY CHEMICAL METHODS

Nitrogen in diazo compounds cannot be detected by the usual method of melting the sample with potassium to yield potassium cyanide which is subsequently converted to Prussian blue, because under the reaction conditions, even at low temperatures, the diazo compounds decompose with nitrogen evolution[1].

A. *Diazoalkanes, α-Diazoketones and α-Diazoesters*

Diazoalkanes can be detected by the vigorous liberation of nitrogen when treated in the cold with dilute hydrochloric or sulphuric acid. Nitrogen evolution also takes place on heating with water. α-Diazoketones similarly liberate nitrogen when heated with acetic acid[2]. The stability of aliphatic diazo compounds towards trichloroacetic acid is of interest in this connection and has been found to be in the following order: diazoalkanes < diazoketones < diacyldiazomethanes < diethyl diazomalonate[3]. Aliphatic diazo compounds can also be identified by the products they yield with various reagents (equation 1)[2].

$$\left.\begin{aligned} \mathrm{RCHN_2 + HCl} &\longrightarrow \mathrm{RCH_2Cl + N_2} \\ \mathrm{RCHN_2 + ArOH} &\longrightarrow \mathrm{RCH_2OAr + N_2} \\ \mathrm{R^1CHN_2 + R^2CO_2H} &\longrightarrow \mathrm{R^1CH_2OCOR^2 + N_2} \\ \mathrm{R^1COCHN_2 + R^2CO_2H} &\longrightarrow \mathrm{R^1COCH_2OCOR^2 + N_2} \end{aligned}\right\} \qquad (1)$$

Diazoalkanes (1–50 mg), as well as diazoketones and diazoesters, are detected by reaction with aqueous 4-(4-nitrobenzyl)pyridinium perchlorate, followed by dilution with alkali, which precipitates blue-black crystals of *N*-alkyl-4-(4-nitrobenzylidene)-1,4-dihydropyridines, which in various solvents have characteristic absorption maxima in the visible region[4].

B. Arenediazonium Salts

Arenediazonium salts generally liberate nitrogen on heating with water or with a dilute mineral acid[2]. Some of them, such as those derived from aminoanthraquinones, are very stable under these conditions[2]. With $AuCl_3$ or $PtCl_4$ they furnish complex salts, such as $[ArN_2]^+AuCl_4^-$ and $[ArN_2]_2^{2+}PtCl_6^{2-}$ whereas with $ZnCl_2$, $CaCl_2$ or $SnCl_4$ they yield slightly soluble double salts[2]. When arenediazonium bromides are treated with bromine in a potassium bromide solution, they precipitate crystalline perbromides $[ArN_2]^+Br_3^-$ which serve in their detection and characterization[5]. Their most sensitive method of detection, however, involves coupling with a phenol in a Na_2CO_3 solution, or with an aromatic amine in dilute acetic acid[2] to yield azo dyes[2].

When a weakly acidic solution of an arenediazonium salt is added to an alkaline solution of resorufin (9-hydroxy-3-isophenoxazone), the fluorescence of the latter is quenched as soon as the mixture becomes acidic. Addition of a Na_2CO_3 solution to the above mixture precipitates brown dyestuffs if diazonium ions are present, otherwise the red fluorescence is restored[6].

C. Triazenes

Aromatic triazenes behave chemically in similar fashion to arenediazonium salts, but they are more stable and liberate nitrogen only when treated with strong mineral acids (equation 2)[7].

$$Ar^1NHN{=}NAr^2 \xrightarrow{HX} Ar^1NH_2 + Ar^2N_2^+X^- \longrightarrow Ar^2X + N_2 \qquad (2)$$

In contrast to arenediazonium salts which couple with *m*-phenylenediamine in ethanolic solution to yield azo dyes, aromatic triazenes do so only on addition of acetic acid[7].

Various 3-hydroxytriazenes have been detected by a spot test which involves treatment with 1-naphthylamine in acetic acid, giving at once a pink or red-brown colour, which intensifies on gentle heating[8].

II. DETERMINATION BY CHEMICAL METHODS

A. Elemental Analysis

The Kjeldahl method for the elemental determination of nitrogen cannot be applied to diazo compounds, in particular not to α-diazoketones, since addition of hydriodic acid results in nitrogen evolution even in the cold[9]. Zinneke has however modified the Kjeldahl method in such a manner that the total nitrogen evolved could be trapped and measured in a specially built nitrometer[10].

B. Diazoalkanes and Related Compounds

1. Reaction with acids

Diazoalkanes easily alkylate carboxylic acids and phenols to the corresponding methyl esters and methyl ethers, respectively (equation 1). Thus as early as 1910 diazomethane and diazoethane were determined by adding the diazoalkane in anhydrous ether at 0 °C to an excess of a solution of *p*-nitrobenzoic acid in ether, and after a short time titrating the excess acid with a standard 0·1 N-Ba(OH)$_2$ solution to a phenolphthalein end-point[11]. Later diazoalkanes (CH$_2$N$_2$, MeCHN$_2$, EtCHN$_2$) were similarly estimated in anhydrous ether at 0 °C, using benzoic acid, and back-titrating the excess acid with a 0·1 N-NaOH or KOH solution and phenolphthalein[12]. The method was modified to the micro scale, using excess benzoic acid, 0·01 N-NaOH solution as titrant and phenolphthalein[13]. Recently diazomethane was determined by reaction with benzoic acid and the resulting methyl benzoate was measured by vapour phase chromatography[14]. The deuterium content of CD$_2$N$_2$ was obtained by its reaction with PhCO$_2$D in anhydrous ether, followed by determination of the deuterium content in the formed methyl benzoate, either by n.m.r. or by mass spectrometry[15].

2. Gravimetric determination

Diazoalkanes (CH$_2$N$_2$, MeCHN$_2$, EtCHN$_2$) were also determined by adding an aliquot of an ether solution of the diazoalkane to a cold solution of 3,5-dinitrobenzoic acid. Excess acid was removed by base and after conventional work-up and evaporation to dryness, the diazoalkane was estimated by the weight of the resulting methyl ester, and the latter's purity was assessed by a melting-point determination[12b].

3. Colorimetric determination

Colchiceine affords, with ferric chloride, a deep green colour, not given by its methylated derivative colchicine. This reaction serves in the determination of diazomethane. The solution of diazomethane is added to a known amount of colchiceine, and the excess of unreacted colchiceine is estimated after addition of FeCl$_3$ by colorimetric comparison with colchiceine–FeCl$_3$ solutions of known concentration. The method gives results in good agreement with those obtained by the titration method with benzoic acid[16].

The detection of diazoalkanes by the colour reaction with 4-(4-nitrobenzyl)-pyridinium perchlorate has already been mentioned[4]. In its quantitative version diazoalkanes RCHN$_2$ (R = Me, Et, *n*-Pr, *n*-Bu, allyl) give with this reagent on addition of piperidine a red-violet colour. Measurement of its absorbance at 545 nm and comparison with a calibration curve yields the concentration of the diazoalkane[4].

4. Gasometric determination

Aliphatic diazo compounds on treatment with dilute sulphuric acid liberate nitrogen which is measured in a nitrometer (equation 1)[17]. The method uses up to 1-g samples, but has been adapted to the micro scale, making use of the hydrazino apparatus of Ma and Mattei[18].

C. *Diazonium Salts, Diazophenols and Diazotates*

The most commonly used methods in the determination of diazonium salts include reductometric titrations, coupling titrations and gasometric and colorimetric methods.

1. Reductometric titrations

Most of these reductions must be carried out in the absence of oxygen.

a. *Titanous chloride*. Knecht and Thompson titrated benzenediazonium chloride with a TiCl$_3$ solution in cold dilute hydrochloric acid, using H acid (8-amino-1-naphthol-3,6-disulphonic acid) as an external indicator (equation 3)[19]. The titration can also be carried out by adding an excess of a $TiCl_3$ solution, and back-titrating the excess with a standard acid green solution in the presence of sodium tartrate[19].

$$2\,PhN_2^+Cl^- + 4\,TiCl_3 + 2\,HCl \longrightarrow PhN{=}NNPhNH_2 + 4\,TiCl_4 \qquad (3)$$

The method was modified to the micro scale by adding an excess of the $TiCl_3$ solution to an acetate-buffered solution of the sample at room temperature, and back-titrating the excess $TiCl_3$ with a ferric alum solution, using ammonium thiocyanate as an indicator[20]. It should be pointed out that this method is also applicable to azo groups and to nitroarylhydrazines. Siggia has also described this procedure in detail as a method for the analysis of azo and nitro groups as well as hydrazines and diazonium salts[21].

b. *Chromous chloride.* With this reducing agent diazonium salts are quantitatively reduced to the corresponding hydrazines (equation 4). Excess $CrCl_2$ solution is

$$ArN_2^+Cl^- + 4\,CrCl_2 + 4\,HCl \longrightarrow ArNHNH_2.HCl + 4\,CrCl_3 \qquad (4)$$

added to a weakly acidic or neutral solution of the diazonium salt, and back-titration of the excess $CrCl_2$ is accomplished potentiometrically with a standard ferric alum solution[22]. This reduction method has certain advantages over the popular coupling (Section II.C.2) and gasometric (Section II.C.3) methods because it is fast as well as quantitative. It is, however, also applicable to nitrobenzenes and hydrazines.

c. *Vanadium*(II) *sulphate.* Diazophenols and diazonaphthols containing Cl, CO_2H or SO_3H groups were determined titrimetrically in an inert atmosphere by reduction of their acid solutions with excess VSO_4, and back titration of the excess reducing agent with a ferric alum solution, using safranine as indicator. The reaction requires two equivalents of reducing agent per mole of diazo compound, and is accompanied by a quantitative liberation of nitrogen[23].

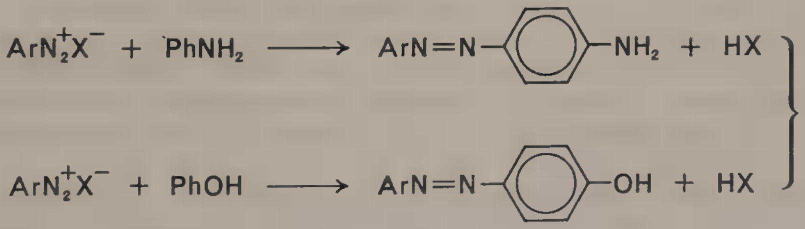
d. *Sodium hyposulphite.* This reagent also served in the quantitative reduction of diazonium salts to arylhydrazines in HCl solution at 0 °C. Excess reagent was used and its excess was back-titrated with a standard acid green solution[19].

e. *Hydriodic acid.* A sample of 20–30 mg diazonium salt is reduced with 57% HI in a sealed tube between 100 and 300 °C (equation 5) and the liberated iodine is back-titrated with a sodium thiosulphate solution and a starch indicator[24].

$$ArN_2^+Cl^- + 2\,HI \longrightarrow N_2 + ArH + HCl + I_2 \qquad (5)$$

2. Coupling reactions

This method is based upon the coupling of arenediazonium salts with aromatic amines or phenols to yield azo dyes (equation 6). The method is very selective



(6)

because only few other compounds couple with these reagents. The determination is carried out below 0 °C by adding the sample to an excess of coupling agent, usually 1-phenyl-3-methylpyrazolin-5-one or 2,4-diaminotoluene in acidic solution, or R-salt (sodium 2-naphthol-3,6-disulphonate) in a Na_2CO_3 solution, and back-titrating the excess reagent with a standard 0·1 N-benzenediazonium chloride solution or a 0·1 N-*m*-nitrobenzenediazonium chloride solution, using an external indicator (H acid or resorcinol in basic solution). The accuracy and precision of the method are lower than those of the gasometric method (Section II.C.3) because of the slow rate of coupling and the difficulty in observing the end-point[25].

Traces of diazonium salts were determined by coupling the salts with R-salt in aqueous solution or with phloroglucinol or naphthol in ethanolic solution. Tenths of a p.p.m. of the formed azo dye were then determined spectrophotometrically[26]. Additional colorimetric determinations based on the coupling method were also reported[27].

The isomeric nitrobenzenediazonium salts in mixtures of azo coupling products were determined by coupling them with 2-naphthol. The products were chromatographed on alumina to separate the *ortho* isomer from the mixture of the *meta* and *para* isomers; the *ortho* isomer was determined spectrophotometrically and the *meta* and *para* isomers were determined by differential spectrophotometry at two different wavelengths. Each isomer was determined with an accuracy of 2–5%[28].

3. Gasometric methods

Gasometric methods are the most general and most specific for measuring diazonium salts and are widely used in industry. An accuracy and precision of about 1% are obtainable, but the procedure is tedious and time consuming. A single analysis may take up to 1 hour.

Solutions of aliphatic and aromatic diazonium salts readily decompose on heating with mineral acids to furnish phenols and nitrogen. When heated with acid and cuprous chloride, chlorobenzenes and nitrogen are obtained. The nitrogen is quantitatively liberated in these reactions and is determined volumetrically in a nitrometer. The method is very selective since few compounds liberate a gas under the above reaction conditions. Siggia has described in detail a general procedure and nitrometer for the determination of diazonium salts by decomposition in the presence of cuprous chloride in concentrated hydrochloric acid[29].

A simple apparatus, based on nitrogen evolution, has been described for the determination of aliphatic and aromatic diazonium salts, stabilized salts, diazotates and triazenes. Nitrogen evolution is effected by boiling the sample with 30% H_2SO_4 and 0·75% Cu_2Cl_2 [30]. Recently another apparatus was devised for the rapid volumetric determination of the nitrogen evolved by HCl–Cu_2Cl_2 from diazonium salts and diazoamino compounds. The reproducibility of the method is ±0·3% and the maximum error is ±1·0% [31].

Siggia and coworkers used a graphical kinetic approach to analyse mixtures of diazonium compounds, which is based on the first-order rates of decomposition in the presence of cuprous chloride. The nitrogen evolved is measured in successive time intervals. In the case of a mixture of two diazonium salts a plot of $\log(100-x)$ versus t (where 100 is the total diazo nitrogen and x is the % diazo nitrogen evolved in time t) is a straight line as soon as most of the faster-reacting component has been decomposed. By extrapolating to $t = 0$, the composition of the mixture can be obtained[32].

Diazo compounds were determined gasometrically on a semimicro scale by decomposing samples by light irradiation in a special apparatus containing a nitrometer. The method had a standard deviation of ±0·07% and the whole procedure required 30–35 min. It has been applied to diazonaphthols which cannot be easily determined by the coupling method[33].

4. Miscellaneous methods

Terent'ev and Tubina described three methods for the determination of arenediazonium salts. The first method involves a direct titration of a solution of a secondary aliphatic amine (hexamethylenimine, piperidine, diethylamine) containing sodium carbonate with the solution of the diazonium salt at 15–20 °C until the colour formed with a 1% solution of sodium 4-amino-5-hydroxynaphthalene-2,7-disulphonate persists for about 30 sec. The second method is based upon the reaction between the diazonium salt and an excess of a secondary aliphatic amine, making the reaction mixture basic, and distilling the excess amine into aqueous 4% boric acid and titrating it with 0·1 N-HCl. The third method involves reaction between the diazonium salt and excess *m*-toluidine, making the solution basic, and steam-distilling the excess amine, which is then brominated and the excess bromine is titrated with sodium thiosulphate and starch as indicator[34].

Arenediazonium salts dissolved in non-aqueous solvents (pyridine, dimethylformamide) were determined by potentiometric titration with 0·1 N-sodium methoxide in benzene–methanol, using a saturated calomel electrode and a glass electrode. A probable reaction (equation 7) has been suggested. The error was less than ± 1·8%[35].

$$\mathrm{ArN_2^+Br^- + MeONa \longrightarrow ArN_2OMe + NaBr} \qquad (7)$$

D. *Triazenes and Tetrazenes*

1. Gasometric methods

Aliphatic triazenes are readily decomposed by mineral acids, liberating nitrogen (equation 8), whereas aromatic triazenes require, in addition, heating in order to liberate nitrogen (equation 2). Aliphatic and aromatic triazenes were determined gasometrically by conventional procedures after boiling samples with concentrated HCl[36] (see also Section II.C.3). Pierce and Rising described a micro-scale modification of the above procedures and an apparatus for the determination of aromatic triazenes[37]. Lohr has observed that the method of Pierce and Rising gave excellent results with pure aryl-substituted triazenes but was not readily adapted to samples which were solutions, slurries or pastes[38]. He made the method applicable to samples in any physical state, using cuprous chloride in concentrated HCl to catalyse the quantitative liberation of nitrogen. Two other similar procedures which are applicable to triazenes as well as to diazonium salts have already been mentioned[30, 31] (Section II.C.3). The determination of 1-aryl-3,3-dimethyltriazenes by the above procedures (Cu_2Cl_2–HCl) has also been reported[39].

$$\mathrm{R^1N{=}NNHR^2 + HCl \longrightarrow R^1Cl + N_2 + R^2NH_2} \qquad (8)$$

2. Miscellaneous methods

If the aromatic amine produced on hydrolysis of an aromatic triazene (equation 2) can be brominated, this can serve as a method for the determination of aromatic triazenes. The triazene is dissolved in glacial acetic acid, HCl and KBr solutions are added, and the mixture is titrated with a 0·5 N-KBr–$KBrO_3$ solution, using KI–starch paper as indicator[40].

Small amounts of 1-aryl-3,3-dialkyltriazenes were determined by hydrolysis to furnish arenediazonium cations (equation 2) which were coupled with *N*-ethylnaphthylamine. The absorbance of the obtained dye was measured spectrophotometrically at the absorption maximum. The accuracy of the method was within ±5% and it has been shown that the rate of hydrolysis of the triazenes depends on the pH and on the electronic character of the substituents on the benzene ring[41]. Similarly, triazenes stabilized with aliphatic amines were hydrolysed with aqueous acetic acid, and those stabilized with aromatic amines were hydrolysed with dilute HCl, and the resulting diazonium ions were coupled with excess 1-phenyl-3-methylpyrazolin-5-one, and the excess of the latter was back-titrated with 0·5 N-$NaNO_2$. The error was less than ±2% and a determination took up to 1 hour[42].

1-Aryl-3,3-dialkyltriazenes were also determined by their hydrolysis with 0·1 N-H_2SO_4 to furnish a dialkylamine which reacted with the acid, and the excess acid was titrated potentiometrically with 0·1 N-NaOH. This procedure was modified in the case the compound contained functional groups, such as carboxyl groups, which interfered with the determination. In that case the reaction mixture was made basic and the dialkylamine formed was steam-distilled into an excess of standard acid and was then determined[43].

4-Amino-1-(5-tetrazolyl)-1-tetrazene hydrate was determined by hydrolysis with sulphuric acid to give amidinohydrazine which was estimated by oxidative titration with 0·1 N-$KBrO_3$, using iodine as indicator[44]. Tetramethyl-2-tetrazene was determined by titration with boron trifluoride etherate, perchloric acid in acetic acid, aluminium chloride in chloroform, or sulphuric acid in acetic acid, using crystal violet as indicator. The titration gave sharp, yet fading, colour changes at a molecular ratio of 1 : 1 [45].

E. Other Diazo Compounds

p-Methoxyphenyl diazothio(2-naphthyl) ether was determined as follows: hydrolysis in alkaline solution yielded *p*-methoxybenzenediazonium ions and 2-naphthalenethiol. The diazonium ion was coupled with 2-naphthol and the dye formed was determined spectrophotometrically. The thionaphthol was determined amperometrically by reacting it with excess silver nitrate and back-titrating the excess of the latter with a standard ethanolic *n*-dodecyl mercaptan solution[46].

III. POLAROGRAPHY

The anodic half-wave potentials of several aryl-substituted diazoalkanes, such as $4\text{-}RC_6H_4CN_2Ph$, $4\text{-}O_2NC_6H_4CN_2R$ and $4\text{-}R^1C_6H_4CN_2C_6H_4R^2\text{-}4$, α-diazoketones, $4\text{-}RC_6H_4CN_2COPh$, and α-diazoesters, $4\text{-}RC_6H_4CN_2CO_2Et$, have been recorded at rotating platinum electrodes and their shifts with change in R have been correlated with substituent constants[47]. Polarographically reduced α-diazoacetophenones gave three waves which have been attributed to three reactions[48].

Arenediazonium salts are reduced at a dropping-mercury electrode. Two half-waves have been observed and tabulated, but they have only qualitative significance since the shapes of the waves are irregular. It has been suggested that the product of reduction is an arylhydrazine (equation 9). In spite of the fact that the waves are too complex, their heights vary directly with the concentration. The first wave has a half-wave potential of less than −0·3 V. It is therefore possible to determine arenediazonium salts at −0·3 V versus SCE, using a dropping-mercury electrode. The diffusion current measured is then compared with a calibration curve of diffusion current against diazonium salt concentration[49].

$$ArN_2^+ + 4e^- + 3H^+ \longrightarrow ArNHNH_2 \qquad (9)$$

Another observation is that the first half-wave of the arenediazonium group occurs at a potential well below that of the azo group. This finding has been utilized in the determination of diazonium salts by a coupling titration in an amperometric titration cell equipped with a dropping-mercury electrode and operating at −0·3 V versus SCE. A known aliquot of 1-phenyl-3-methylpyrazolin-5-one in the cell is titrated with the diazonium salt solution. As long as coupling occurs no reduction of the diazonium salt takes place and no current flows. As soon as the pyrazolinone has been consumed, the end of the titration is indicated by a current flow which is directly proportional to the concentration of excess added diazonium salt. This new technique is more generally applicable than either the gasometric or colorimetric methods of determination of diazonium salts[50, 49].

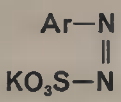
Diazonium salts derived from aniline and from the three isomeric aminobenzoic acids exhibit two polarographic waves in the range of 0 V to −1·5 V versus SCE. At a single pH the diffusion currents are proportional to the concentrations of the diazonium salts.[51] Two distinct waves were obtained in a series of arenediazonium salts and the half-wave potentials of the first wave were tabulated at different pH values together with the diffusion current per unit of concentration[52].

A German patent describes an apparatus containing a polarographic analyser for the continuous determination of diazonium salts in reaction mixtures, and for the automatic regulation of diazo coupling[53].

Aromatic triazenes are reduced at the dropping-mercury electrode at much higher voltages than arenediazonium salts. As a result, it is possible to measure the rate of formation and hydrolysis of triazenes by following the rate of increase or decrease in diazonium ion concentration, using the technique described above[49]. 1-Aryl-3,3-dialkyltriazenes have been determined by reduction at a dropping-mercury electrode, giving well-defined waves at pH 5–7 ($E_{\frac{1}{2}} = -1{\cdot}0$ versus SCE). Results of the polarographic analysis were reliable and compared well with those of other methods[43]. A positive shift of 0·18 V has been observed in the half-wave potentials of triazenes on their polarographic reduction in the presence of tetraalkylammonium ions, in contrast to negative shifts observed in the reduction of other compounds[54].

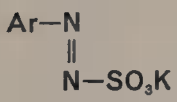
The polarographic method has been used to estimate 1,3-diphenyltriazene in the atmosphere, which accumulates there during production of cellular rubber. Particles collected from the air were extracted with ether and the residue obtained on evaporation of the solvent was nitrated. The triazene in the product was determined polarographically by recording the wave starting from 0·8 V versus SCE and comparing it with a calibration curve of diffusion current against triazene concentration[55].

Measurement of polarographic half-wave potentials of isomeric diazosulphonates indicates that the isomers form an interconvertible *syn–anti* pair **1** and **2**, rather than



$$\begin{array}{r}\mathrm{Ar{-}N}\\ \|\\ \mathrm{KO_3S{-}N}\end{array}$$

(1)



$$\begin{array}{l}\mathrm{Ar{-}N}\\ \ \ \ \ \ \ \|\\ \ \ \ \ \ \ \mathrm{N{-}SO_3K}\end{array}$$

(2)

$ArN{=}N{-}OSO_2K$

(3)

a diazosulphonate (**2**)–diazosulphite (**3**) pair. The more stable *anti* isomers **2** are reduced at a more negative potential than the labile *cis* forms **1**[56].

The polarographic reduction of azodicarbonitrile (**4**) to the azodicarbonitrilide radical anion (**5**) is a reversible one-electron process at $E_{\frac{1}{2}} + 0{\cdot}40$ V versus SCE[57].

$NCN{=}NCN$

(4)

$NCN{=}NCN^{\bullet -}$

(5)

IV. SEPARATION AND CHROMATOGRAPHIC METHODS

A. *Diazoalkanes, α-Diazoketones and α-Diazoesters*

The aliphatic diazo group, in view of its instability, is not expected to occur in nature. Nevertheless several antibiotics containing this group have been isolated. Thus azaserine (*O*-diazoacetyl-L-serine)[58] and 6-diazo-5-oxo-L-norleucine[59] were isolated and purified by chromatography on pretreated alumina, followed by chromatography on carbon columns and recrystallization from aqueous ethanol or methanol. Azaserine was also analysed by Craig countercurrent distribution between water and phenol, and the norleucine derivative was analysed by paper chromatography and paper ionophoresis. Alazopeptin [L-alanyl-(6-diazo-5-oxo)-L-norleucyl-(6-diazo-5-oxo)-L-norleucine] has been isolated from fermentation broths of *Streptomyces griseoplanus* by crystallization[60].

Bicyclic α-diazoketones were purified by chromatography on basic alumina and recrystallization[61]. Several unsaturated α-diazoesters were separated from their reaction mixtures by chromatography on Florisil and recrystallization, whereas other similar esters decomposed on chromatography on the same adsorbent[62]. Diethylphosphonodiazomethane was purified by distillation (69–70 °C at 0·35 mm)[63].

B. *Arenediazonium Salts and Diazotates*

Arenediazonium salts are relatively rarely isolated and are generally handled in solution because of their instability and tendency to explode in the solid. They can, however, be isolated free of inorganic salts when diazotization is carried out with organic diazotizing agents, such as amyl nitrite in ethanol, and are then precipitated by ether. They should be dried and handled carefully in small quantities only. Nowadays the solid diazonium salts used in industry have been superseded by the so-called stabilized diazonium salts, as well as by the diazotates, and, above all, by the diazoamino compounds. They can also be stabilized as complex salts with inorganic salts[64].

Stabilized arenediazonium salts were separated by paper chromatography using as solvent a mixture of 95% EtOH–concentrated HCl–distilled H_2O (30 : 0·5 : 43·5), and the spots were developed with Naphthol AS. R_f values and colours of spots were reported[65].

Arenediazonium chlorozincates and fluoroborates were separated by thin layer chromatography on silica gel G plates. The best solvent mixtures were Me_2SO–$MeCO_2H$–H_2O (6 : 1 : 1) and Me_2SO–88% HCO_2H–$CHCl_3$–dioxane (25 : 1 : 5 : 20). Spots were developed with a blue-dye-forming coupler (2,3-dihydroxynaphthalene), followed by treatment with ammonia. The diazonium salts were also recovered preparatively from thick plates[66].

Arenediazonium salts were analysed by pyrolysis gas chromatography on Chromosorb 103 at temperatures between 160 and 300 °C. The pyrolysis products were identified by infrared or laser Raman spectroscopy of the trapped peaks. For routine analysis the samples were pyrolysed at 160 °C and the nitrogen from the pyrolysis was eluted on a column of Molecular Sieve 5A and determined quantitatively by comparison of nitrogen peak areas with calibration curves of injected nitrogen samples. Precision and accuracy of the method were comparable to those of analyses by other methods[67].

anti-Diazotates are obtained by adding solutions of diazonium salts to highly concentrated solutions of alkali hydroxides at room or higher temperatures. They are then isolated by either salting out or precipitation with ethanol[68].

C. Triazenes and Tetrazenes

Aromatic triazenes are light yellow solids when pure but upon precipitation from a reaction mixture are often orange to deep red in colour[69]. In earlier years mixed methyl- and dimethyldiazoaminobenzenes[70] and nitrodiazoaminobenzenes[71] have been precipitated in pure form by cadmium hydroxide in methanol. More recently chromatography on alumina has been recommended for purification[69]. Thus bisthiadiazolyltriazenes have been separated quantitatively on alumina by elution with pyridine–glacial acetic acid (92 : 8)[72].

Various aromatic triazenes were separated by paper chromatography. Thus diazoaminobenzenes substituted in the benzene rings[73] and *para*-substituted 1-aryl-3,3-dimethyltriazenes[74] were separated using a variety of solvent systems and detecting agents. R_f values were given.

Several phenyltriazenes and nitrophenyltriazenes found as contaminants in 1-phenyl-3,3-dimethyltriazene and in 1-(*p*-nitrophenyl)-3,3-dimethyltriazene were separated from these two compounds by thin layer chromatography on silica gel using xylene and benzene as solvents, and ultraviolet detection[75].

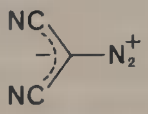
Mixtures of various tetraalkyl-2-tetrazenes were quantitatively separated and recovered as pure compounds by gas chromatography on polyethylene glycol on firebrick at 70 °C. A linear relationship was found between peak area and amount of compound injected[76].

V. INFRARED AND RAMAN SPECTROSCOPY

A. Diazoalkanes, α-Diazoketones, α-Diazoaldehydes, α-Diazoesters, Diazocyclopentadienes and Related Compounds

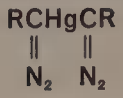
All the bands in the infrared spectra of gaseous CH_2N_2, $CHDN_2$ and CD_2N_2 have been recorded and assigned[77]. The strongest band in these spectra is the stretching vibration of the NN bond, which appears in the vapour phase at 2102 cm^{-1} in CH_2N_2, at 2097 cm^{-1} in $CHDN_2$ and at 2096 cm^{-1} in CD_2N_2 [77b]. In CCl_4 solution this band occurs in CH_2N_2 at 2075 cm^{-1} [78]. The assignments of the major bands of the above three compounds have been tabulated[79]. The infrared spectrum of $CH_2N^{15}N$ has also been recorded[77b].

The spectra of several monoalkyl-, alkylaryl- and diaryldiazomethanes in CH_2Cl_2 display their strongest band, namely the stretching vibration of the NN bond in the 2070–2010 cm^{-1} region[78]. 4-Diazooctane displays the NN stretching vibration in CCl_4 at 2050 cm^{-1} [80], whereas in diazopropyne it appears at 2075 cm^{-1} [81]. Bis(trifluoromethyl)diazomethane and bis(perfluoroethyl)diazomethane exhibit this band at 2137 and 2119 cm^{-1}, respectively[82]. Dicyanodiazomethane displays the band at 2140 cm^{-1} which indicates considerable contribution from the diazonium methylid structure **6**. The high symmetry of this molecule is reflected in the simplicity of the spectrum which contains only four bands in KBr at 2225, 2140, 1240 and 1215 cm^{-1} [83]. Three 5-nitro-2-furyl diazo compounds were shown to display the NN band in the region 2110–2070 cm^{-1} [84]. Mercury derivatives of diazomethyl compounds **7** exhibit



(6)

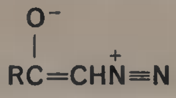
the NN band in the region of 2080–2037 cm^{-1}, whereas germanium, tin and lead substituted diazomethanes show it in the 2050–1950 cm^{-1} region[85].



$$\underset{N_2}{\overset{\|}{RCH}}g\underset{N_2}{\overset{\|}{CR}}$$

(7)

Yates and coworkers[78] and Fahr[86] tabulated the infrared spectra of a large number of α-diazoketones and compared them with those of related types of compound. The α-diazoketones show a mutual interaction between the carbonyl and diazo groups, which can be represented by resonance contributions from structures of



$$R\overset{O^-}{\overset{|}{C}}{=}CH\overset{+}{N}{\equiv}N$$

(8)

type **8**. This leads to lower carbonyl frequencies and to higher values of the NN diazo frequency, which by now possesses some triple bond character. Thus diazoketones of type $RCOCHN_2$ (R groups may be alkyl or aryl) display a strong band in the region of 2100–2080 cm^{-1}, whereas those of type $R^1COCR^2N_2$ exhibit a strong band in the range of 2075–2050 cm^{-1}. The intense carbonyl band for both types of diazoketone occurs in the range of 1645–1605 cm^{-1}, with the exception of diazocamphor and diazoacenaphthenone which have this band around 1680 cm^{-1}. The α-diazoketones also exhibit a very intense band in the 1390–1380 cm^{-1} region which in some compounds is a composite band and in others is composed of two strong bands. Fahr also discussed the mutual interaction of the diazo and carbonyl groups in the infrared spectra of bisdiazo compounds, $N_2CHCO(CH_2)_nCOCHN_2$, and in analogous compounds[87]. It has also been found that with increasing contribution from diazonium structures **8** the integrated intensity of the NN stretching band decreases[88]. α-Diazoketones also display a strong band between 2·356 μm and 2·444 μm which is attributed to the first overtone of the asymmetric diazo stretching vibration[89].

The diazo stretching vibration of α-diazoaldehydes, RCN_2CHO (where R is alkyl), falls in the region of 2100–2080 cm^{-1}, and the carbonyl band appears around 1690–1650 cm^{-1}. Both bands are split, which may be due to the presence of *cis–trans* conformers, resulting from the partial double bond character of the bond between the carbon attached to the diazo group and the carbonyl carbon[90].

The NN stretching frequencies of many other α-diazoketones have been tabulated[90a, 85, 91], as well as those of 2-diazo-1,3-diketones[91], α-diazo-β-oxophosphonyl compounds[91] and mercury derivatives of diazomethyl compounds (**7**, when R is acyl or aroyl)[85]. The NN stretching vibration of α,β-unsaturated α-diazoketones occurs in the region of 2101–2066 cm^{-1} [92]. The diazo and carbonyl bands of 2-oxo-1-diazocycloalkanes were tabulated[93]. 16-Diazoandrostan-3β-ol-17-one exhibits bands at 2075, 1650 and 1324 cm^{-1} [94], whereas the bands of diazoisofenchone occur at 2092, 1698 and 1335 cm^{-1} [95]. The absorption frequencies of several cyclic 2-diazo-1,3-dicarbonyl compounds were also recorded and these display two bands around 2180 and 2140 cm^{-1} [96].

The interaction between diazoketones and hydroxylic solvents was investigated by infrared spectroscopy[97]. Infrared studies showed that diazoketones, $RCOCHN_2$, donate and accept protons in hydrogen bonding[98]. The conformations of hindered α-diazoketones were derived from infrared spectra and dipole moments[99].

α-Diazoesters exhibit the NN stretching frequency practically in the same region as α-diazoketones and α-diazoaldehydes[78, 90a, 100, 101, 62, 102, 85].

The NN stretching frequency of diazomethylene sulphones occurs in the range of 2145–2109 cm^{-1}[91] and that of phosphonyl- and phosphono-diazomethanes falls in the range of 2132–2075 cm^{-1}[85].

The strongest band in the infrared spectra of diazocyclopentadiene in CCl_4 lies at 2082 cm^{-1}[103, 104]. The NN stretching frequency of many substituted diazocyclopentadienes has been reported[104, 105]. A complete vibrational analysis has been made for diazocyclopentadiene and its perdeuterated analogue[106]. The diazo band of α-diazoanthrone lies at 2070 cm^{-1} and that of the carbonyl group at 1647 cm^{-1}[107].

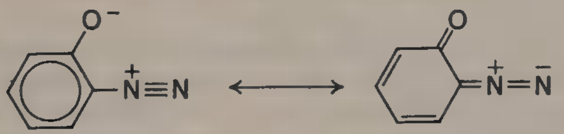
B. Diazonium Salts, Diazophenols, Diazotates, Diazosulphonates and Diazoethers

Arenediazonium salts in Nujol mulls exhibit the NN stretching frequency around 2260 ± 20 cm^{-1}[108], occasionally in the range of 2295–2110 cm^{-1}[109]. It is observed that changes in the anion produce only negligible shifts in this band, whereas changes of substitution in the benzene ring result in a marked effect on the frequency of the band[109]. The infrared spectra of benzenediazonium tetrafluoroborate, tetrachloroborate and tetrabromoborate have been recorded[110]. A systematic relationship between the NN stretching frequency of methoxy-substituted benzenediazonium cations and σ^+ constants has been observed, which is useful in the identification and classification of these compounds[111]. The NN stretching frequencies of several substituted arenediazonium salts[112] and of several *o*-dialkylaminobenzenediazonium salts[113] have been recorded. The infrared spectra of 20 *para*-substituted benzenediazonium cations measured as solid $[HgCl_4]^{2-}$ salts indicated that electron-donating *para*-substituents caused increase in the Ar–N stretching frequency at 1400–1300 cm^{-1} and decrease in the NN stretching frequency, whereas electron-attracting substituents were less effective in causing such shifts. A linear correlation was also found between these frequencies and Hammett σ_p values[114].

The $^{15}N{\equiv}^{15}N$ stretching band of the $^{15}N_2$-benzenediazonium ion in a KBr pellet was observed at 2227·5 cm^{-1}, i.e. shifted 74·5 cm^{-1} from the respective $^{14}N{\equiv}^{14}N$ frequency. Its $C_6H_5{-}^{15}N$ stretching fundamental was at 1478 cm^{-1} and the band due to the in-plane bending of the $C{-}^{15}N{\equiv}^{15}N$ moiety was found at 511 cm^{-1}. The corresponding bands in the unlabelled compound were at 1500 and 518 cm^{-1}, respectively[115].

The NN stretching frequencies of fourteen substituted ethylenediazonium salts were observed[116] to occur in the range of 2260–2110 cm^{-1}.

Diazobenzenes with hydroxyl groups in *ortho* or *para* position, the so-called diazophenols and diazonaphthols, exhibit their NN stretching frequency in the range of 2175–2015 cm^{-1}, whereas their carbonyl frequency occurs in the range of 1640–1560 cm^{-1}, the latter being close to the carbonyl frequency of simple tropolones. This indicates that they exist as a resonance hybrid **9**[117]. With increasing contribution from the diazonium structure **9a** the diazo frequency is shifted to higher values[118].



(9a) **(9b)**

The infrared spectrum of potassium *syn*-methanediazotate has been recorded in a Nujol mull: it has strong bands at 1393, 1335, 1140 and 1115 cm^{-1}, and additional bands at 1600, 1587, 1013, 938 and 777 cm^{-1} [119]. Potassium *syn*-1-phenylethanediazotate has in a Nujol mull bands at 1600, 1490, 1375, 1160, 1150, 1087, 758 and 697 cm^{-1}, whereas the *anti*-diazotate has bands at 1600, 1490, 1410, 1300, 1166, 1079, 1015, 760, 695 and 611 cm^{-1} [120].

In earlier years Le Fèvre and coworkers recorded and tabulated the infrared spectra of potassium *syn*- and *anti*-benzenediazotate, sodium *p*-nitrobenzenediazotate, and potassium *p*-methoxybenzenediazotate in the 1800–600 cm^{-1} region. These authors were however unable to make definite spectral assignments for the NN stretching vibration[121]. The infrared spectra of two crystalline modifications of potassium *syn*-benzenediazotate and of two crystalline modifications of potassium *syn*-*p*-toluenediazotate were recorded and tabulated[122]. A very thorough infrared study of *syn*- and *anti*-arenediazotates has been made by utilizing ^{15}N-labelled compounds. It has been found in this study that the intense NN stretching vibration occurs around 1350 cm^{-1} in the *syn* compounds and around 1375 cm^{-1} in the *anti* compounds. The band is shifted by substituents on the benzene ring but the metallic cations have no effect on its location. The NO stretching vibration in these diazotates displays two close and strong bands in the region of 1200–1120 cm^{-1}. It has been concluded that in both the *syn*- and *anti*-diazotates the bond order of the NN bond exceeds markedly that of the NO bond, and that the *anti*-diazotates have a planar *trans* structure with respect to the NN bond, while the *syn*-diazotates possess a non-planar distorted *cis* structure[123].

The infrared spectra of several arenediazosulphonates were recorded and tabulated but no definite NN band assignments could be made[121]. The infrared spectrum of *p*-nitrobenzenediazo methyl ether, $p\text{-}O_2NC_6H_4N{=}NOMe$, was recorded and tabulated[123]: the NN stretching vibration occurs as a shoulder at 1508 cm^{-1} and the NO stretching vibration as an intense band at 995 cm^{-1}.

C. Diazocyanides and Diazoisocyanides

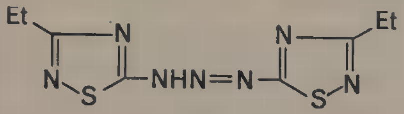
The infrared spectra of several *cis*- and *trans*-arenediazocyanides were reported[124, 121] and the band occurring around 2170 cm^{-1} was assigned to the C≡N stretching vibration[124]. It has however been claimed that the assignments in Reference 124 were erroneous and that the stable and labile forms of arenediazocyanides were actually nitrile–isonitrile isomers[125]. Recently the original conclusions that the labile and stable pairs of arenediazocyanides were geometrical stereoisomers have been reaffirmed[126]. Thus it has been shown that the unstable *cis* isomers exhibit the cyano stretching vibration at 2175–2150 cm^{-1}, which shifts to 2195–2190 cm^{-1} as they isomerize to the more stable *trans* isomers. The diazo stretching vibration occurs in the *cis* isomers at 1480–1420 cm^{-1} and in the *trans* isomers at 1460–1390 cm^{-1} [126]. The above-mentioned band at 2195–2190 cm^{-1} in the *trans* isomers of *p*-chlorobenzenediazocyanide and in *p*-bromobenzenediazocyanide, which is absent in the *cis* isomers, has been used to determine them in solution during their formation in the isomerization of the *cis* isomers[127].

Azodicarbonitrile (**4**) and its stable radical anion **5** exhibit infrared bands at 2217 and 2165 cm^{-1}, respectively[57].

The spectra of *p*-chlorobenzenediazoisocyanide and *p*-bromobenzenediazoisocyanide have been reported. Their most intense band is split, and its two parts occur in the ranges of 2135–2130 cm^{-1} and 2100–2095 cm^{-1}. This band has been assigned to the NC isocyanide stretching vibration while a band occurring at 1440 cm^{-1} has been assigned to the NN diazo stretching vibration. Several other bands have been tentatively assigned and resonance contributions to the structure of the diazoisocyanides have been discussed[128].

D. Triazenes and Tetrazenes

Diazoaminobenzene displays its bands at 3·1, 3·3, 6·2, 6·6, 6·8, 6·9, 7·0, 8·0, 8·3, 8·5, 9·3, 11·2, 13·0, 13·3 and 14·5 μm [129]. The infrared spectra of several triazenes have been reproduced and tabulated in the 1800–600 cm^{-1} region, and tentative band assignments have been made, the NN diazo band presumably occurring around 1400 cm^{-1} and/or 1600 cm^{-1} [121]. The spectrum of the diazoaminothiadiazole **10** has



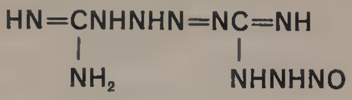
(10)

been recorded. This compound and its analogues show a strong broad band in the 2700 cm^{-1} region, indicating strong hydrogen bonding[72].

Tautomeric equilibria of triazenes substituted in the benzene rings have been calculated by comparing integrated intensities of ^{14}NH and ^{15}NH bands in the 3300 cm^{-1} region in specifically labelled compounds[130].

Infrared group frequencies of triazenes, ArN=NNHAr, have been assigned by laser Raman spectroscopy. Thus the band in the range of 3500–3300(w) cm^{-1} was assigned to the NH stretch; the band at 1522(m) cm^{-1} to the NH bend; and the band at 1178(m) cm^{-1} to the CN stretch[131].

In a study of infrared spectra of compounds of high nitrogen content, the spectrum of 1-guanyl-4-nitrosoaminoguanylisotetrazene (**11**) was obtained. A band at



$$\mathrm{HN{=}\underset{\displaystyle NH_2}{C}NHNHN{=}N\underset{\displaystyle NHNHNO}{C}{=}NH}$$

(11)

1062 cm^{-1} was assigned to the NN diazo stretching vibration. Other assignments were also made[132].

VI. ELECTRONIC SPECTROSCOPY, FLUORESCENCE AND PHOSPHORESCENCE

A. Diazoalkanes, Diazocyclopentadienes, α-Diazoaldehydes, α-Diazoketones and α-Diazoesters

The spectra of diazomethane and diazoethane were recorded in the vapour phase[133]. Their spectra as well as the spectrum of 1-diazopropane were also recorded in hexane and in other solvents[134]. Their absorption begins around 550 nm, displaying a broad and diffuse maximum in the 450 nm region, which is of very low intensity (ε 3–10). Alkyl substitution shifts the band slightly bathochromically, whereas aryl substitution causes a large shift. This is manifested in the change in colour from the yellow diazomethane, to the yellow-red 2-diazopropane, and to the blue-red diphenyldiazomethane[135]. At wavelengths shorter than 300 nm a second region of rapidly increasing absorption is found[133]. The vacuum ultraviolet absorption spectrum of gaseous diazomethane and deuterated diazomethane were obtained in the 135–200 nm region[136].

The concentration of diazomethane in ether solution has been determined spectrophotometrically at 410 nm from the molecular extinction coefficient, ε 7·2 [15].

The ultraviolet spectra of three 5-nitro-2-furyl diazo compounds have been tabulated and recorded[84]. The ultraviolet spectrum of dicyanodiazomethane in acetonitrile shows absorption at 241 and 313 nm (ε 12,400 and 107)[83]. The spectra of several diaryldiazomethanes were recorded[137].

Crystalline diazocyclopentadiene (m.p. −23 to −22 °C) is yellow but is red as a liquid. Its electronic spectrum in isooctane displays a maximum at 298 nm (log ε 4·17) and a long tailing absorption into the visible, the latter being responsible for its red colour[103].

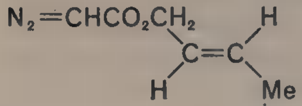
The ultraviolet and visible absorption spectra of diazocyclopentadiene and several of its substitution products were tabulated. As with other aromatic compounds, substitution with conjugating substituents on the diazocyclopentadiene ring resulted in bathochromic shifts[104]. The ultraviolet spectra of several polyphenyldiazocyclopentadienes were reported and reproduced[105c, d].

The ultraviolet spectra of seven α-diazoaldehydes have been tabulated. They exhibit two short wavelength bands at approximately 250 and 280 nm ($\varepsilon \sim 10^4$ and 5×10^3–10^4), in addition to a long wavelength band of low intensity in the region of 360–400 nm ($\varepsilon \sim 40$). As with α-diazoketones there is a marked influence of solvents on the relative intensities of the short wavelength bands[90b].

The ultraviolet spectra of numerous α-diazoketones belonging to several classes have been tabulated[137]. Conjugation of the diazo and carbonyl groups shifts the long wavelength weak band hypsochromically relative to this band in diazoalkanes, while the short wavelength intense band is bathochromically shifted. 1-Diazo-2-butanone absorbs at 247, 269 and 360 nm (ε 7650, 7110 and 21) and α-diazoacetophenone absorbs at 250 and 294 nm (ε 12,300 and 13,500). Substituted diazoacetophenones have two bands in the 240–270 and 270–300 nm regions with molecular extinction coefficients, ε 10^4–3×10^4 [137]. The ultraviolet spectra of several cyclic 2-diazo-1,3-dicarbonyl compounds were reported[96]. 16-Diazoandrostan-3β-ol-17-one has in ethanol bands at 250 and 297 nm (ε 4139 and 3592)[94]. α-Diazobenzyl phenyl ketone absorbs at 267, 317 and 417 nm (ε 19,953, 5012 and 100)[138].

The ultraviolet and visible spectra of numerous diazoacetophenones in several solvents have been reported. They all show maxima at approximately 210, 250 and 290 nm, and a low-intensity band at about 400 nm. The hypsochromic shift of the long wavelength band in polar solvents may result from an $n \rightarrow \pi^*$ transition, due to the diazo group[139]. The interaction of diazocarbonyl compounds with hydroxylic solvents has been investigated, and it has been concluded that their behaviour in the ultraviolet and infrared are reasonably consistent with the possible intervention of conformational isomeric forms[97, 140]. In fact, it has been shown quantum-mechanically that the ultraviolet spectra of α-diazoketones, such as diazoacetone and α-diazoacetophenone, can be interpreted satisfactorily if it is assumed that they exist in *cis* and *trans* conformations[141].

Ethyl diazoacetate absorbs in ethanol at 249 and 377·5 nm (ε 10,050 and 16)[142]; its spectrum in water has been reproduced[143]. Azaserine, another α-diazo ester, exhibits a maximum at 250·5 nm (ε 19,700) at pH 7 in water[58]. The ultraviolet spectra of the following esters have been reported: **12** (in ethanol) has maxima at 213 and 248 nm (ε 4860 and 16,200); **13** (in *n*-hexane) at 220 and 245 nm (ε 7850 and 12,650), and **14**



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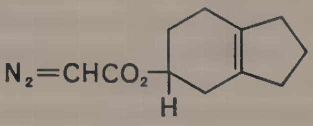

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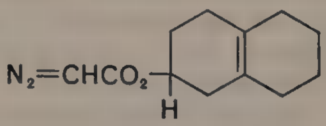


(14)

(in *n*-hexane) at 217 and 245 nm (ε 8100 and 12,700)[62]. Several α-substituted α-diazoesters have two bands in ethanol in the regions of 262–264 and 360–415 nm. Thus ethyl benzyldiazoacetate absorbs at 263 and 415 nm[102]. Diethyl diazomalonate absorbs in cyclohexane at 252 and 352 nm (ε 7400 and 23), and dimethyl diazomalonate absorbs in cyclohexane at 225(sh), 250 and 352 nm (ε 7300, 7900 and 22)[100].

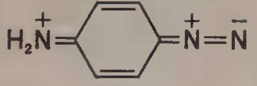
B. Arenediazonium Salts, Diazophenols, Diazotates, Diazosulphones and Diazosulphonates

Arenediazonium chlorides in 0·1 N-HCl display maxima in the 220–300 nm region (ε 10^4–2×10^4), which are strongly dependent on ring substituents and their position. The unsubstituted benzenediazonium chloride absorbs at 262 nm (ε 12,390)[144]. Benzenediazonium fluoroborate in acetonitrile absorbs at 261 and 296 nm (log ε 4·09 and 3·28)[145]. Its spectrum and that of several mono and polymethoxy derivatives have been recorded in the 200–450 nm region and assignments of electronic transitions were made by means of molecular orbital theory[145]. The electronic spectra of *para*- and *meta*-substituted benzenediazonium fluoroborates were recorded and tabulated. The *para* series has a single band in the range of 260–380 nm (log $\varepsilon > 4{\cdot}0$), and the *meta* series has two bands around 270 nm (log $\varepsilon \sim 4{\cdot}0$) and in the range of 300–350 nm (log ε *c.* 3·5). As indicated before, the maxima are strongly dependent on substituents and their positions. Molecular orbital calculations were made to correlate these transitions with substituents[146]. The electronic spectra of several *o*-dialkylaminobenzenediazonium tetrafluoroborates show two bands at about 275 and 440 nm (log $\varepsilon \sim 3{\cdot}75$ for both maxima)[113].

Stabilized arenediazonium salts as their zinc chlorides have been accurately determined spectrophotometrically by their maximum absorbance at 380 nm. The method does not require pretreatment and compares favourably with results obtained by the gasometric method. Beer's law is followed at 380 nm for aqueous solutions of 1–10 p.p.m. concentrations. The method can be applied to other substituted benzenediazonium salts with maxima in the 350–400 nm region, since decomposition products and other impurities do not absorb in this region[147].

It has been reported that several arenediazonium salts exhibited fluorescence at room temperature and phosphorescence at liquid nitrogen temperatures[148].

The ultraviolet spectra of diazophenols and diazonaphthols have been reported. It has been argued from these spectra and from dipole moment measurements that these compounds are resonance hybrids with contributions from quinonoid resonance structures **9b**[149, 150]. A similar conclusion has been reached from the electronic spectra of *p*-aminobenzenediazonium salts, which should be assigned the quinonoid structure **15**[151].



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The ultraviolet spectra of *syn*- and *anti*-diazotates in aqueous alkaline solution differ markedly. The *anti* isomers have absorption maxima between 270 and 280 nm (log ε *c.* 4·1), whereas the *syn* isomers show a very broad inflexion in that region, the centre of which has log ε *c.* 3 [152]. The ultraviolet spectra of several *syn*- and *anti*-diazotates obtained on alkaline equilibration of diazonium salts have been tabulated. It is observed that the spectral shifts on going from the diazonium salts to the diazotates depend strongly on the substituents and their positions. The ultraviolet spectra indicate that in strong alkali the predominant species in these equilibria is the isodiazohydroxide[144]. The ultraviolet spectra of the components in equilibrium (equation 10) in the alkaline solution of *p*-nitrobenzenediazonium ions have been obtained

$$p\text{-}O_2NC_6H_4N_2^+ \underset{}{\overset{OH^-}{\rightleftharpoons}} (p\text{-}O_2NC_6H_4N{=}N{-}OH) \underset{}{\overset{OH^-}{\rightleftharpoons}} p\text{-}O_2NC_6H_4N{=}NO^- + H_2O \quad (10)$$

by computation. Whereas the diazonium salt exhibits maxima at 260 and 311 nm (log ε 4·14 and 3·24), the corresponding *anti*-diazohydroxide, and the *syn*- and *anti*-diazotates display their maxima at 315, 305 and 332 nm (log ε 3·70, 3·92 and 4·10), respectively[153].

The electronic spectra of several diazosulphones, $Ar^1N{=}NSO_2Ar^2$, have been recorded, and it appears from these spectra that the diazo group has the *trans* configuration[154]. Benzyl benzenediazosulphone has maxima at 290 and 438 nm (ε 14,200 and 129) in cyclohexane[155].

The electronic spectra of ten pairs of alkali salts of isomeric diazosulphonates have been recorded. In aqueous solution the *syn*- and *anti*-*o*-chlorobenzenediazosulphonates exhibit maxima at 238, 300 and 448 nm (log ε 3·7, 3·2 and 2·3), and at 228, 292 and 428 nm (log ε 3·8, 3·9 and 2·3), respectively. Small differences only are found in the ultraviolet spectra of each pair[156]. The electronic spectra of numerous *ortho*-, *meta*- and *para*-substituted *anti*-benzenediazosulphonates have been tabulated. The unsubstituted isomer absorbs at 219, 255, 290 and 416 nm (log ε 3·93, 3·14, 4·07 and 2·25). The two long wavelength bands have been assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. The effects of substitution on the spectra have also been discussed[157].

C. Diazocyanides and Diazoisocyanides

Electronic spectra of five pairs of isomeric *cis* and *trans* halo- and nitrobenzenediazocyanides have been obtained. They display three bands in the regions of 220–270, 300–340 and 390–480 nm (log ε ~ 3, 3–4 and 4). The difference between the spectra of each pair is small[158]. The spectra of *cis*- and *trans*-*p*-chlorobenzenediazocyanides have been reported. They are quite similar but the maxima of the *trans* isomer are bathochromically shifted and are of somewhat higher intensity as compared with those of the *cis* isomer. This indicates that the *cis* isomer has steric hindrance, inhibiting resonance[156]. The electronic spectra of *cis*- and *trans*-diphenyl-4-diazocyanides have been recorded. They are very similar but not identical, and show the differences expected of geometrical isomers[159]. Azodicarbonitrile (**4**) and its radical anion **5** display maxima in acetonitrile at 240 and 445 nm (ε 7830 and 18), and at 222, 372 and 525 nm (ε 5270, 4560 and 120), respectively[57].

The ultraviolet spectra of *p*-chlorobenzenediazoisocyanide and its *p*-bromo analogue have been reported. They indicate that the rigid, semipolar-bonded isocyanide group ($N^+{\equiv}C^-$) is non-chromophoric in character[128].

D. Triazenes and Tetrazenes

The electronic spectra of 19 substituted derivatives of 1,3-diphenyltriazenes have been determined. They all display three bands, in the regions of 230–240, 280–300 and 340–360 nm (ε ~ 2 × 10⁴, 10⁴ and 2 × 10⁴). No conclusions could be drawn from this study about their structure in solution[160]. The spectra of 1-aryl-3,3-dimethyltriazenes display the same bands as the above series, but it was concluded here that the compounds possess a *trans* configuration about the —N=N— bond[161]. Electronic spectra of numerous triazenes have been recorded, such as those of ArN=

NN(Ph)X (Ar = *p*-anisyl, 1-naphthyl; X = H, Me, Ac)[162a]; $NO_2C_6H_4N{=}NNHC_6H_4X$ (X = H, Me, Ph, Cl, MeO, NHAc, NO_2)[162b]; $RO_2CC_6H_4N{=}NNHC_6H_4X$ (R = H, Me; X = H, Me, Ph, Cl, MeO, NHAc, CO_2H, CO_2Me, NO_2)[162c]; isomeric chlorophenyltriazenes[162d], and polysubstituted diazoaminobenzenes[162e].

1-Aryl-3,3-bis(2-hydroxyethyl)triazenes, used in dyeing and printing, were analysed spectrophotometrically. Their ultraviolet spectra in ethanolic or aqueous solution exhibit maxima from 220 to 245 nm and from 315 to 390 nm, occasionally also a maximum in the 280–295 nm region. In acid solution, a band corresponding to a diazonium cation is observed. The conversion of these triazenes to the diazonium salts is accompanied by an isosbestic point, indicating a quantitative relationship between the triazenes and the diazonium compounds. The dissociation products of the triazenes (a diazonium salt and an amine) do not interfere in the determination when the long wavelength absorption band is used[163]. 1-Aryl-3,3-dialkyltriazenes have been determined in concentrations down to 50 μM (in 96% EtOH) by absorbance measurements at wavelengths between 217 and 380 nm [164].

The ultraviolet spectra of tetramethyl-2-tetrazene and tetraethyl-2-tetrazene in ethanol display maxima at 277 nm (ε 8300) and at 285 nm (ε 7600), respectively. The tetrazenes are basic in nature and can act as proton acceptors, affording in proton donor solvents a new band around 240 nm [45]. The purity of tetra-alkyl-2-tetrazenes, which were separated by gas chromatography of their mixtures, was determined from the ratio of their absorbance in basic aqueous solution at 248 and 277 nm [76].

VII. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

A. *Diazoalkanes, α-Diazoketones, α-Diazoesters, α-Diazosulphones and Diazocyclopentadienes*

Diazomethane in CCl_4 displays a singlet at δ 3·20 p.p.m. [165] As compared with allenes and ethylenes this is a large upfield shift which may be due to resonance structures with a negative charge on the carbon. This is also manifested in the nucleophilic character of diazomethane[166]. The chemical shifts of several diazoalkanes have been tabulated[167]. The chemical shifts of the α-protons fall in the range of 3·0–5·0 p.p.m., and it can be seen that they are shifted downfield when the negative charge on the α-carbon can be stabilized by appropriate substituents, as, for example, in phenyldiazomethane (δ 4·58) or in ethyl diazoacetate (δ 4·96) [167].

The ^1H chemical shifts of several 5-nitro-2-furyl diazo compounds have been reported[84], as were also the ^{19}F chemical shifts of bis(trifluoromethyl)diazomethane and bis(perfluoroethyl)diazomethane[82]. Trifluoromethyldiazomethane exhibits a quartet in the ^1H spectrum at 4·6 p.p.m. ($CDCl_3$, J_{HF} 4·0 Hz) and a doublet in the ^{19}F spectrum at −54·45 p.p.m. (in $CDCl_3$ solution, with $CFCl_3$ as external standard)[168].

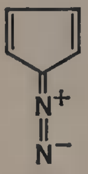
In the ^1H spectrum α-diazoacetone exhibits the methine singlet at 5·18 p.p.m. and the methyl singlet at 2·00 p.p.m. [169] The α-methine protons of α,β-unsaturated α-diazoketones resonate in the range of 5·2–5·7 p.p.m. [92] It has been shown that the methine proton of aryl α-diazoketones resonates in CCl_4 at about 5·8 p.p.m., in benzene at about 4·9 p.p.m. and in $(CD_3)_2SO$ at about 6·9 p.p.m. [98]

Nuclear magnetic resonance at different temperatures has demonstrated that α-diazoaldehydes, α-diazoketones and α-diazoesters exist as equilibrium mixtures of *cis* and *trans* conformers. In diazoacetone the *trans*-methine proton resonates around 5·2 p.p.m., about 0·5 p.p.m. upfield from the *cis*-methine[170].

The methine protons of methyl and ethyl diazoacetate resonate at 4·96 p.p.m.[167] The same proton in several other similar α-diazoesters was found to display singlets in the region of 4·6–4·7 p.p.m.[62] The methine proton of α-diazo-*N*,*N*-diethylacetamide resonates at 2·40 p.p.m.[101] The methyl group on the double bond of ethyl 2-methyldiazoacetate resonates at 1·55 p.p.m.[101], whereas the methylene of the benzyl group of ethyl 2-benzyldiazoacetate resonates at 3·61 p.p.m.[102]

The methine protons of *m*-tolyldiazosulphone and of *t*-butyldiazosulphone resonate in CCl_4 at 5·07 and 4·79 p.p.m., respectively[98]. In diethylphosphonodiazomethane this proton resonates at 4·23 p.p.m. (J_{PCH} 11 Hz)[63].

The aromatic protons of diazocyclopentadiene exhibit two multiplets centred at 6·7 (α-protons) and 5·8 p.p.m. (β-protons)[104, 167]. It has been concluded that diazocyclopentadiene has very little contribution from structure **16**, but that it possesses almost complete carbanion character in the ring as indicated in structure **17**[167].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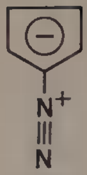
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The ^1H chemical shifts of 9-diazofluorene have been reported[167]. The ^1H chemical shifts of several nitro- and iodo-substituted diazocyclopentadienes[104] and of polyphenyl-substituted diazocyclopentadienes[105c, d] have also been reported.

B. *Diazonium Salts and Diazotates*

The first example of ^1H and ^{19}F n.m.r. spectra of an alkyldiazonium ion has been reported[168]. Trifluoromethyldiazomethane in fluorosulphonic acid exhibits at −60 °C in its ^1H spectrum a quartet at 6·3 p.p.m. (J_{HF} 6·1 Hz), which has been assigned to the methylene group of the 2,2,2-trifluoroethyldiazonium ion (**18**). In

$$CF_3CH_2N_2^+$$

(18)

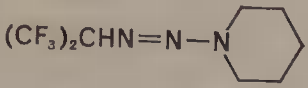
the ^{19}F spectrum it exhibits the CF_3 signals as a triplet at −64·58 p.p.m. from $CFCl_3$ (J_{HF} 6·1 Hz).

The ^1H n.m.r. spectra of *p*-methoxy-, *p*-methyl-, *p*-chloro- and *p*-nitro-benzenediazonium salts in D_2O were reported. The chemical shifts of the aromatic protons are in the region of 7·7–9·2 p.p.m., and the *ortho* coupling constants are about 9 Hz. The effects of the substituents on the ^1H chemical shifts in the diazonium ions and in the corresponding amines and ammonium salts are in the same direction. The chemical shifts are also closely related to the Hammett σ constants[171]. The aromatic multiplets of several *o*-dialkylaminobenzenediazonium fluoroborates fall in the region of 6·5–8·2 p.p.m.[113]

The methyl singlets of potassium *syn*- and *anti*-methanediazotates occur at 3·18 and 3·70 p.p.m., respectively[172, 165]. The methine, methyl and aromatic protons of potassium *syn*-1-phenylethanediazotate resonate at 1·19 (doublet), 5·58 (quartet) and 7·05–7·43 (multiplet) p.p.m. (J_{CH-CH_3} 6·8 Hz), whereas those of the *anti* isomer have their signals at 1·36 (doublet), 4·79 (quartet) and 7·09–7·44 (broadened singlet) p.p.m. (J_{CH-CH_3} 6·8 Hz)[120].

C. Triazenes

The triazene **19** exhibits in its ^{19}F n.m.r. spectrum a doublet centred at 4·27 p.p.m. (J 8 Hz), upfield from $CFCl_2CFCl_2$; its ^1H n.m.r. spectrum contains a septet at δ 4·13 (1H) (J 8 Hz) and two singlets at 3·40 p.p.m. (4H) and at 1·35 p.p.m. (6H)[82].



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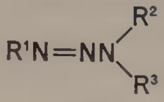
The methyl chemical shifts of several 1-aryl-3,3-dimethyltriazenes occur in $CDCl_3$ in the 3·5 p.p.m. region. These triazenes exhibit hindered rotation about the $N_{(2)}—N_{(3)}$ bond because of its partial double bond character, as concluded from low temperature n.m.r. studies[173]. In a series of papers Wiberg and Pracht[174] studied silyltriazenes **20**. They have tabulated ^1H chemical shifts of numerous substituents[174a]



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and have shown by variable temperature n.m.r. that where $R^1 = R^2 =$ Me and $R^3 = SiMe_3$, $SiEt_3$ and $SiMeEt_2$, only a single methyl singlet appears and that this is due to fast fluctuations of the silyl group R^3 between $N_{(1)}$ and $N_{(3)}$ [174a, b]. The same authors also applied low temperature n.m.r. to demonstrate that silyltriazenes, where $R^2 = R^3 = SiMe_3$ and $SiMeEt_2$, exist as *cis–trans* isomers, which can be isolated at low temperatures[174c]. Finally they have shown that in the last-mentioned group of triazenes hindered rotation occurs about the NN single bond, as evidenced from low temperature n.m.r. studies[174d]. Values of free energy of activation were presented for the different processes reported in these studies.

VIII. MASS SPECTROMETRY

A. Diazoalkanes, α-Diazoketones and α-Diazoesters

The mass spectral peaks and relative intensities of diazomethane have been tabulated. Its strongest peaks are due to $CH_2N_2^+$, N_2^+ and CH_2^+, the relative intensities being 96·5, 50·0 and 100·0, respectively. The spectrum is to a large extent similar to that of diazirine, with the exception that the $CH_2N_2^+$ and N_2^+ peaks are more intense in diazomethane[175].

The more abundant peaks of several α-diazoketones and their relative intensities were schematically presented. These peaks are listed below for each of the diazoketones and the most abundant peak of each spectrum is underlined:

$PhCOCHN_2$: $\underline{PhCOCHN_2^+}$, $PhCOCH^+$, $PhCO^+$, $C_7H_6^+$, Ph^+, 52, CHN_2^+, N_2^+;

CCl_3COCHN_2: $CCl_3COCHN_2^+$, CCl_3CO^+, CCl_3^+, $\underline{COCHN_2^+}$, CHN_2^+, N_2^+;

$CH_2ClCOCHN_2$: $CH_2ClCOCHN_2^+$, $CH_2COCHN_2^+$, CH_2ClCO^+, $\underline{COCHN_2^+}$, CH_2ClCH^+, CH_2Cl^+, CHN_2^+ and $COCH^+$, N_2^+;

$MeCOCHN_2$: $MeCOCHN_2^+$, $COCHN_2^+$, $MeCOCH^+$, $MeCO^+$, $COCH^+$ and CHN_2^+, $\underline{N_2^+}$, Me^+.

From the above it is seen that all of these molecules have molecular peaks as well as N_2^+ and CHN_2^+ peaks. Ionization potentials and bond dissociation energies of these compounds were also presented, and it was concluded that fragmentation in the mass spectrometer involved a competitive intervention of a mechanism of direct electron impact at the diazo compound, and a process of primary ionization of the carbonyl fragment formed on thermal cleavage[176].

The mass spectral peaks and relative intensities of several diazo-1,3-dicarbonyl compounds were tabulated. The molecular ions are of low abundance, but the compounds give peaks at $[M-N_2]^+$ and $[M-N_2-CO]^+$, the latter being due to an electron-impact induced Wolff rearrangement. A ^{13}C-labelled compound was used to investigate the migration mobility of substituents in this rearrangement[177]. In a study of the major fragmentation patterns of diazoketophenanthrenes it was observed that the more abundant ions were M^+, $[M-N_2]^+$, $[M-N_2-CO]^+$, $[M-N_2-CO-H]^+$ and $[M-N_2-CO-HC{\equiv}CH]^+$ [178].

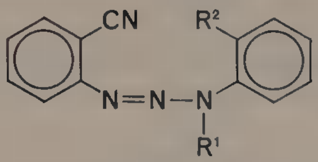
The mass spectral peaks of diazoesters **12–14** were reported. Molecular peaks are absent in their spectra but they exhibit $[M-N_2]^+$ and CHN_2^+ peaks[62]. The mass spectral patterns of several 2-diazo-1,3-ketoesters were tabulated but, in contrast to the diazo-1,3-dicarbonyl compounds mentioned above, the fragments $[M-N_2]^+$ do not give a Wolff rearrangement[177].

B. *Diazophenols*

The zwitterions of diazotized *o*- and *p*-aminophenol are volatile and give intense molecular ions and strong $[M-N_2]^+$ and $[M-N_2-CO]^+$ peaks, which are formed via the quinonoid structures of these molecules. By contrast, the *meta* isomer which cannot be stabilized through a quinonoid structure yields a complex mass spectrum. The zwitterions of diazotized anthranilic acid and diazotized sulphanilic acid did not afford molecular ion peaks[179].

C. *Triazenes*

The mass spectra of four diaryltriazenes **21** (R^1 = H or alkyl) give molecular ions of low abundance, presumably because of their rapid central cleavage to the abundant ions **22** and **23**. The tautomerism in triazenes **21** (R^1 = H) is also reflected in their mass spectra, but it is not known whether the tautomers are formed before or after electron impact. Elimination of nitrogen as $(M-N_2)^+$ or $(M-R^1N)^+$ peaks is also common in these triazenes[180].



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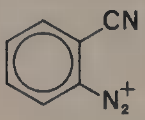

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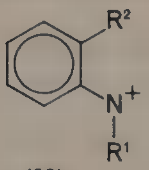

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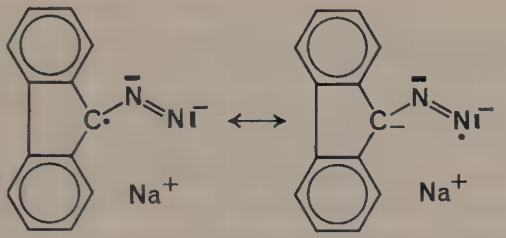
IX. ELECTRON SPIN RESONANCE SPECTROSCOPY AND CHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION

Many diazo compounds are unstable and decompose easily with evolution of nitrogen. Until recent years only chemical and indirect physical methods were available to the chemist to study which of the reactions of diazo compounds proceed by a free-radical mechanism. With the emergence of the powerful spectroscopic methods of this section, it has become possible to probe into this problem in a straightforward manner. This section, however, will be restricted only to those cases where the diazo compounds themselves become free radicals, leaving out the majority of cases where the primary reaction products are free radicals.

On shaking diazofluorene with sodium in ether solution it yields a deep blue, oxygen-sensitive free radical, **24**, which has been detected by e.s.r. Diphenyldiazomethane behaves similarly, yielding a free radical, which probably has a contributing structure **25**[181].



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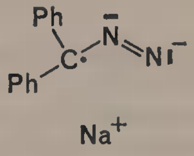

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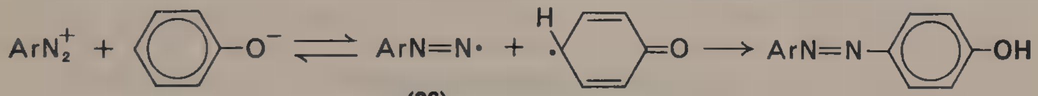
In the diazo coupling between an arenediazonium fluoroborate and methanolic sodium phenoxide which yields a *p*-hydroxyazobenzene, it has been shown by CIDNP that the first step of the reaction involves a reversible electron transfer reaction (equation 11) to give two free radicals which then combine to yield the azo compound. This was proved by using a diazonium salt, ^{15}N-labelled at both positions, and detecting not only enhanced absorption of the azo product, but also enhanced absorption and emission of the first formed aryldiimine radical **26**[182]. This reaction was also studied by ^{13}C and ^{15}N CIDNP, which as above showed not only polarization of formed products, but also enhanced absorption of the ^{13}C and ^{15}N resonances of the original diazonium ion. A mechanism was proposed for this reaction, involving diazoethers[183]. In similar fashion ^{13}C CIDNP of *p*-methoxybenzenediazonium ions (labelled with ^{13}C at $C_{(1)}$) showed, on addition of a sodium hydroxide solution, not only emission from the formed anisole but also enhanced absorption which has tentatively been attributed to $C_{(1)}$ in the original diazonium ion. This indicates participation by the above type of aryldiimine radical **(26)**[184].



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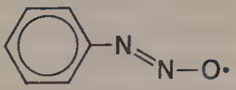
(11)

A phenyldiazotate σ radical **27** has been observed by e.s.r. in the decomposition of *N*-nitrosoacetanilide[185].



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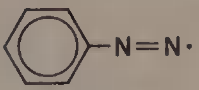
^{15}N CIDNP of the thermal decomposition of labelled diazoaminobenzene shows in addition to polarization of the formed products also enhanced absorption of the starting material, but only in the central nitrogen atom. This presumably originates from recombination of free radicals **28** and **29**. Radical **28** must however be very different from radical **26**, generated in the decomposition of arenediazonium fluoroborates in alkaline solution[182, 183], because in the latter, atoms $C_{(1)}$, $N_{(1)}$ and $N_{(2)}$ are equally polarized, whereas in the diazoaminobenzene only the $N_{(2)}$ is polarized[186].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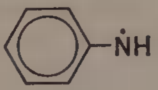
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X. ELECTRON SPECTROSCOPY

Electron spectroscopy is used to study the sequence of molecular orbitals and their energies in molecules. It has also found analytical and structural applications, but as yet it has presumably not been used in the analysis of diazo compounds[187].

The ultraviolet photoelectron spectra of 2-diazopropane and diazocyclopentadiene have been obtained. From these spectra it has been possible to conclude that in these two compounds, as well as in diazomethane itself, the highest occupied orbital is a non-bonding $b_2(\pi)$ orbital[188].

The X-ray photoelectron spectrum (ESCA) of benzenediazonium fluoroborate displays two nitrogen 1s peaks with a peak separation of 1·3 eV. It has been concluded that the higher binding energy peak is associated with the nitrogen atom directly attached to the phenyl group[189].

XI. DIPOLE MOMENTS

Dipole moments have contributed to structural, configurational and conformational assignments of organic molecules.

Dicyanodiazomethane has a dipole moment of 3·8 D, which indicates a considerable contribution from the diazonium methylid structure **6** to the ground state of the molecule[83].

The dipole moments of diazoacetone and its three chloromethyl derivatives have been determined, and from these values it has been inferred that the molecules possess a rigid planar $COCHN_2$ structure, where the CO and CN_2 groups may have either the *cis* or *trans* conformation. Diazoacetone itself exists in both conformations, but in the chloro derivatives only the *cis* conformers are present. Comparison of experimental and theoretical dipole moment values for $CH_2ClCOCHN_2$ and $CHCl_2COCHN_2$ led to angles of 150° and 40°, respectively, between the molecular plane containing the $COCHN_2$ grouping, and the plane defined by C(carbonyl)—C(alkyl)—X (X = Cl in the former molecule, X = H in the latter molecule)[190]. Dipole moments of *para*-substituted phenyldiazoketones showed that the *cis–trans* equilibrium at the $COCHN_2$ grouping is almost entirely shifted to the *cis* conformation, in contrast to diazoacetone[191]. Dipole moment measurements of hindered diazoketones also point to occurrence of two pseudo *cis–trans* (distorted) conformations[99]. Diethyl diazomalonate has a dipole moment of 2·66 D [101].

Of the configurational pairs of arenediazocyanides, the stable forms have the larger dipole moment and therefore possess the *trans* configuration, whereas the labile forms have the *cis* configuration[192, 124a, 159].

The dipole moments of 1-aryl-3,3-dimethyltriazenes indicate that they presumably have a *trans* configuration about the —N=N— bond[161, 69a].

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CHAPTER 6

Basicity, acidity and hydrogen bonding

J. F. McGarrity

Institute of Organic Chemistry, University of Lausanne, Lausanne, Switzerland

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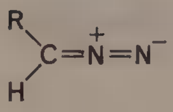
I. INTRODUCTION

The electron distribution in primary diazoalkanes is often represented by resonance forms **1a**–**1d**.



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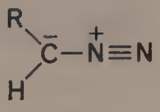

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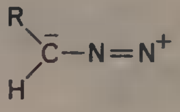

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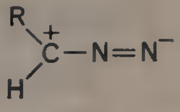


(1d)

Forms **1b** and **1c** dictate the reactivity of diazoalkanes to acids and electrophiles, with forms **1a** and **1d** playing a minor role. Proton abstraction by bases is governed by form **1a** whereas reactions with nucleophiles are best rationalized by consideration of forms **1b** and **1c**. In the equations that follow, the choice of representation will depend on the reaction in question, and does not imply a predominance of that form in the overall electron distribution.

The structure of the discussion follows largely that of the classic review of Huisgen[1]. Emphasis is however placed on quantitative evaluation of basicity and acidity. When there is a lack of thermodynamic data, as is often the case for the compounds discussed, kinetic results are examined. Qualitative examples are presented as illustrations of specific points, and do not represent a complete coverage of the subject. Extensive reference is made to comprehensive[2, 3] and more recent[4, 5] reviews.

II. BASICITY OF ALIPHATIC DIAZO COMPOUNDS

A. Gas Phase Basicity of Diazoalkanes

In contrast to its elusive behaviour in solution, the methanediazonium ion (**2**) can be directly observed and induced to react in the gas phase.

The most unequivocal methods of formation are by nucleophilic displacement processes[6], and by fragmentation of the azomethane molecular ion[7]:

$$N_2+CH_3\overset{+}{F}H \longrightarrow \underset{(\mathbf{2})}{CH_3N_2^+}+HF \tag{1}$$

$$[CH_3N{=}NCH_3]^+ \longrightarrow CH_3{-}\overset{+}{N}{\equiv}N+{\cdot}CH_3 \tag{2}$$

This latter means of generation of the methanediazonium ion lends itself admirably to the study of subsequent proton transfer reactions forming diazomethanes, by ion cyclotron resonance spectroscopy[8]. Thus at 13 eV (4·2 eV above the appearance potential of the methanediazonium ion), an increase in the pressure of azomethane results in its protonation by the diazonium ion:

$$CH_3N_2^+ + CH_3N{=}NCH_3 \longrightarrow CH_2N_2+CH_3\overset{+}{N}H{=}NCH_3 \tag{3}$$

As is often the case for the chemistry of alkyl diazonium ions in solution, the loss of a proton is accompanied by competitive loss of nitrogen. The species so formed are characteristic fragments of the trimethyldiazenium ion (3), initially produced by a nucleophilic displacement of nitrogen.

$$CH_3N_2^+ + CH_3N{=}NCH_3 \longrightarrow \underset{(\mathbf{3})}{(CH_3)_2\overset{+}{N}{=}NCH_3}+N_2 \tag{4}$$

The proton affinity (P.A.) of diazomethane, shown to be inferior to that of azomethane by observation of the reaction given by equation (3), was found to be intermediate between those of methylamine and ammonia, by the reactions observed upon introduction of each of these bases into the azomethane system, (equations 5–8).

$$CH_3N_2^+ + CH_3NH_2 \longrightarrow (CH_3)_2\overset{+}{N}H_2 + N_2 \qquad (5)$$

$$CH_3N_2^+ + CH_3NH_2 \longrightarrow CH_2N_2 + CH_3\overset{+}{N}H_3 \qquad (6)$$

$$CH_3N_2^+ + NH_3 \longrightarrow CH_3\overset{+}{N}H_3 + N_2 \qquad (7)$$

$$CH_3N_2^+ + NH_3 \xrightarrow{\quad\times\quad} CH_2N_2 + {}^+NH_4 \qquad (8)$$

Hence

$$\text{P.A.}\,(NH_3) < \text{P.A.}\,(CH_2N_2) < \text{P.A.}\,(CH_3N{=}NCH_3) < \text{P.A.}\,(CH_3NH_2) \qquad (9)$$

The existence of the methanediazonium ion in the gas phase, as an intermediate or part of a transition state, in the reaction of hydrogen halides with diazomethane (equation 10), is much less evident.

$$CH_2N_2 + HX \longrightarrow CH_3X + N_2 \qquad (10)$$

The estimated upper limit of 24·8 kJ/mol for the activation energy of this reaction involving hydrogen iodide was considered to be compatible[9] with a simple polar transition state such as **4**.

$$HI + CH_2N_2 \longrightarrow \underset{(4)}{\overset{\delta-}{I} - - - - \overset{\delta+}{H} - - - - \overset{\delta-}{CH_2} \overset{\delta+}{\cdots N \equiv N}} \longrightarrow CH_3I + N_2 \qquad (11)$$

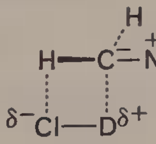
The extreme rapidity of these reactions even at −78 °C limited the measurements of rate constants in this study to ratios based on competitive experiments. Thus at 300 K:

$$\frac{k_{HBr}}{k_{HCl}} = 9 \pm 2 \quad \frac{k_{HI}}{k_{HBr}} = 4 \pm 2 \quad \frac{k_{HI}}{k_{HCl}} = 50 \pm 15$$

Rate constants for the reactions of hydrogen chloride and hydrogen bromide with diazomethane have, however, been determined[10]:

$$k_{HCl} = (7{\cdot}0 \pm 1{\cdot}0) \times 10^5\ \text{cm}^3\ \text{mol}^{-1}\ \text{sec}^{-1},$$
$$k_{HBr} = (3{\cdot}0 \pm 1{\cdot}0) \times 10^6\ \text{cm}^3\ \text{mol}^{-1}\ \text{sec}^{-1}$$

The significance of these figures is obscured by the contribution of a wall reaction, providing an experimentally-observed negative activation energy of −1·6 kJ/mol. Experiments with deuterium chloride and diazomethane provided evidence that the first associative step is reversible[11]. All three deuterated species of the product methyl chloride were obtained. When deuterium chloride was injected with an excess of diazomethane, which was subsequently quenched with hydrogen bromide, there was 20% deuteration of the methyl bromide. This hydrogen isotopic exchange was considered to be impossible via an intermediate complex of the form **4**. The alternative complexes postulated[11] did not include **5**, which nevertheless merits consideration as it allows for both competing substitution and deprotonation reactions, with a minimum of structural reorganization.



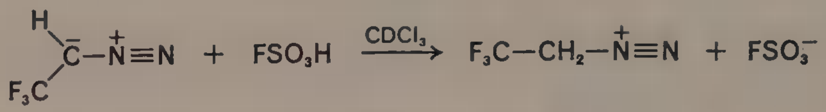
(5)

B. Solution Basicity of Diazoalkanes

I. Site of protonation in 'super-acid' media

Of the two potentially basic sites in simple diazoalkanes, reaction at one—the carbon in limiting structures (**1b**) and (**1c**)—leads to the habitually observed products of reactions with acids[12]. The alternative site—the nitrogen of limiting structures (**1a**) and (**1d**)—is not apparently involved. An earlier postulate of *N*-protonation[13] was subsequently revised in the light of more extensive data[14, 15].

Protonation of 2,2,2-trifluorodiazoethane in fluorosulphonic acid–deuteriochloroform gave a solution of the carbon-protonated species[16] indicated by the ^1H and ^{19}F n.m.r. spectra.



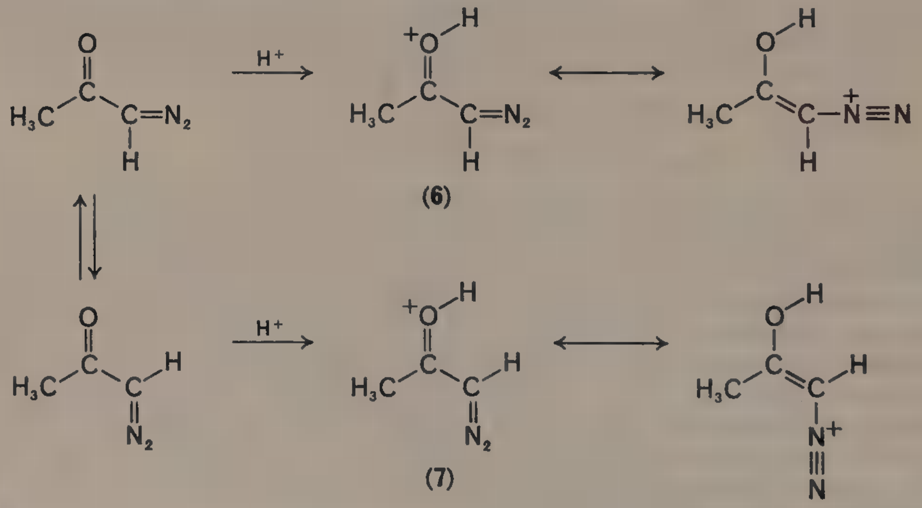
(12)

$\delta_H = 4{\cdot}6$ p.p.m., $q\ J = 4{\cdot}0$ Hz $\delta_H = 6{\cdot}3$ p.p.m., $J = 6{\cdot}1$ Hz

$\delta_{F^{19}} = +54{\cdot}45$ d $\delta_{F^{19}} = +64{\cdot}58$, $t\ J = 6{\cdot}1$ Hz

The principal evidence for this protonation site was the presence of a triplet in the F^{19} spectrum. Analogous C-protonated diazonium ions were formed from 1,1,1,3,3,3-hexafluoro-2-diazopropane at −70 °C in FSO_3H–$CDCl_3$[17], and for 1-phenyl-2,2,2-trifluoro diazoethane at −60 °C in SO_2–$HFSO_3$[18]. From the spectral data presented for these examples, an *N*-protonated species cannot be so rigorously excluded.

When the diazo group is adjacent to a carbonyl group, another potential site of protonation is introduced. Thus on admixture of diazoacetone with HF–SbF_5 in SO_2 at −80 °C, protonation occurs on the carbonyl oxygen, to give a mixture of *Z* and *E* diazonium ions, (**6**) and (**7**), in the ratio 4 : 1[19].



(13)

(14)

For 6:

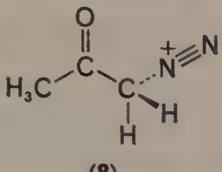
$\delta_{CH_3} = 2{\cdot}05$ p.p.m., $\delta_{CH} = 5{\cdot}9$, $J = 2$ Hz, $\delta_{OH} = 9{\cdot}47$, $J = 2$ Hz

For 7:

$\delta_{CH_3} = 2{\cdot}19$, $\delta_{CH} = 6{\cdot}1$, $J = 1$ Hz, $\delta_{OH} = 9{\cdot}29$ p.p.m.

The observation of geometrical isomers renders improbable protonation on carbon or nitrogen as in **8** and **9** respectively.

The difference in coupling constants between the methine proton and that derived from the acid in **6** and **7** tends to confirm O-protonation. In FSO_3H–SbF_5–SO_2 at -60 °C neither this H–H coupling nor, indeed, the resonance of the OH proton could be observed due to its rapid exchange with the solvent protons.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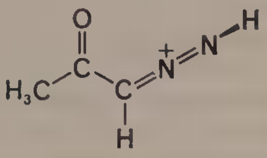
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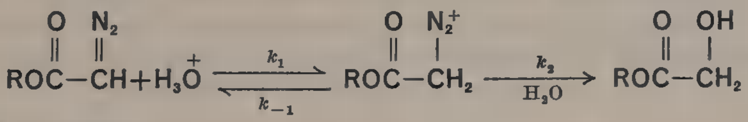
Protonation on oxygen was also observed for a series of aryl primary diazoketones of general formula $ArCOCHN_2$ and for alkyl diazoketones, primary[20] and secondary[19]. The p.m.r. spectra of 2-diazo cholestan-3-one derivatives in FSO_3H–$CDCl_3$–SO_2 at -70 °C were interpreted as indicating protonation on carbon[21]. The principal evidence cited as argument against oxygen protonation, i.e. the dissimilarity of the chemical shift of the acidic proton at $\delta = 9{\cdot}3$ p.p.m. to that for protonated ketones, is, in the light of subsequent values for oxygen-protonated diazoketones[19], of $\delta = 8{\cdot}2-9{\cdot}3$ p.p.m., probably invalid. The rapid proton exchange with the solvent, on warming the solution, is also more compatible with O rather than C protonation.

2. Thermodynamic basicity of diazoalkanes

For direct observation of alkyl diazonium ions in solution, they must possess features protecting them against spontaneous decomposition into molecular nitrogen and carbocations, and must be able to exist in weakly nucleophilic media. In the examples cited above, the first criterion was fulfilled by strongly electron-withdrawing groups diminishing the stability of possible carbocationic products. The second was assured by the extremely feeble nucleophilicity of the counterions SbF_6^- and FSO_3^-, extrapolated from their extremely weak basicity[22]. These conditions have so far prevented the establishment of a directly observable equilibrium. In the highly acidic media mentioned above, the diazo compounds studied were completely protonated; in more basic solutions the equilibrium concentrations of the diazonium ions are too low. Thus the protonation equilibrium preceding the rate-determining loss of nitrogen, in the hydrolysis of ethyl diazoacetate[23–25] **(10)** (equation 15), cannot be directly observed, even in 2·5-molar aqueous perchloric acid[26].



$$\mathrm{RO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\overset{\overset{\mathrm{N_2}}{\|}}{\mathrm{C}}\mathrm{H}+\mathrm{H_3}\overset{+}{\mathrm{O}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{RO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\overset{\overset{\mathrm{N_2^+}}{|}}{\mathrm{C}}\mathrm{H_2} \xrightarrow[\mathrm{H_2O}]{k_2} \mathrm{RO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\overset{\overset{\mathrm{OH}}{|}}{\mathrm{C}}\mathrm{H_2} \qquad (15)$$

(10, $R = C_2H_5$**)**

The overall rate constant for this reaction is given by equation (16):

$$k_{\text{obs}} = \frac{k_2\,k_1[\mathrm{H_3O^+}]}{k_{-1}+k_2} \qquad (16)$$

Furthermore, as in this case $k_2 \ll k_{-1}$

$$k_{\text{obs}} = \frac{k_2\,k_1[\mathrm{H_3O^+}]}{k_{-1}} = Kk_2[\mathrm{H_3O^+}] \qquad (17)$$

where $K = k_1/k_{-1}$.

Thus the observed rate constant contains the protonation equilibrium constant K, multiplied by k_2, the rate constant for the displacement of nitrogen, which has been shown to be nucleophile assisted for this substrate[27]. Although the value of k_2 is inaccessible directly, its sensitivity s to the strength of the participating nucleophile n, as expressed by the Swain–Scott equation[28], has been determined[27]. Identical s values for two nucleophilic substitutions indicate a common sensitivity of the transition states to reactant properties. This is equated by the Leffler postulate[29, 30], to a common position of the transition states along the reaction coordinate, the position being governed by the difference in free energy between reactants and products. The activation free energy is determined by this energy difference and a number of factors, including steric, solvational and entropy changes dependent on the transition-state structure. It has been proposed that substituent effects on structurally related diazonium ions are small[12]. If one accepts this proposition, it follows that the reactions of water with structurally related diazonium ions, displaying similar sensitivity to substitution by other nucleophiles, should have similar activation energies. This resemblance in transition state structures (with identical entering and leaving groups) implies similar free energies of reaction dominated by the free energy of formation of molecular nitrogen, and common interactions unique to the transition state. Hence the s values for the hydrolysis of **10** and diazoacetone (**11**) of 0·3 and 0·4 [27] imply approximately equal values of k_2 for nitrogen displacement. Consequently, comparison of the overall second-order hydrolysis rate constants of **10** and **11** give a measure of the relative acidity of their corresponding diazonium ions.

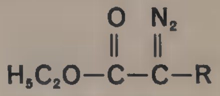
$$\log k_{\mathrm{obs}}(\mathbf{11}) - \log k_{\mathrm{obs}}(\mathbf{10}) = -\mathrm{p}K(\mathbf{10}) + \mathrm{p}K(\mathbf{11}) \simeq 1{\cdot}3 \tag{18}$$

This type of comparison cannot be justifiably extended to the hydrolysis of primary aryldiazosulphones $ArSO_2CN_2H$, which although following the same mechanism have a somewhat higher s value[31].

An estimate of the acid dissociation constants of alkanediazonium ions can be made in some cases, where the deprotonation is less rapid than the competitive loss of nitrogen. This situation is characterized by rate-determining protonation. When $k_2 \gg k_{-1}$, equation (16) becomes:

$$k_{\mathrm{obs}} = k_1[H_3O^+] \tag{19}$$

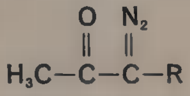
An increasing concentration of additional base may, however, sufficiently accelerate the deprotonation, so as to make the second step partially rate determining, i.e. the dependence of the observed rate constant on acid concentrations may change. This situation was realized in the hydrolysis of diazoacetate anion (**12**) in the presence of hydroxide ion[32], and in the hydrolysis of 2-diazo butan-3-one (**14**) and ethyl diazopropionate[33] (**13**) in the presence of acetic acid/acetate buffers.



$H_5C_2O{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{N_2}{\|}}{C}{-}R$

(10) R = H

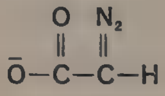
(13) R = CH_3



$H_3C{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{N_2}{\|}}{C}{-}R$

(11) R = H

(14) R = CH_3



$\bar{O}{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{N_2}{\|}}{C}{-}H$

(12)

Analysis of the kinetic data[32, 34] provides values for k_{-1}/k_2, which, with certain approximations, allow estimates of k_{-1}. Combination with the known k_1 value gives limiting values of $K < 10^5$ mol/l, $K < 5 \times 10^3$ mol/l and $K < 1$ mol/l for the protonated forms of **14**, **13** and **12**, respectively, i.e. p$K < -5$, p$K < -3{\cdot}7$ and p$K < 0$.

A more involved analysis of kinetic data for general acid-catalysed hydrolyses of diazo compounds can lead, in principle, to an estimate of the pK_a's of the conjugate acids. The significance and limitations of this approach will be discussed in Section II.B.6.

3. Acid-catalysed hydrogen–deuterium exchange

Primary deactivated diazoalkanes of the form $RCHN_2$ where $R = -CO_2R$ [23, 24], $-COR$ [35–38], $-SO_2R$ [39, 40], $-CF_3$ [41], establish an acid–base equilibrium with aqueous acid, prior to nitrogen loss. This equilibrium is principally demonstrated by a kinetic isotope effect $k_{H_2O}/k_{D_2O} \simeq 0{\cdot}4$ [42], or by hydrogen–deuterium exchange in a deuterated solution, either in the diazo compounds or products derived therefrom. For simple diazoalkanes, precise kinetic measurement is difficult due to their extreme acid lability, and so the second probe is more often used.

In the case of diazomethane, the results obtained appear somewhat confusing. Whereas it undergoes exchange in a two-phase system of alkaline D_2O and dibutyl ether or tetrahydrofuran[43, 44], in a system of chloroform–D_2O there is no exchange unless catalytic quantities of a weak acid, such as phenol, ammonium chloride or benzoic acid, are added[45]. In dioxane–D_2O, reaction of diazomethane with an acid or phenol gives the trideuterated ester or ether respectively[45]. Monodeuteration on carbon is observed in deuterated acetic acid[46], while a pre-equilibrium is reported to be established with benzoic acid in toluene[47]. In strong aqueous acid solution, only one deuterium is incorporated[11, 48].

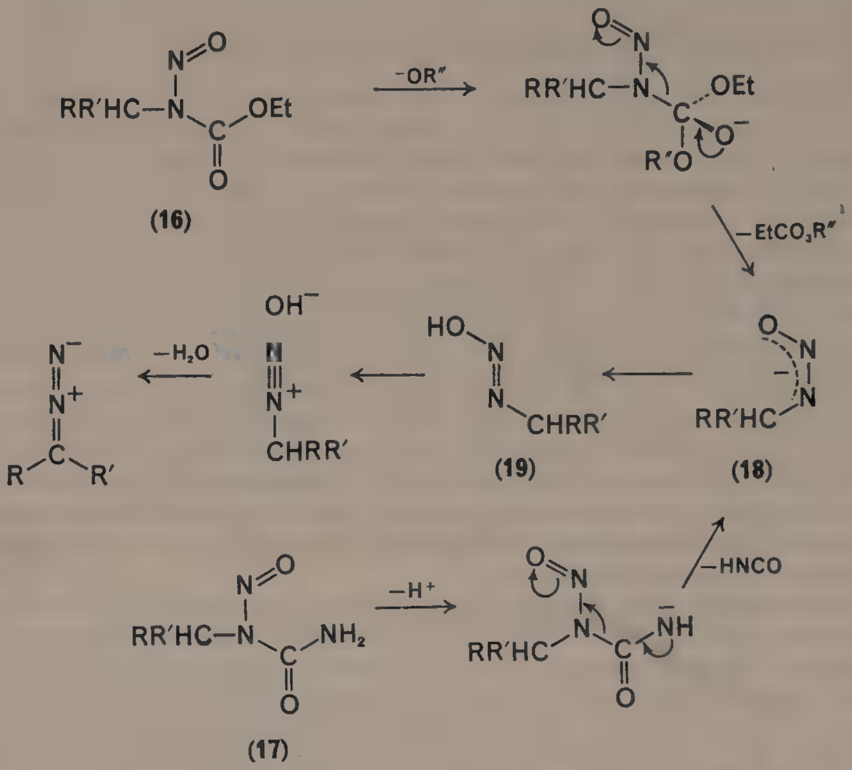
That the exchange occurs via the conjugate base of diazomethane (see Section IV) cannot be excluded *a priori*. However, the implication of acidic catalysis by weak acids, but not by D_3O^+, suggests that the determining factor is the strength of the conjugate base of the catalyst. Certain diazocarbonyl compounds, **12** [32], **14** [49]and benzoyl phenyldiazomethane (**15**)[50, 51] have been shown to undergo protonation by water and, at least in the first two cases, subsequent regeneration by the hydroxide ion. For bases stronger than water, deprotonation is favoured over nucleophilic substitution. In support of this argument, the methanol isolated after the hydrolysis of diazomethane in dioxane–D_2O is monodeuterated on carbon when the hydrolysis is carried out at pH 3, trideuterated for pH 13, and contains a mixture of mono-, di- and trideuterated species when the reaction is performed between pH 6 and 7 [52].

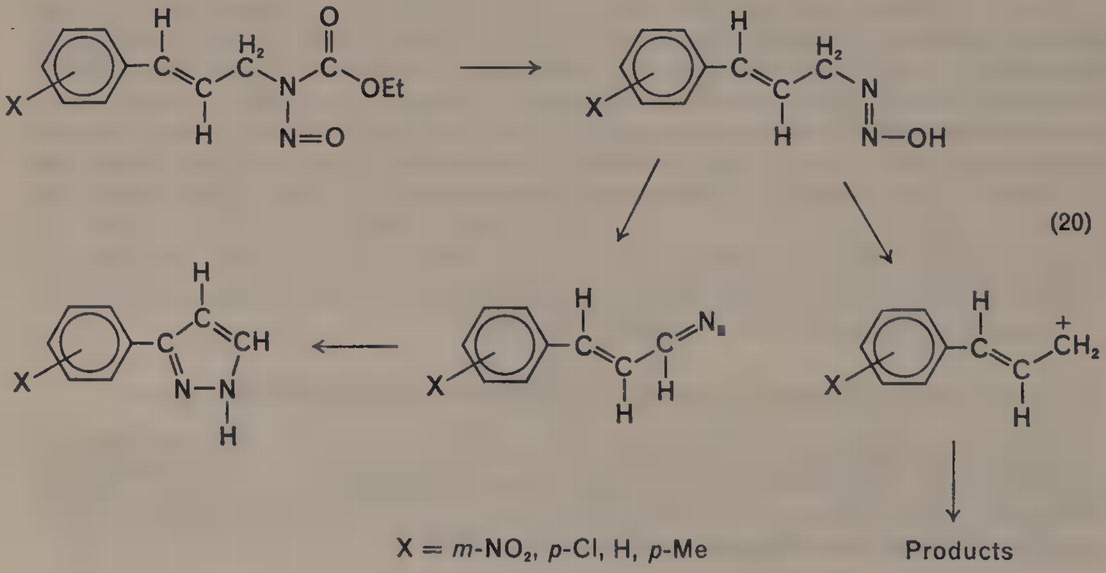
The same phenomenon has been more precisely defined by a study of the methanolysis of diazobutane[53]. In neutral or acidic deuterated solution there is no exchange, however in strongly basic solutions (up to 1·8 M-NaOMe) exchange is observed to the extent of 87%. The approximate inverse proportionality of the observed overall rate to methoxide ion concentration (except at concentrations 1·0 M) suggests establishment of a partial pre-equilibrium dependent on base concentration. The alternative interpretation of base-catalysed exchange may be supported by the deviation from linearity of the ratio $CD_2HOMe : CDH_2OMe$ against $[OMe^-]$ at base concentrations of approximately 1·5 M. At these concentrations, however, it is difficult to decide what confidence can be placed in kinetic equations, not corrected for variations in the activity of the substrates[54].

4. Base-catalysed decomposition of *N*-nitrosourethanes and ureas

The alkanediazonium ion–diazoalkane equilibrium in basic solution can be established by preliminary formation of the acidic species by another reaction sequence. This situation is realized, in principle, by the decomposition in basic solution of *N*-nitrosourethanes[55] (**16**) and ureas[56] (**17**).

The implication of diazotates (**18**) as intermediates in this scheme follows from their isolation in the reactions of differently substituted *N*-nitrosourethanes in ethereal solution[53, 57], and their subsequent conversion into previously obtained products in basic protic solvents. The exact status of the diazohydroxide (**19**) and the diazonium ion, either free or in an ion pair, as precursors of the diazoalkane will be discussed later. The reactions of the diazohydroxide leading to the formation of the diazoalkane compete with its decomposition to nitrogen, solvated hydroxide ions and carbonium ions. Thus the yields of substituted diazoalkanes will be dependent not only on the substituent effect on their stability, but also on that of the





(20)

X = m-NO_2, p-Cl, H, p-Me

alternative carbonium ions. For example, in the formation of pyrazoles derived from diazoalkenes[58], the observed effect of electron-withdrawing groups of increasing the pyrazole yield is compatible with destabilizing the incipient carbonium ion, or in facilitating development of the negative charge in the transition state for diazoalkane formation. The effects of alkyl substituents, complementary in stabilizing carbonium ions and inductively destabilizing the diazo group, are evident for examples **20**, **21**, **22**, **26** and **27** of Table 1.

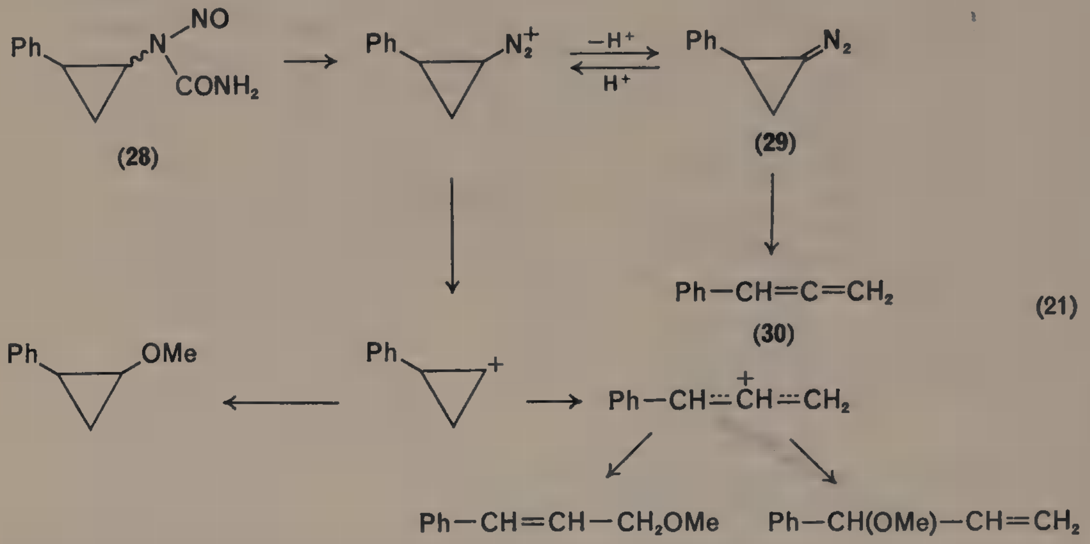
TABLE 1. Yields of diazoalkanes from basic hydrolysis of the corresponding diazotates

$RR'CN_2$	R	R'	$[OH^-]$	Yield (%)	Reference
20	H	H	unknown	100	57
21	*n*-Pr	H	3 M	60	53
22	*n*-Octyl	H	3 M	31	53
23	Cyclopropyl	H	3 M	0	59
24	Ph	H	unknown	100	57
25	Vinyl	H	3 M	100	53
26	*n*-Hexyl	CH_3	3 M	3 [a]	60
27	Cyclohexyl		3 M	0	53
28			3 M	100 [a]	53

[a] From deuterium-incorporation experiments.

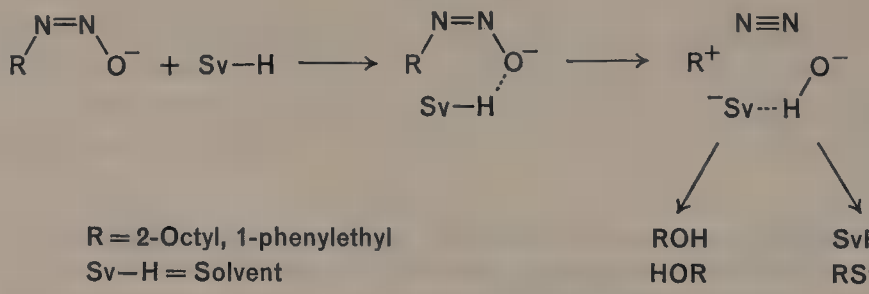
Separation of the two effects can apparently be made for examples **23**, **24**, **25** and **28**. The stability of the cyclopropyl carbinyl cation[61] accounts for its preferential formation, and, on the contrary, the relative instability of the cyclopropyl cation[62] allows the establishment of the diazo compound **28** as an intermediate in the reaction. The stability conferred to alkyl carbonium ions by substituent phenyl or alkyl groups does not, however, determine the direction of reaction of the diazohydroxides. The quantity of phenyl- and vinyl-diazomethane formed may rather be due to a dominant stabilization of the transition state in the base-catalysed elimination, reflecting a conjugative stabilization of the product diazo group. The above argument[53] is entirely dependent on the assumption that the benzyl and allyl cations are as readily formed in water as is the 2-octyl cation which is generated in preference to 2-diazooctane. Solvolysis rates in nucleophilic solvents, where the bimolecular contribution to the rate-determining step is unknown[63], offer debatable support to this thesis. Gas-phase heats of formation from the corresponding alkanes[64] (ΔH_f $Ph-\overset{+}{C}H_2 =$ 854 kJ, $H_2C{=}CH-\overset{+}{C}H_2 = 940$ kJ, $C_3H_7-\underset{\overset{|}{H}}{\overset{+}{C}}-CH_3 = 906$ kJ) in the absence of solvational energies offer a support only for the benzyl cation. For this particular example the alternative diazoalkane product was obtained at unspecified base concentration ('five- to six-fold excess'); at a lower, equally unspecified base concentration, there was minor formation of benzyl alcohol.

That the diazoalkane formation is dependent on base concentration and strength is supported by the observation that when cyclohexane diazotate is quenched in methanol rather than water, providing a more basic medium, diazocyclohexane is observed[53]. It is worth noting, in this respect, that cyclopropyldiazomethane (**23**), completely by-passed in the aqueous diazotate hydrolysis, is prepared by reaction of the corresponding *N*-nitrosourethane with a concentrated solution (2 M) of sodium triethylene glycolate in triethylene glycol at −25 °C [59]. For the octane-2-diazotate system, the inferred yields of diazooctane increased from 3% to 15% with increasing base concentration[60]. The effect of base on the partition between the two reactions in methanol was examined by Kirmse for a series of cyclopropyl[65, 66, 67] and alkenyl[68] substituted diazoalkanes.



(21)

The yield of allene **30**, derived from diazoalkane **29**, increased from 0·52% to 80% for both *cis* and *trans* starting ureas (**28**) with increasing base strength. The importance of the diazonium ion, either free or in an ion pair as the immediate precursor of the diazoalkane, as depicted above, is controversial. As regards secondary alkyl diazotates, it has been established from results with optically pure and labelled substrates that carbonium ion products are not derived from diazonium ions, but rather from a solvated diazotate species[69]

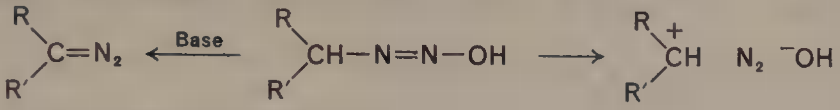


R = 2-Octyl, 1-phenylethyl
Sv—H = Solvent

(22)

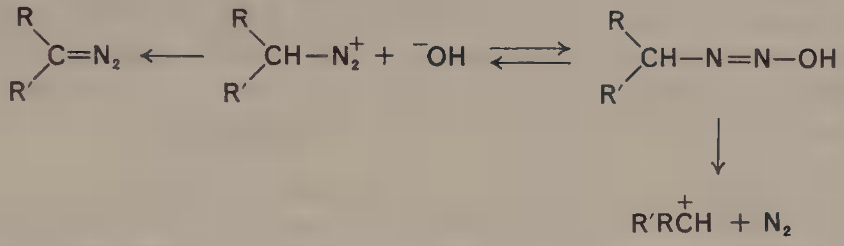
The influence of diazo group and carbonium ion stability on the reaction course implies that both sets of products are formed from a common intermediate—the diazotate species favoured by Moss[69] or free diazonium ion preferred by Kirmse[56, 70].

An alternative explanation is that an equilibrium between the two intermediates is established rapidly relative to the two competing product-forming reactions



(23)

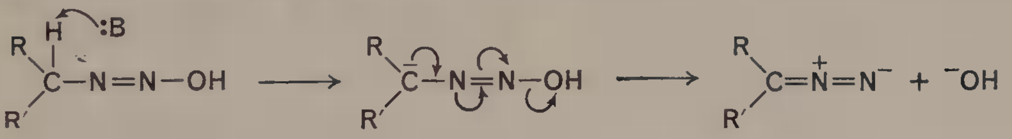
or



(24)

18-Oxygen labelling experiments showed, among other things, that this equilibrium is not established in secondary diazotate hydrolysis[69]. As the benzyl and alkyl cation-forming processes are presumed to have activation energies lower than, or equivalent to, those for secondary cations, the equilibrium must also be excluded in these cases (assuming equivalent diazonium ion stability). This conclusion is in part supported by the observed base catalysis. The equilibrium will be displaced to the diazohydroxide form by increasing base concentration. This, combined with the expected first-order dependence of the proton abstraction reaction on base, would give an overall zero-order dependence for diazoalkane formation, which is not observed. The irrefutable evidence, from trapping experiments[70] for free diazonium ions in the systems, is restricted to cyclopropyl diazonium ions, which may arise from diazocyclopropane rather than diazohydroxide precursors.

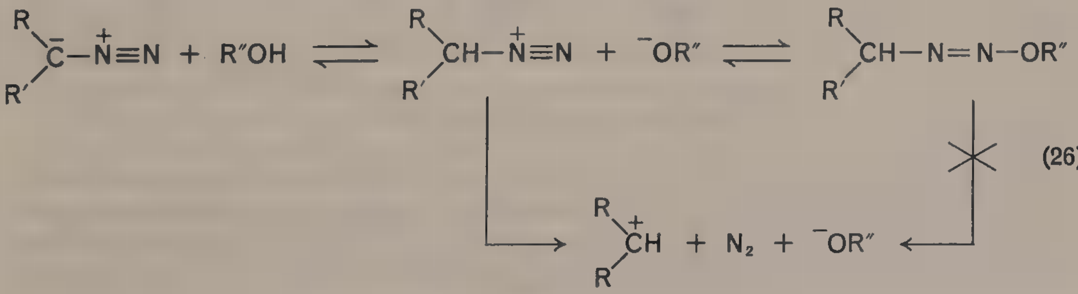
The partition of the two reaction sequences appears to occur at the diazotate–diazohydroxide stage. The mechanism for the base-catalysed elimination of water has been formulated as a two-step process[58].



(25)

This however would appear to present no advantages over a concerted scheme similar, in essence, to that proposed for the base-catalysed cleavage of **15**[71].

It should be noted that when diazoalkanes are decomposed in basic alcohol solutions[53] diazonium ions, and not diazotic esters analogous to **19**, are the carbonium ion precursors. This follows from the inverse-order dependence of reaction rate on base concentration (rather than zero order).



(26)

In conclusion the partition of diazotates in basic solution, between diazoalkane and carbonium ion products, appears to be dominated by the base strength, and substituent effects on the carbonium ions, rather than by diazonium ion acidity.

5. Acidic species alkylated by diazoalkanes

The acid strength and reaction conditions necessary to protonate diazoalkanes vary largely with their substituents. Whereas diazomethane methylates readily and smoothly carboxylic acids and phenols, their reactions with diazoesters and diazoketones require gentle warming. Likewise, dialkyloxonium salts are efficiently methylated in dichloromethane[72] according to:

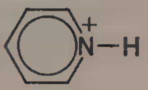
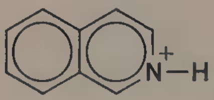
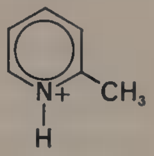
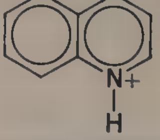
$$(CH_3)_2\overset{+}{O}H[SbCl_6^-]+CH_2N_2 \longrightarrow (CH_3)_3\overset{+}{O}[SbCl_6^-]+N_2 \qquad (27)$$

In contrast, the efficiency of quaternization of protonated amines, by diazoacetophenone (31) in alcohol, varies apparently as a function of the acid strength as indicated in Table 2.

(31)

(28)

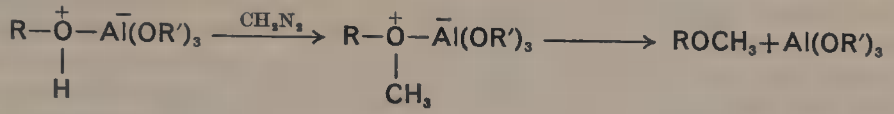
Table 2. Efficiency of quaternization of pyridinium salts by **31** (equation 28)

Acid	pK_a[74]	Yield[73] (%)
	5·2	88
	5·4	68
	5·95	27
	4·90	21[a]

[a] See discussion in Section II.B.6.

Diazomethane reacts at room temperature with alcohols[75], the efficiency and rapidity of reaction increasing with substitution of electron-withdrawing groups in the latter. Reduction of the already feeble acidity of the hydroxyl group by solvation may prevent reaction; thus trichloroethanol is methylated in heptane but not in ether[76].

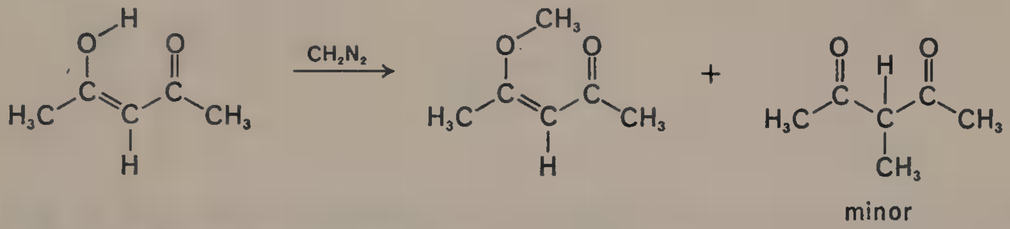
On the other hand, increase of the proton acidity by prior complexation of the hydroxyl oxygen with an electrophilic species dramatically increases the efficiency of the process[75, 77].



$$R-\underset{\displaystyle H}{\overset{+}{O}}-\overset{-}{Al}(OR')_3 \xrightarrow{CH_2N_2} R-\underset{\displaystyle CH_3}{\overset{+}{O}}-\overset{-}{Al}(OR')_3 \longrightarrow ROCH_3+Al(OR')_3 \qquad (29)$$

Similar catalysis, preferably by boron trifluoride, renders amines sufficiently acidic to undergo this reaction[78, 77].

Whereas certain carbon acids such as acetylacetone react with diazoalkanes through their enolic forms[79] (equation 30), sufficiently acidifying but non-enolizable substituents such as sulphone[80, 81] and nitro[82] groups allow direct methylation on carbon.



(30)

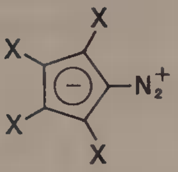
6. Kinetic basicity of aliphatic diazo compounds

In contrast to the paucity of thermodynamic data related to diazoalkane basicity, there exists a wealth of relevant kinetic data. This results from the facility of rate measurements by following the evolution of nitrogen, or currently by monitoring the diazo ultraviolet absorptions. A comparative analysis of the data is not, however, as straightforward as their measurement. The second-order rate constant may be simply a measure of the protonation rate (equation 19) as for an $A S_E 2$ reaction.

Alternatively, for A-2 and A-1 mechanisms, it may be expressed by equation (17) where k_2 is respectively dependent on or independent of the nature and concentrations of nucleophiles present. Examples of all three kinetic forms and intermediate situations[32, 33, 83] have been found for acid-catalysed diazoalkane hydrolysis[12]. Consequently in the ignorance of the exact mechanism, caution should be exercised in drawing conclusions as to structure/reactivity relationships. For example, in the reaction of protonated pyridines with **31** (Table 2), the reduced yield for the 2-picolinium ion relative to the pyridinium homologue may represent not only its inferior acidity, but also a diminished nucleophilicity of its conjugate base due to steric hinderance. Independent evidence suggests that this diazo compound hydrolyses by an A-2 mechanism[38], although a conflicting opinion has been expressed[84].

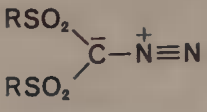
The increasing reactivity in the order diazomethane–diazoethane–diazopropane towards phenol in toluene[85] may not only be a reflection of increased basicity, but also of more rapid nitrogen loss from the intermediate diazonium cation. The inertness of a diazo compound to acid, for example diazomalonitrile to sulphuric acid in anhydrous acetonitrile[86] allows no extrapolation to its behaviour in a protic nucleophilic medium.

Similarly, the acidity scale developed on the basis of reaction rates of a series of acids with weakly basic diazoalkanes[87–89], such as **32** and **33**, in chlorinated hydrocarbon solvents, is not necessarily a function uniquely of acid strength. Such a situation would be realized only if the protonation of the diazoalkanes in question were rate determining, or if the decomposition of the diazonium ion formed were unassisted. In the first case the observed rate constants would indeed be measures of kinetic acidities; in the second, in that they would depend on the equilibrium concentration of the diazonium ion, they would be measures of thermodynamic acidity. In view of the quantitative conversion of 1,1,1,3,3,3-hexafluorodiazo-2-propane (**34**) into its conjugate acid in highly acidic media[17], and the subsequent S_N2 type displacement of nitrogen from the latter by the feebly nucleophilic fluorosulphonate anion, both these possibilities seem to be unlikely. It should be noted that the observed linear $\log k_{obs}$–pK_a plots[87–89] are consistent also with the remaining A-2 type mechanistic possibility. Both the thermodynamic strength of the acid, and the kinetic nucleophilicity of its conjugate base which are included in the rate constant, can be related to the aqueous acid strength by linear free energy relationships.



(32)

X = Cl, Ph



(33)

R = Ph etc.

$(CF_3)_2CHN_2^+$

(34)

The data in Table 3, and the subsequent discussion, refer to hydrolysis of diazoalkanes where protonation by the hydrated proton has been shown to be rate determining. For several substrates, data for various sets of reaction conditions are included as minor differences in the latter can significantly affect the former.

The reactivity of differently substituted stabilized diazo compounds within the same class towards strong acids in non-nucleophilic solvents has been correlated with the N=N stretching frequency in the i.r. spectrum[107]. The hydrolysis rates for series of primary diazoketones and sulphones have been similarly correlated[108]. Generally, the higher the absorption frequency, the more the electron distribution described by the form $\overset{-}{C}-\overset{+}{N}\equiv N$ is predominant in the ground state[109]. This is favoured by electron-withdrawing groups attached to the carbon; *ipso facto*, these decrease the acid lability. For reactions that proceed by a rate-determining protonation step there is a general trend in this sense[108], but extrapolation from one class of compounds to another allows only qualitative comparison[105] of ground-state effects by this means.

In the series $PhCN_2R$ the protonation rate decreases in the order R = H, Ph, CN, CF_3, $Si(Ph)_3$, $(EtO)_2PO-$, $(Ph)_2PO-$, $R'O-\overset{\overset{O}{\|}}{C}-$, $-R'\overset{\overset{O}{\|}}{C}-$. This variation represents well the expected different degrees of stabilization of the ground state, by electron withdrawal (except for the triphenylsilyl substituent which may also provide a steric retardation of the reaction).

It is interesting to note that for the unique series where the effect on the protonation rate of an alkyl group relative to a hydrogen substituent has been directly measured, the protonation of 1-*p*-nitrophenyldiazoethane is slower by a factor of almost 10 than that of *p*-nitrophenyldiazomethane. The substitution of a methyl group has apparently less effect for diazoketones. Whereas protonation rates of primary diazoketones are normally inaccessible, that of diazoacetone has been measured by hydrogen isotopic exchange rates[101]. Furthermore, in the hydrolysis of 7-(2′-diazo-)acetyl-bicyclo[2.2.1]hept-2-ene (**37**), the protonation is rate determining due to acceleration of the subsequent nucleophilic displacement of nitrogen by participation of the neighbouring double bond[100]. In both cases, protonation is

TABLE 3. Kinetic parameters for proton transfer from H_3O^+ to diazoalkanes

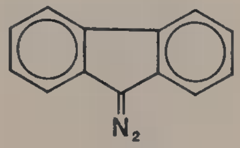
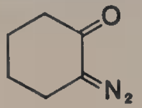
Substrate	Solvent	T (°C)	μ^a	k_2 (l mol^{-1} sec^{-1})	k_{H_2O}/k_{D_2O}	$\Delta H^{\neq}$	$\Delta^{\neq}$	Reference
$^-O_2CCN_2H$	A	25	$1{\cdot}1\times10^{-1}$	$6{\cdot}5\pm1\times10^4$				32
$C_6H_5CN_2H$	B	0	$2{\cdot}0\times10^{-3}$	$7{\cdot}5\times10$	2·64			90
p-$NO_2C_6H_4CN_2H$	B	0	$2{\cdot}0\times10^{-3}$	$2{\cdot}4$				90
	B	20	$2{\cdot}0\times10^{-3}$	$1{\cdot}3\times10^{\,b}$	2·81	56·6	−39·1	90
	C	20	$4{\cdot}0\times10^{-4}$	$8{\cdot}3^{\,c,\,d}$	3·8			91
p-$NO_2C_6H_4CN_2CH_3$	C	20	$2{\cdot}0\times10^{-3}$	$9{\cdot}1\times10^{-1\,c,\,d}$	2·70			91
$C_6H_5CN_2C_6H_5$ **(35)**	C	20	$2{\cdot}0\times10^{-3}$	$5{\cdot}5\times10^{-1\,c,\,d}$				92
	C	20	0	$5{\cdot}4\times10^{-1\,e}$				92
	D		$1{\cdot}9\times10^{-1}$	$7{\cdot}5\pm0{\cdot}2\times10^{-1}$				93
	E	29·5	$1{\cdot}4\times10^{-4}$	$3{\cdot}8\times10^{\,c}$	3·41			94
	E	29·5	$1{\cdot}0\times10^{-4}$	$2{\cdot}8\times10^{\,c,\,f}$	2·28			95
 **(36)**	F	25	5×10^{-2}	$6{\cdot}7\times10^{-2\,c,\,d}$	1·37	76·2	-20 ± 6	96
	C	20	5×10^{-2}	$3{\cdot}5\times10^{-2\,c,\,\blacksquare}$				92
$C_6H_5CN_2CF_3$	B	25	9×10^{-2}	$1{\cdot}3\times10^{-1}$	2·13	61·3	−67	18
$C_6H_5CN_2CN$	A	25	5×10^{-1}	$2{\cdot}5\times10^{-3}$	2·2			97
$CH_3COCN_2CH_3$	A	25	5×10^{-2}	$7{\cdot}4\times10^{-1}$	2·5			98
	G	25	1×10^{-2}	$3{\cdot}1\times10^{-1}$	2·5	67·2	−33	99
$CH_3COCN_2C_2H_5$	G	25	1×10^{-2}	$2{\cdot}4\times10^{-1\,c}$	2·4			99
CH_3COCN_2Pr-i	G	25	1×10^{-2}	$4{\cdot}8\times10^{-1\,c}$	2·6			99
	B	25	1×10^{-2}	$4{\cdot}2\times10^{-1\,c}$	2·0			99

TABLE 3 (*cont.*)

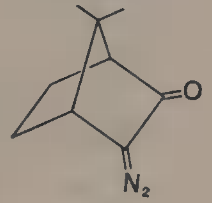
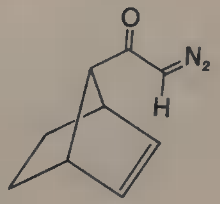
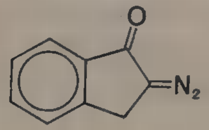
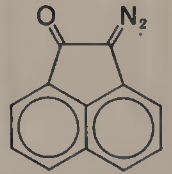
Substrate	Solvent	T (°C)	μ^a	k_2 (l mol^{-1} sec^{-1})	k_{H_2O}/k_{D_2O}	$\Delta H^{\neq}$	$\Delta S^{\neq}$	Reference
	G	25	5×10^{-3}	$2{\cdot}4^{c}$	1·9			99
 (37)	B	25	1×10^{-1}	1·67 [illegible]	1·8			100
CH_3COCN_2H	A	0	1×10^{-1}	$2{\cdot}2 \times 10^{-1\,g}$				101
$C_6H_5COCN_2CH_3$	C	20	1×10^{-2}	$3{\cdot}3 \times 10^{-2\,c,\,d}$	2·42			102
p-$NO_2C_6H_4COCN_2CH_3$	C	20	1×10^{-2}	$5{\cdot}6 \times 10^{-3\,c,}$ [illegible]	2·3			102
	B	25	5×10^{-1}	$2{\cdot}8 \times 10^{-2\,c,\,d}$	2·0			99
	C	2·0	7×10^{-2}	$8{\cdot}1 \times 10^{-3\,c,\,d}$	2·3			103
p-$NO_2C_6H_4COCN_2C_2H_5$	C	20	7×10^{-2}	$6{\cdot}6 \times 10^{-3\,c,\,d}$	2·4			103
p-$NO_2C_6H_4COCN_2$Pr-*n*	C	20	7×10^{-2}	$3{\cdot}6 \times 10^{-3\,c,}$ [illegible]	2·4			103
p-$NO_2C_6H_4COCN_2$Pr-*i*	C	20	7×10^{-2}	$3{\cdot}9 \times 10^{-3\,c,\,d}$	2·4			103
	G	25	5×10^{-2}	$1{\cdot}5 \times 10^{-1}$	1·8			99

TABLE 3 (*cont.*)

Substrate	Solvent	T (°C)	μ^a	k_2 (l mol^{-1} sec^{-1})	k_{H_2O}/k_{D_2O}	$\Delta H^{\neq}$	$\Delta S^{\neq}$	Reference
	C	20	$2{\cdot}7\times10^{-1}$	$1{\cdot}1\times10^{-3\,c,\,d}$				92
$C_6H_5COCN_2C_6H_5$	C	20	2×10^{-1}	$2{\cdot}9\times10^{-3\,d}$	1·4			92
	C	20	1×10^{-1}	$2{\cdot}2\times10^{-3\,d}$				83
	A	25		$5{\cdot}3\times10^{-4}$	2·6	81·5	−29	50
$H_3CCOCN_2C_6H_4NO_2$-*p*	C	20	1×10^{-1}	$6{\cdot}7\times10^{-5}$	1·5			83
$C_2H_5OCOCN_2CH_3$	A	25	1×10^{-3}	$1{\cdot}9\times10$	2·5			98
	A	25	5×10^{-2}	$2{\cdot}1\times10$				98
$CH_3OCOCN_2C_6H_5$	B	25	5×10^{-1}	$8{\cdot}5\times10^{-3}$	1·6			104
$C_2H_5OCOCN_2C_6H_5$	C	20	1×10^{-1}	$2{\cdot}1\times10^{-3}$				105
$C_2H_5OCOCN_2C_6H_4NO_2$	C	20	8×10^{-1}	$3{\cdot}2\times10^{-4\,c,\,d}$				83
$(C_6H_5)_3SiCN_2C_6H_5$	C	20	1×10^{-1}	$6{\cdot}9\times10^{-2\,c,\,d}$	2·5			106
$(C_6H_5)_2POCN_2C_6H_5$ (38)	C	20	1×10^{-1}	$4{\cdot}2\times10^{-3\,c,\,d}$	2·3	84·0	−25	105
$(C_2H_5O)_2POCN_2C_6H_5$ (39)	C	20	5×10^{-2}	$9{\cdot}0\times10^{-3\,c,\,d}$	1·7	82·3	−29	105

Solvent: A, water; B, dioxane–water 60–40 v/v; C, dioxane–water 2–1 v/v; D, dimethylsulphoxide–water 4–1 w/w; E, water 2·2 M in acetonitrile; F, ethanol–water 93·8% w/w; G, dioxane–water 40–60 v/v; H, toluene.

[a] Ionic strength mol/l.
[b] Extrapolated from Arrhenius plot.
[c] Measured with one acid concentration only.
[d] Reaction followed by nitrogen evolution.
[e] Value extrapolated from data for differing salt concentrations.
[f] The acid added, *p*-toluene sulphonic acid may not be completely dissociated in this system.
[g] Measured by hydrogen isotopic exchange.

three- to four-times more rapid than for methyl-substituted diazoketones measured under the same conditions. This behaviour contrasts with the accelerating influence of alkyl substitution on the overall reaction of diazoalkanes with phenol in toluene[85].

The stabilizing effect of benzoyl relative to carboethoxy groups is dependent on the nature of other substituents present. Thus the effect of their different electron-withdrawing capacity is diminished by introduction of an additional stabilizing group:

$$\frac{k_{\mathrm{CH_3CN_2CO_2C_2H_5}}}{k_{\mathrm{CH_3CN_2COC_6H_5}}} \simeq 570 \qquad \frac{k_{\mathrm{C_6H_5CN_2CO_2C_2H_5}}}{k_{\mathrm{C_6H_5CN_2COC_6H_5}}} \simeq 1{\cdot}0 \tag{31}$$

The more rapid proton–deuterium exchange of primary arylsulphonyldiazomethanes relative to the corresponding diazoketones[40], though not a direct measure of protonation rate, indicates a superior stabilization provided by the carbonyl group.

The variation of protonation rate with nuclear substituents in several series of aryldiazoalkanes give normally good correlations with Hammett σ values (Table 4). The rho (ρ) values derived therefrom are generally in the range $-1{\cdot}5$ to $-1{\cdot}8$, indicating a large sensitivity to electron availability. The correlation in the diazofluorene[111] (**36**) examples with Hammett parameters modified as by Taft[112] is indicative of the non-benzenoid nature of the aromatic substituent site rather than any peculiarity of the proton transfer. On the other hand, the correlation for diaryldiazoketones[83] with the σ^+ parameters of Brown[113] is inconsistent with the simply visualized C-protonation mechanism. It should be noted however that as the rate constants for the hydrolysis of these compounds are successfully correlated with those for aryldiazophosphonate esters[105], which are themselves correlated with ordinary σ values, there appears to be a lack of sensitivity to the constants used. Likewise while the one electron oxidation potentials of several series of aryl-substituted diazo compounds correlate with σ^+[114, 115], for diaryldiazoalkanes they are also proportional to the logarithms of the protonation rates, themselves dependent on σ.

Other traditional indices of transition-state structure in relation to reactants and products are not immediately definitive. It is a commonly held thesis that primary hydrogen isotope effects for proton transfer attain their maximum value for approximately 'symmetric' transition states, with a continuous decline for increasingly exo- or endo-energetic reactions[116]. One might then expect decreasing overall solvent isotope effects for increasingly 'uphill', hence slow, reactions for a series of related compounds. This is not apparent from the data presented, although within a series of substituted aryldiazoketones there is some relation[83]. With specific reference to 3-diazobutan-2-one (**14**) and ethyl diazopropionate (**13**), despite a difference in reaction rate of 28, the measured solvent isotope effects are 2·5 and 2·46 respectively[98].

Furthermore, an analysis of this global isotope effect, from experiments in H_2O–D_2O mixtures[117], for transfer to the two substrates respectively, produces almost identical fractionation factors[118], $\phi_1 = 2{\cdot}1 \pm 0{\cdot}03 \times 10^{-1}$ and $2{\cdot}08 \times 10^{-1}$, and $\phi_2 = 7{\cdot}78 \pm 0{\cdot}04 \times 10^{-1}$ and $7{\cdot}85 \pm 0{\cdot}12 \times 10^{-1}$, for the proton 'in flight' and residual protons of the lyonium species. The latter results give values of α_i, a parameter describing the position of the transition state along the reaction coordinate, of 0·27 and 0·29, surprisingly close to that of 0·30 for the much more reactive diazotate anion[117] (**12**). This similarity is extended to the values of the exponent α_{B} in the Brönsted relation

$$\log k_{\mathrm{HA}} = \alpha_{\mathrm{B}} \log K_{\mathrm{HA}} + C \tag{32}$$

Here K_{HA} is the dissociation constant of an acid, whose reaction with a substrate has a rate constant k_{HA}, and α_{B}, describing the sensitivity of the latter to the former,

TABLE 4. Hammett rho (ρ) values for diazoalkane protonations

Substrate series	Substituent constant	Solvent[a]	Number of substituents	ρ	Acid	Reference
$XC_6H_4CN_2H$	σ	B	3	$-1{\cdot}6$	H_3O^+	90
$C_6H_5CN_2C_6H_4X$	σ	D	4	$-1{\cdot}10$	H_3O^+	93
	σ	D	4	$-1{\cdot}43$	$HCCl_2CO_2H$	93
	σ	D	4	$-1{\cdot}34$	H_3CCO_2H	93
	σ	D	4	$-1{\cdot}36$	C_6F_5OH	93
	σ	D	4	$-1{\cdot}30$	3,4,5-$Cl_3C_6H_2OH$	93
	σ	E	11	$-1{\cdot}99$	H_3O^+	95
	σ	H	11	$-1{\cdot}57$	$C_6H_5CO_2H$	110
$CH_3CN_2COC_6H_4X$	σ_p	C	4	$-1{\cdot}0$	H_3O^+	102
$C_6H_5CN_2COC_6H_4X$	$\sigma_p + R(\sigma_{p^+} - \sigma_p)$	C	7	$-0{\cdot}812$	H_3O^+	83
$XC_6H_4CN_2COC_6H_5$	σ_{p^+}	C	6	$-2{\cdot}05$	H_3O^+	102
$XC_6H_4CN_2PO(OC_2H_5)_2$	σ_p	C	5	$-1{\cdot}641$	H_3O^+	105
$XC_6H_4CN_2CF_3$	σ_p	B	4	$-1{\cdot}74$	H_3O^+	18
(36)	$(\sigma I + a\sigma R)$	F	11, 11, 13[b]	$-1{\cdot}63$–$-2{\cdot}1$[b]	H_3O^+	111

[a] Solvent index given in Table 3.

[b] Data for three series of substituents in positions 2, 3 and 4.

has been interpreted in the same fashion as α_t above. The values in question, for reaction with carboxylic acids, are 0·61 ± 0·03, 0·59 ± 0·04 and 0·51 ± 0·03 for **14**, **13** and **12** respectively. The identity of these values, within experimental error, for the diazoketone and ester is surprising in view of their reactivity difference and the values, reflecting the degree of proton transfer in the transition state, appear incompatible with such a thermodynamically unfavourable reaction. (The acid dissociation constants of the diazonium ions formed are $<10^5$, $<5\times10^3$, <1, whereas K_{HA} of the acid catalysts $<6\times10^{-4}$.) The disparity between the values of α_B and α_t is a result of the greater acid strength of the hydronium ion relative to carboxylic acids. For proton transfer from the stronger acid, the transition state is expected to be more 'reactant like', in the oft-quoted terms of the Hammond postulate[119] or its more quantitative formulation[29, 30], and to be characterized by a lower value of α.

A more refined free energy of activation–free energy of reaction relationship derived by Marcus[120], equations (34) and (35), has met with some success in the analysis of diazoalkane protonation data. For the reaction

$$\underset{\text{(I)}}{\mathrm{S+HA}} \underset{W^r}{\rightleftharpoons} \underset{\text{(II)}}{\mathrm{S\ldots H{-}A}} \underset{\Delta F_R{}^0}{\rightleftharpoons} \underset{\text{(III)}}{\mathrm{S^+{-}H\ldots A^-}} \underset{W^p}{\rightleftharpoons} \underset{\text{(IV)}}{\mathrm{S^+{-}H+A^-}} \qquad (33)$$

$$\Delta F^{\ddagger}_{HA} = W^r + \Delta F^{0\ddagger}\left(1+\frac{\Delta F^0_R}{4\Delta F^{0\ddagger}}\right)^2 \quad \text{for } 1>\frac{\Delta F^0_R}{4\Delta F^{0\ddagger}}>-1 \qquad (34)$$

$$\Delta F^{\ddagger}_{HA} = W^r \quad \text{for } -1>\frac{\Delta F^0_R}{4\Delta F^{0\ddagger}} \qquad (35)$$

$$\Delta F^{\ddagger}_{HA} = W^r + \Delta F^0_R \quad \text{for } \frac{\Delta F^0_R}{4\Delta F^{0\ddagger}}>1 \qquad (36)$$

$\Delta F^{\ddagger}_{HA}$ is the free energy of activation observed for the proton transfer from HA to S, i.e. from state (I) to state (IV).

W^r is the energy that must be supplied to form the 'reactant complex', i.e. state (II) from state (I), and involves diffusion, desolvational energy and distortion of bonds, if necessary to allow the proton to be transferred.

ΔF^0_R is the standard free-energy difference within the reaction complex, i.e. ΔF^0 state (III) $-$ ΔF^0 state (II) and is ostensibly equal to $\Delta F^0_{HA} - \Delta F^0_{SH^+}$.

$\Delta F^{0\ddagger}$ is the activation free-energy within the reaction complex for the case where $\Delta F^0_R = 0$.

From this equation, the rate of change of α with differing ΔF^0_R is inversely proportional to $\Delta F^{0\ddagger}$ which measures the inherent reactivity of the system. The data for the hydrolysis of **12** catalysed by phenols for which $\alpha = 0{\cdot}74$, carboxylic acids where $\alpha = 0{\cdot}51$ [121], and a series of protonated amines displayed in Figure 1 [122], allowed calculation of $\Delta F^{0\ddagger}$, and hence the other parameters of equation (35).

The corresponding parameters could be calculated from the data for hydrolysis of **13** and **14**, with inclusion, however, of the data for catalysis by H_3O^+ [34], and for hydrolysis of diphenyldiazomethane (**35**), catalysed by carboxylic acids and phenols[93]. The collected parameters are listed in Table 5.

The first points of note are the values of $\Delta F^0_{SH^+}$, i.e. the free energies of the reactions:

$$\mathrm{SH^+ + H_2O} \rightleftharpoons \mathrm{S + H_3O^+} \qquad (37)$$

In all cases they are unacceptably large: for **14** and **13** they correspond to dissociation constants 10^{10} mol/l and 10^8 mol/l, respectively, compared to independently estimated values of $<10^5$ mol/l and $<5\times10^3$ mol/l (Section B.2). Furthermore, the variation of the values derived for protonated diazoacetate anion indicates that these values do not have an absolute thermodynamic significance. Their significance is rather in the context of the reaction complex, in that differently organized reactant complexes, in solvational and hydrogen-bonded terms (state II), may be formed with different types of acids. Such a variation with acid type should dictate a variation in $\Delta F^{0\ddagger}$ and, more obviously, in W^{r}. Although the values of $\Delta F^{0\ddagger}$ obtained by the above analyses are probably underestimated due to simplifications made in the algebraic derivation[123, 124, 125], their significance, relative to the term W^{r} for related compounds, is nevertheless a valid point of comparison.

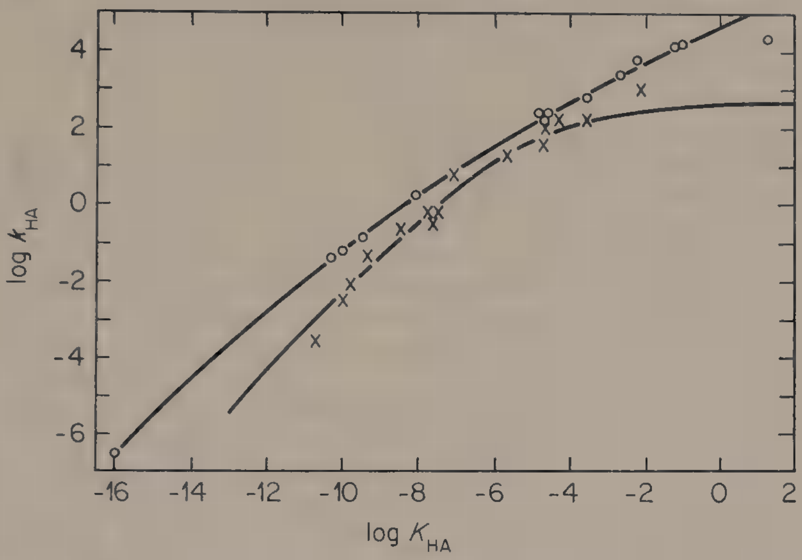


FIGURE 1. Predicted and experimental relations between log k_{HA} for the hydrolysis of **12**, and log K_{HA} of the catalysing acid. The ○ are points for oxygen acids, the × for protonated amines. The solid lines are predicted from equation (35) by insertion of the parameters listed in Table 5. Reprinted with permission from M. M. Kreevoy and S. Oh, *J. Amer. Chem. Soc.*, **95**, 4805 (1973). Copyright by the American Chemical Society.

TABLE 5. Parameters of the Marcus formalism for diazoalkane hydrolysis

Acid HA	Base	$\Delta F^{0\ddagger}$ (kJ/mol)	W^{r} (kJ/mol)	$\Delta F^{0}_{\mathrm{SH}^+}$ (kJ/mol)
$R^1R^2R^3NH^+$	**12**	5·9	58	−28·5
RCO_2H, ArOH	**12**	17·0	34	−14·7
RCO_2H, H_3O^+	**14**	8·0	71	−24·8
RCO_2H, H_3O^+	**13**	8·0	60	−19·8
RCO_2H, ArOH	**35**	5·5	72·3	−25 ± 2

The magnitude and variation of the values of W^{r} are the most significant features of the data in Table 5. They are markedly superior to the free energies estimated for the diffusion together of substrate and acid, and desolvation of the latter, i.e. between 37·2 kJ/mol[121] and 42 kJ/mol[125]. The difference in hydrolysis rate for **13** and **14** is seen thus to stem primarily from the different work terms W^{r}. It is also this term that represents the stabilizing effect of the aryl groups in **35**. The major

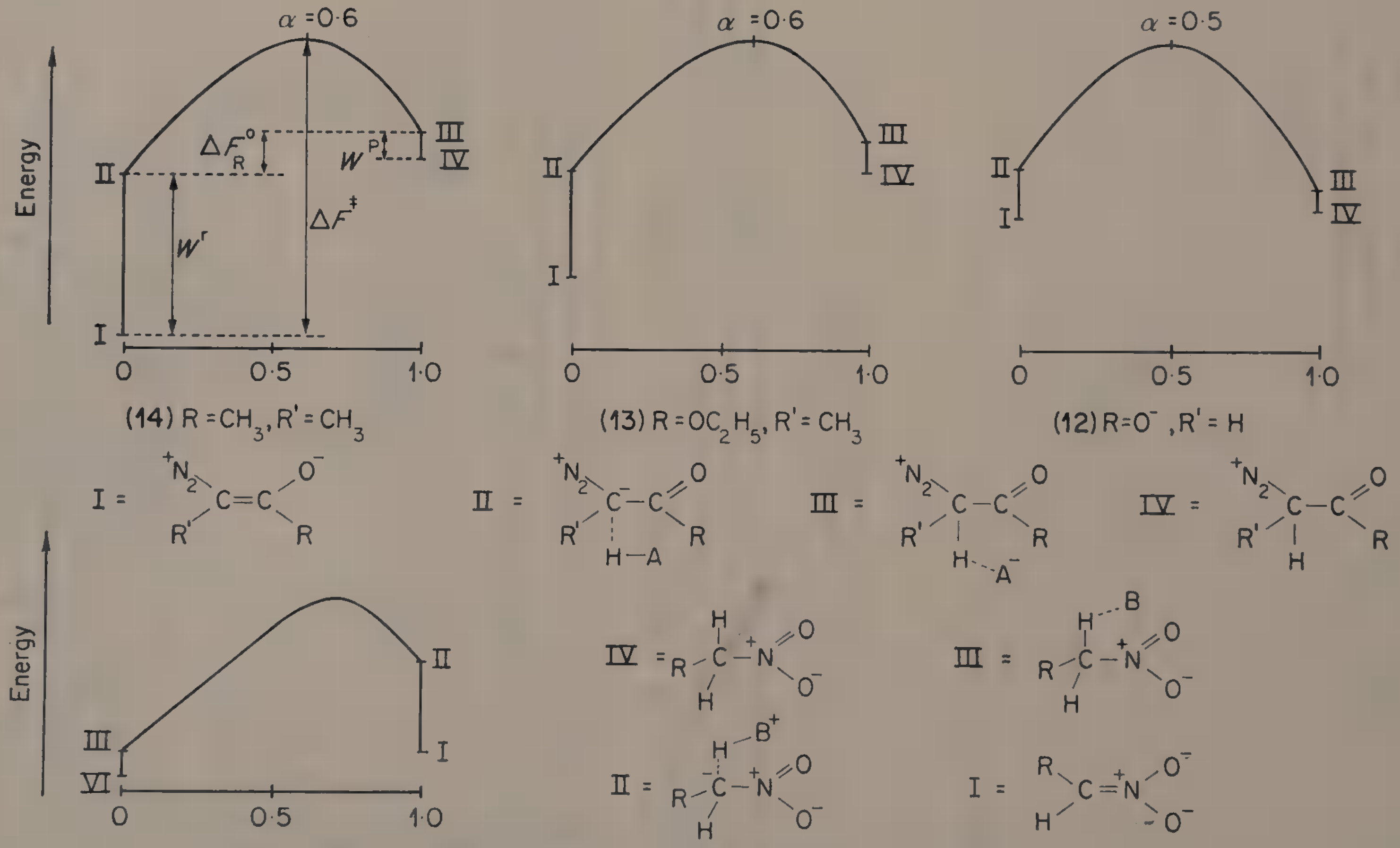


FIGURE 2. Schematic representation of the energy profiles for protonation of diazocarbonyl compounds, and for nitroalkane deprotonation.

kinetic consequence of these large work terms is that no matter how thermodynamically favoured be the proton transfer, depending on the acid strength, the rate can never approach the diffusion limit[122]. Differing interpretations of the high values of W^r in terms of hydrogen bond formation in the reaction complex[93, 122], and non-equilibrium solvated species[34] appear to be complementary. Evidence for the former is derived from an analysis of the Hammett ρ values for solvolysis of **35**. This value can be separated by use of certain approximations into ρW^r and ρc terms[93], the latter referring to the actual proton transfer, state (II) → state (III). It was found that the ρW^r term was by far the more important, indicating that the aryl substituent effects are primarily felt in the H-bond formation. The differences in hydrolysis rates of **12**, **13** and **14** can be attributed to differing degrees of electron delocalization from the diazo group into the adjacent carbonyl substituents. The reflection of these differences in the work terms W^r and not $\Delta F^{0\ddagger}$, for the same acid types, implies that this electron delocalization is reversed before the proton transfer occurs[34].

This interpretation demands an intermediate with negative charge located on the diazo carbon, but available for hydrogen bonding, and with a consequently rearranged solvation sphere. The energy changes along the reaction profile are illustrated schematically in Figure 2.

A corresponding energy diagram for nitroalkane deprotonation is included. This represents the same electron reorganization phenomenon, but in a reversed sense in that the tetrahedral carbanionic species (state III) formed by proton transfer, relaxes into the π-delocalized anion[126]. In this case, kinetic evidence for the scheme includes substituent effects of different magnitude on the transition state, leading to the carbanionic structure (III) and on the final state (IV) of the nitronate anion. This behaviour leads to values of $\alpha_B > 1$ and < 0, inexplicable conventionally[126, 124] in terms of 'degree of proton transfer'. Similar results of anomalous α values for diazonium ion deprotonation would be expected, but are as yet unobtainable.

The above diagram shows how differing diazo compounds, despite differences in overall reactivity towards acids, can have identical indices of transition-state position along the reaction coordinate within the 'reaction complex'.

III. LEWIS BASICITY OF ALIPHATIC DIAZO COMPOUNDS

A. Kinetics of Electrophilic Addition

The problems involved in defining a basicity scale for diazoalkanes towards Lewis acids are more complex than those concerning proton basicity. As before, instability of the adducts formed preclude direct determination of their equilibrium concentrations. Kinetic measurements may be subject to specific solvational effects. Uncertainty may exist as to the nature of the rate-determining step, or even of the electrophilic species. Whereas the effective catalytic species in the $Cu^{II}(CF_3CO_2)_2$-catalysed decomposition of diazoalkanes has been claimed[127] to be Cu^I, a contrary conclusion has been drawn concerning catalysis by $Cu^I[P(OR)_3]_n$ complexes[128]. $HgCl_2$ reacts with diphenyldiazomethane (**35**) more rapidly than HgI_2 in an ether–hexane solution[129], but less rapidly than $HgBr_2$ in tetrahydrofuran, and does not react at all in ether[129]. A qualitative order of reactivity of a series of electrophiles towards **35** in ether–hexane or acetonitrile has been established and is reproduced in Table 6.

The comparative reactivity of differently substituted diazoalkanes towards a single electrophile appears to follow their reactivity towards proton sources. Introduction of a *p*-methoxy substituent increases the reaction rate of diphenyldiazomethane (**35**) with $HgCl_2$ in tetrahydrofuran, and, whereas **35** is unaffected by the less electrophilic alkylmercury chlorides, diazomethane reacts readily in their presence[130]. Decomposition of *p*-toluyldiazomethane by zinc(II) halides is more rapid than that of phenyldiazomethane[131].

TABLE 6. Relative rates of catalysed diphenyldiazomethane decomposition in ether–hexane or acetonitrile solution. Reprinted with permission from D. S. Crumrine, T. J. Haberkamp and D. J. Suther, *J. Org Chem.*, **40**, 2274 (1975). Copyright by the American Chemical Society

Rate[a]	Catalyst
Very fast	$AlCl_3$, $TiCl_4$, $SnCl_4$, $BF_3.O(Et)_2$
Fast	$HgCl_2$, $Hg(NO_3)_2$, $CuBr_2$, $FeCl_3$, ZnI_2, CuIP(OPr-*i*)$_3$, CuCN[MeCN][b]
Moderate	HgI_2, $ZnCl_2$, CuCl[ether], $CuCl_2.2H_2O$, $SnCl_2.H_2O$, Hg_2Cl_2[MeCN]
Slow	CuCN, $CrCl_3.6H_2O$, $AlCl_3.6H_2O$
No reaction	Hg_2Cl_2[ether], $CdCl_2$, $Zn(CN)_2$, $Cr(OAc)_3.6H_2O$, $NiCl_2.6H_2O$, $Co(NO_3)_2.6H_2O$, $CoCl_2.6H_2O$, $MgCl_2.6H_2O$, $CaCl_2$, LiCl, LiBr, NH_4Cl

[a] Very fast, reacts completely in less than 1 min. Fast, reacts in less than 15 min. Moderate, reacts in less than 4 h. Slow, reacts while standing for 24 h.

[b] Brackets indicate solvents in which the reactivity order differed. Taken from Reference 129.

The related zinc(II) halide-catalysed decomposition of diphenyldiazomethane and diazofluorene in acetonitrile, proceeds by a rate-determining association[132] (equation 38)

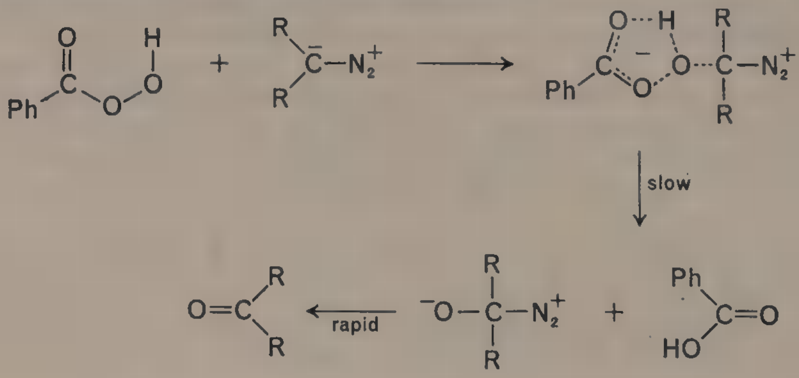
$$Ph_2CN_2 + ZnX_2 \xrightarrow{\text{slow}} Ph_2CN_2^+Zn^-X_2 \xrightarrow[-N_2]{\text{rapid}} [Ph_2C^+Zn^-X_2] \qquad (38)$$

In contrast, the adducts formed by each of these two substrates with copper(II) bromide are in equilibrium with the reactants before decomposition[133].

$$Ph_2CN_2 + CuBr_2 \rightleftharpoons Ph_2CN_2^+Cu^-Br_2 \xrightarrow[-N_2]{\text{slow}} [Ph_2C^+Cu^-Br_2] \qquad (39)$$

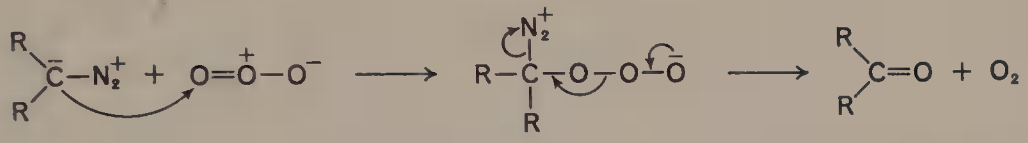
For the former reaction (equation 38 where X = Cl), it is interesting to note that the Hammett ρ values for diazofluorene and diphenyldiazomethane substituents are quite dissimilar ($-2{\cdot}45$ and approximately $-1{\cdot}0$), despite the minor (7-fold) difference in rate. Also striking is the observation that the order of kinetic catalytic efficiency, $ZnCl_2 < ZnBr_2 \ll ZnI_2$, does not follow the equilibrium Lewis acidity (towards dibenzacridine[132]).

A situation somewhat less complicated kinetically was encountered in the reaction of diphenyldiazomethane with peroxybenzoic acid[134].



(40)

The effect of substituents in the aryl groups of the diazoalkane on the reaction rate, as reflected by their ρ value of $-0{\cdot}96$, is less marked than on the corresponding proton transfer reaction. That the electrophilic attack was indeed by oxygen and not by a proton, was supported by the similarity of the kinetic isotope effect $k_{\mathrm{RO_3H}}/k_{\mathrm{RO_3D}} = 1{\cdot}33$ and of the solvent dependence of reaction rate to those of other peroxide oxidations. A similar mechanism is probably operative for the reaction of peroxybenzoic acid with diazoketones[135]. Other examples of electrophilic oxygen attack on diazoalkanes are provided by the reactions of ozone[136] and singlet oxygen[137].



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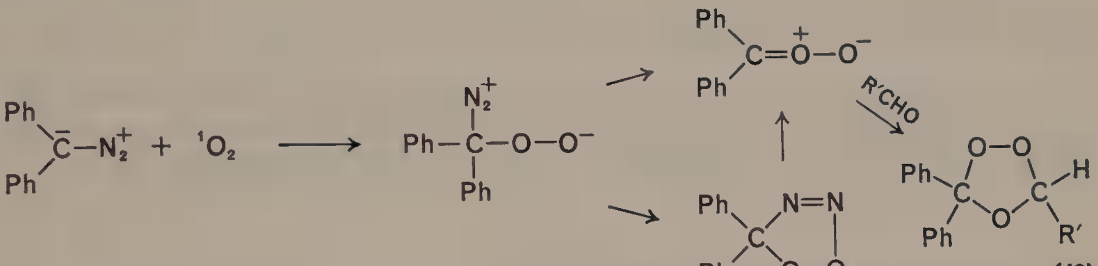
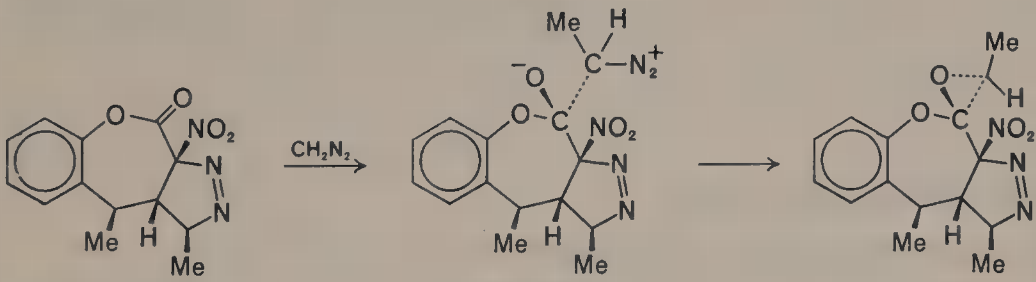


(42)

B. *Reactions with Electrophilic Carbon*

I. Reactions with esters

The reactions of diazoalkanes with electron-deficient carbon centres in carbonium ions[3], acid derivatives[138, 5] and carbonyl groups[3, 139, 140] have been reviewed frequently. In the last-mentioned category, there exist few examples of reaction with the carbonyl group of esters. Whenever electron-withdrawing substituent groups such as trihalomethyl[141] or nitro[142] are attached, the reactivity of the carboxyl group is sufficiently enhanced to allow addition and subsequent epoxide formation as for ketones.



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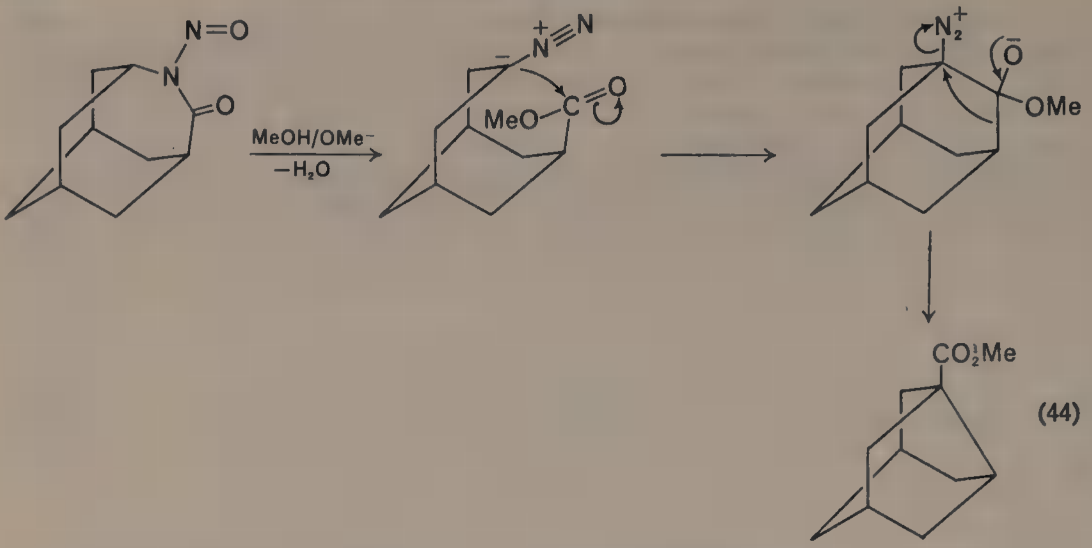
Addition of diazo groups to esters may be favoured by other circumstances, for example the close proximity of the two groups in the same molecule[143–145].

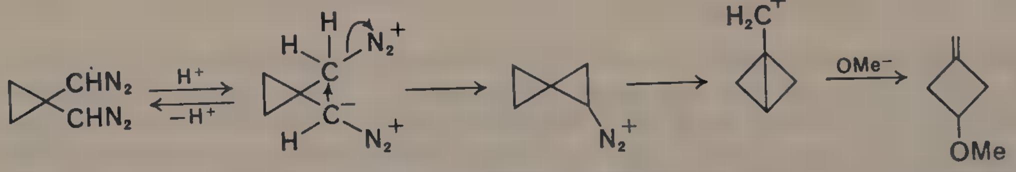


(44)

As these reactions were however carried out in the presence of base, necessary for the initial nitrosolactam decomposition, the possibility of nucleophilic catalysis, by attack on the terminal diazonitrogen[146], cannot be excluded (see Section V.C).

2. Reaction with aliphatic diazonium ions

Similar intramolecular proximity can lead to the reaction of an aliphatic diazonium ion with an unprotonated diazo group[147, 148].



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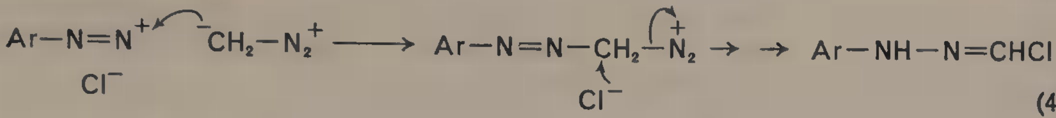
Another diazoalkane–diazonium ion reaction has been proposed to explain azine formation from dipotassium diazomethane disulphonate in water[149]. There are, however, significant differences between this example and the above. Here the alkyl diazonium ion is presumed to react intermolecularly with the diazo group (in water), and through nitrogen rather than carbon as the electrophilic site. There exists ample precedent, however, for the formation of azines by direct reaction of two diazo compounds (Section V.C).

C. *Site of Electrophilic Attack*

1. Reaction with aromatic diazonium ions

Aromatic diazonium ions are well established as electrophilic partners in diazoalkane reactions[150]. Whereas, as is usually observed, the majority of products implicate carbon as the nucleophilic site (equation 47), in the case of diazomethane, the formation of a tetrazole by-product indicated attack at nitrogen (equation 48).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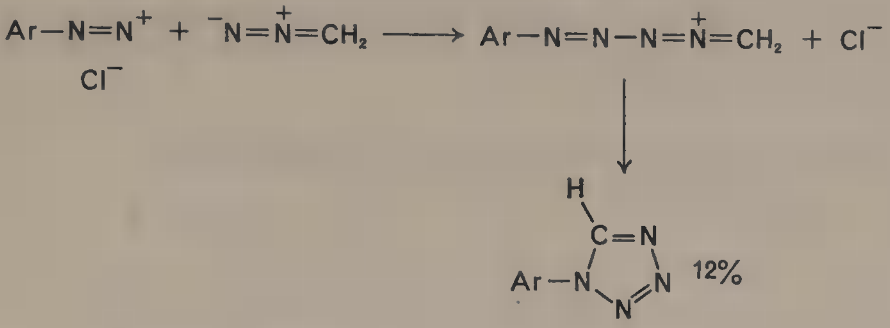
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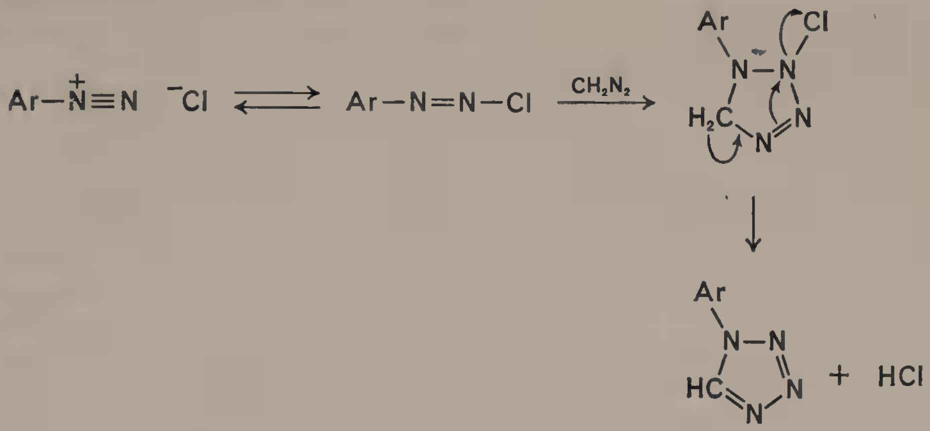
It has, however, been pointed out[151] that this product could be generated by a 1,3-dipolar cycloaddition of diazomethane to the arenediazochloride, in equilibrium with the separated ions.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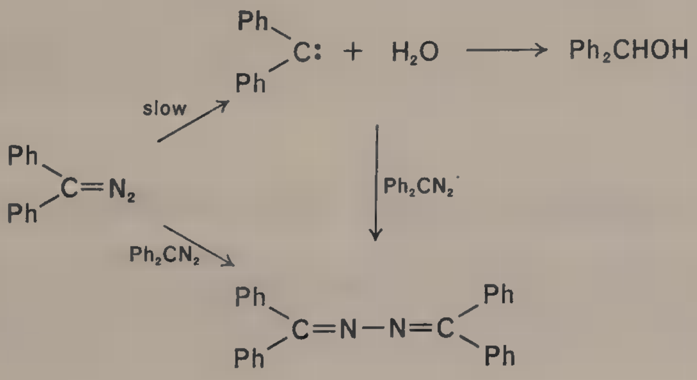
2. Reactions with carbenes

The only unequivocal examples of electrophilic attack at the terminal nitrogen of diazoalkanes involve carbenes. The formation of azines in the thermolysis of diazoalkanes does not necessarily involve the prior formation of a carbene. Indeed, the singlet carbene from phenyldiazoethane forms styrene rather than the azine observed as the major thermolysis product[152]. The dimerization could result from an excited state–ground state interaction[153], or from an electrophilic attack of one diazo group


(49)

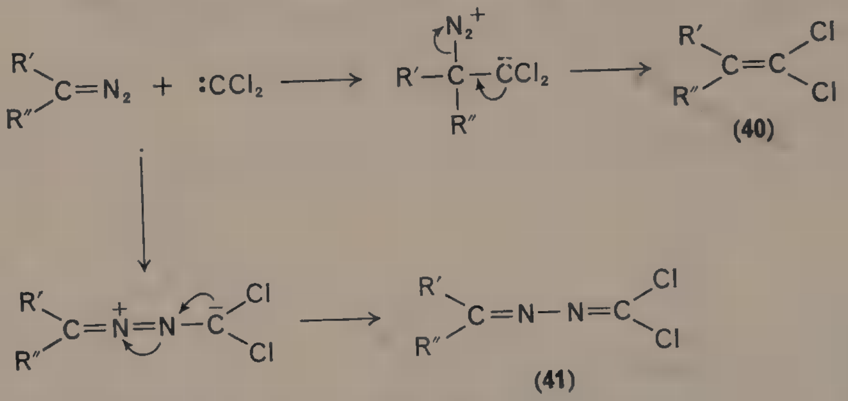
on another (Section V.C.) Kinetic evidence exists, however, that the formation of benzophenone azine from diphenyldiazomethane is in part due to a carbene mechanism[154], and in part to dimerization[155].

Carbenes with dihalo-[156] and a variety of other[157] substituents react preferentially at the nucleophilic carbon site of diazoalkanes, including diphenyldiazomethane and diazofluorene. An increase in the bulk of the substituents at this carbon, however, may direct reaction to the nitrogen terminus.

TABLE 7. Variation of product distribution, with increasing bulk of aryl substituents, in reaction (50)

R^1	R^2	40 (%)	41 (%)
Ph	H	85·0	0
Ph	α-Naphthyl	52·0	7·0
α-Naphthyl	α-Naphthyl	6·1	14·5

This is illustrated by the results in Table 7, for the influence of α-napthyl substituents on the distribution, between olefin (**40**) and azine (**41**) products, for the reactions of diaryldiazoalkanes with dihalocarbenes (equation 50).



(50)

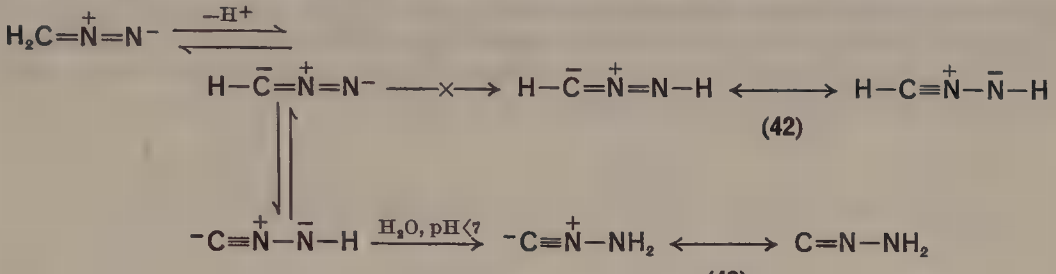
Accordingly, reaction of phenyl-α-naphthyl-methylene with its diazo parent yields azine rather than olefin[158]. Thus steric hindrance to reaction at carbon could well explain the preferential formation of azine in the reaction of diphenyldiazomethane with its corresponding carbene, and especially carbenoid, species[132]. Compilation of reactions of diazoalkanes with electrophiles with subsequent retention[5], or loss[159] of nitrogen exist, and will not be repeated here. The rapidly developing area of substitution at a metallated diazo carbon[5], where the mechanism is uncertain[160, 161], will also be left untreated. Discussion of these reactions and of interactions of diazo compounds with metals in general will be found in Chapter 7 on 'Complex Formation' in this volume.

IV. PROTON ACIDITY OF DIAZOALKANES

Diazomethane is deprotonated by triphenylmethylsodium[162], methyllithium or phenyllithium[163] in ether at 0 °C to form the corresponding alkali metal salts.

$$H_2C{=}\overset{+}{N}{=}N^- + (Ph)_3C^-\ Na^+ \longrightarrow H\overset{-}{C}{=}\overset{+}{N}{=}N^-\ Na^+ + (Ph)_3CH \qquad (51)$$

Whereas hydrolysis of these salts with alcohol–water at room temperature produces a 35% yield of diazomethane, hydrolysis at −15 °C with a concentrated, weakly acidic buffer solution (of ammonium chloride or potassium dihydrogen phosphate) yields a colourless diazomethane isomer. This ‘isodiazomethane’, originally considered to possess a nitrilimine[164, 165] structure (**42**), is now identified as an *N*-amino-isocyanide (**43**) on the basis of spectroscopic[166] and chemical[167, 168] evidence.



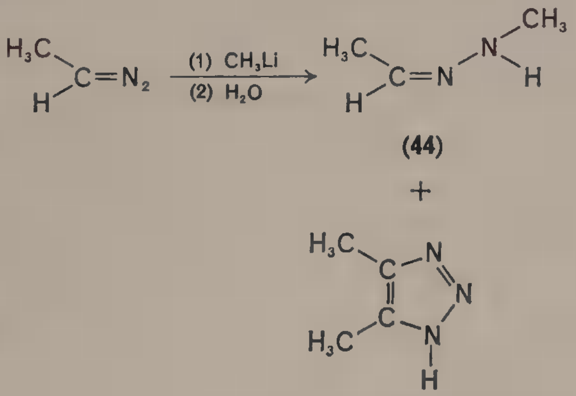
(42)

(43)

$$(43) + H_2O \xrightarrow{pH \approx 7} HCONHNH_2 + N_2H_4 \qquad (52)$$

Diazomethane is re-formed immediately and quantitatively by treatment of ‘isodiazomethane’ with solid potassium hydroxide in ether[163]. Reaction with a buffered aqueous neutral solution, however, generates formylhydrazine and hydrazine[163]. Thus ‘isodiazomethane’ is the kinetically controlled product of protonation of the diazomethane anion, while under equilibrating conditions diazomethane is favoured. The possibility that the experimental conditions of the isomerization, involving the presence of a heterogeneous basic system, may upset the equilibrium in favour of diazomethane (**20**) is unlikely as **20** is in part reformed from **43** in a basic aqueous buffered solution[163]. SCF–MO calculations using a LW [533 ; 3] gaussian lobe basis set do not reproduce the energetics of the above situation[169]. Thus **43** is calculated to be 136 kJ more stable than **20**.

Substituted diazomethanes do not form isolable salts, but evidence of their deprotonation by organometallics is to be found in the reaction products. Diazoethane on treatment with methyllithium yields acetaldehyde *N*-methylhydrazone (**44**), and 4,5-dimethyl-1,2,3-triazole (**45**)[170]. The corresponding triazole is the unique isolable product of the reaction of phenyldiazomethane with biphenylyl-phenyl-ketone disodium[162].



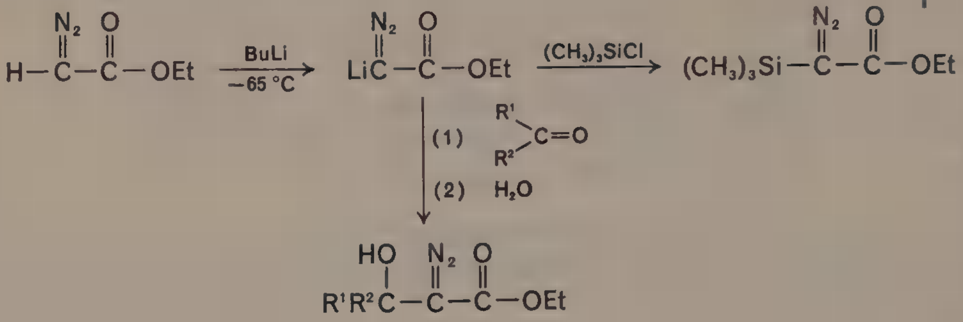
(44)

(45)

(53)

The hydrazone product is readily visualized as arising from nucleophilic attack of the base on the terminal nitrogen of the diazo system. This process, also observed to the extent of 15% for the diazomethane–methyllithium system[171], will be discussed in Section V.C. The triazole product has been postulated to be the result of the nucleophilic attack of the diazoethyl anion on its conjugate acid[170], however a 1,3-dipolar cycloaddition of diazoethane onto the hydrazone formed concurrently is a more appealing possibility.

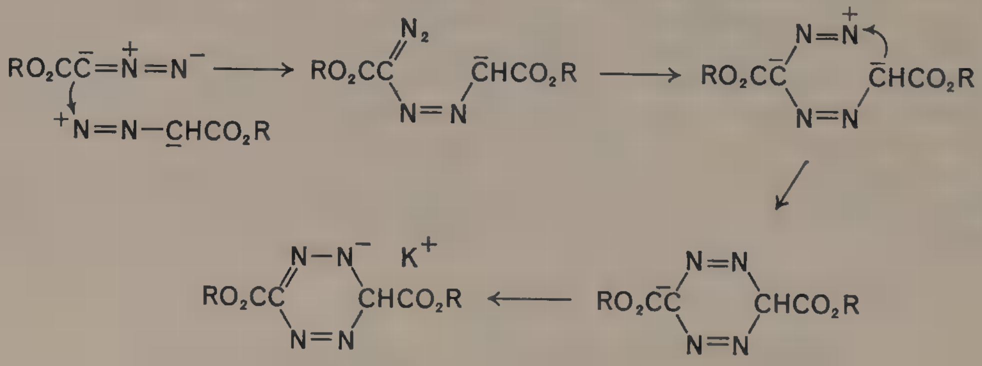
As would be expected, ethyl diazoacetate is more acidic than simple diazoalkanes in that it can be lithiated with butyllithium at −110 °C[172]. The salt formed is, however, thermally unstable† at temperatures above −50 °C[172] as witnessed by previous unsuccessful attempts at preparation[173]. Below this temperature it is sufficiently reactive to undergo metal exchange with trimethylsilyl and tributyltin chloride and to condense with ketone carbonyl groups.



(54)

This latter reaction can be conveniently effected by treatment of a mixture of diazoester and ketone with butyllithium at −65 °C. Similar types of condensations occur under the influence of weaker bases, but with more electrophilic carbonyl bonds. Thus ethyl diazoacetate condenses with aldehydes in ethanolic potassium hydroxide solution at room temperature[174]. These conditions are unsuitable for the corresponding reactions with ketones, due to the unfavourable equilibrium established between reactants and product adduct. Reaction does proceed, however, with small ring or α-carbonyl ketones[174]. Metallation of ethyl diazoacetate with Grignard reagents occurs at −70 °C[172] whereas at 0 °C, only nucleophilic addition to the terminal nitrogen is observed.

Ethyl diazoacetate has long been known to dimerize in ethereal potassium alkoxide solution[175]. The most reasonable mechanism proposed[1] involves its reaction as Brönsted and Lewis acids at carbon and nitrogen centres respectively.



(55)

(46)

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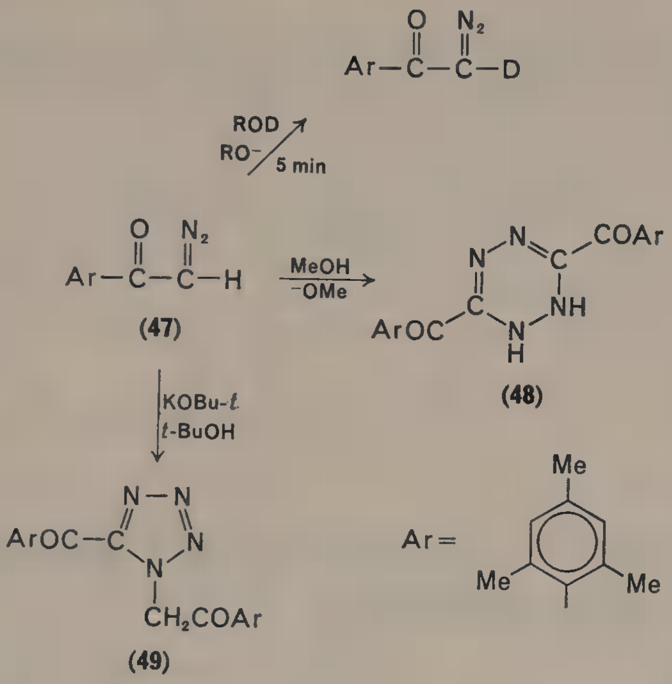
† The formation of thermally stable, metallated diazoesters, where the metal is Ag or Hg etc., which do not proceed by initial proton abstraction, is discussed in Chapter 7 on Complex Formation'.

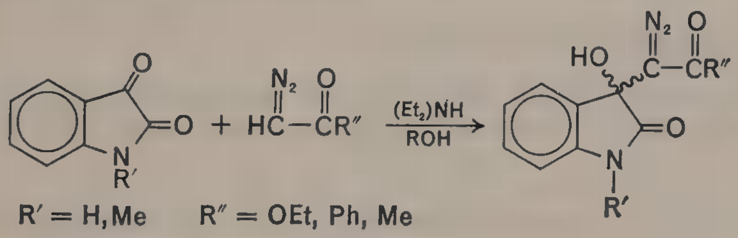
Primary α-diazoketones display a similar balance of reactivity as acids and electrophiles towards bases. 2,4,6-Trimethyl-ω-diazoacetophenone **(47)** undergoes base-catalysed proton deuterium exchange rapidly in alcoholic solution[176], as do primary diazosulphones[40]. The reaction product with methoxide in methanol is the tetrazine **(48)**[177], analogous to **46**, however with *t*-butoxide in *t*-butanol the tetrazole dimer **(49)** is formed[178]. Both types of dimer are also produced by diazoacetophenone, but with potassium hydroxide in dimethylsulphoxide and with potassium *t*-butoxide in *t*-butanol, respectively[178]. The influence of different bases and conditions on the reaction course has not been clarified as both of the above dimers can be considered to arise from initial proton abstraction or nucleophilic addition by the base.



(56)

Dimerization subsequent to proton abstraction is also observed in the reaction of diazoketones with lithium diisopropylamide at −70 °C, however if a ketone is also present, condensation occurs to form the α-hydroxy diazoketone[172]. For this reaction butyllithium is an unsuitable metallation reagent as it competitively adds to the terminal diazo nitrogen[174].

Base-catalysed condensation of diazoketones, diazophosphonate esters and diazophosphineoxides[179] with carbonyl groups is observed under mild conditions if the latter are sufficiently activated, e.g. in isatin derivatives[180], or held in the immediate vicinity of the diazo group[181]. This condition allows even attack at a carboxyl function.



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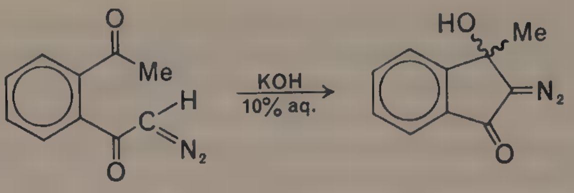

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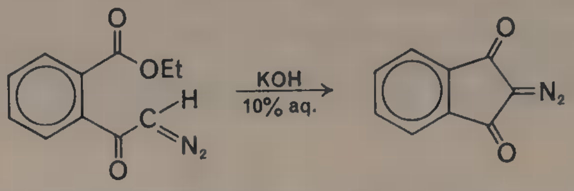

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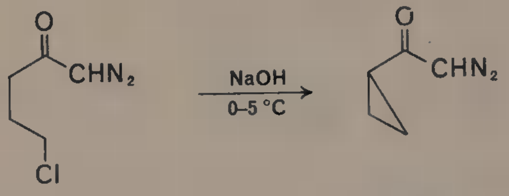
It should finally be noted that the presence of an α-diazo group does not exclude normal base-catalysed reactions, e.g. intramolecular alkylation[182], or Darzens condensation[183].



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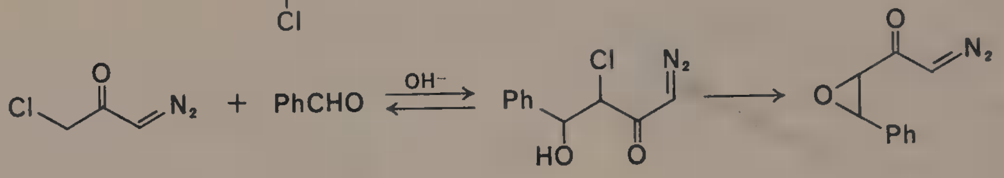

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V. LEWIS ACIDITY OF DIAZO AND DIAZONIUM GROUPS

A. Coupling of Aromatic Diazonium Ions

1. Introduction

The reactions of the aromatic diazonium group with nucleophiles can be considered as substitutions or additions. The former class does not provide an index of the Lewis acidity of the group and, as it has recently been reviewed[184], will not be considered further here. General considerations of terminal addition to the diazonium group by nucleophiles, such as hydroxide, alkoxide, phenoxide, cyanide, azide, thiolate and bisulphite anions, phosphites, phosphines, ammonia and substituted amines, have been extensively discussed[185]. Quantitative thermodynamic aspects of these reactions are presented elsewhere in this volume. The coverage of the literature on azo-coupling to aromatic[186] and aliphatic carbon nucleophiles[187–189] will not be repeated. The following discussion will be limited to more recent results, which may define the relative 'kinetic acidity' of several classes of nucleophiles.

2. Reactions with nucleophilic carbon

Generally the principal factor influencing the ease of coupling with aliphatic carbon bases is the nature of the substituents in the base, rather than in the diazonium salt.

$$\mathrm{Ar\overset{+}{N}{\equiv}N + {}^{-}CHR_2 \longrightarrow ArN{=}N{-}CHR_2 \longrightarrow Ar{-}NH{-}N{=}CR_2} \qquad (62)$$

The rate constants for hydrazone formation for the anions of nitroethane[190], acetoacetanilide[191], acetylacetone[192] and acetone[193] with a series of diazonium salts have been determined. Furthermore, good correlations of reaction rates for each anion with Hammett's σ parameters were obtained. As was noticed for coupling to aromatic nuclei, the most reactive diazonium ions have negative deviations from this relation as the diffusion rate limit is approached. This phenomenon was ascribed to lack of additivity of substituent constants rather than to incursion of diffusion control (with one exception), or to a change of ρ values with decreasing activation free energy[194]. Such a change in ρ with the overall reactivity of each anion type was however observed. Coupling to the highly reactive anion of acetone ($pK_a = 19$–20) was associated with a value of 1·89, compared to a value of 3·45 for acetylacetone. In fact the ρ values were observed to decrease regularly with increasing rate constant, even when data for coupling to aromatic nucleophiles were included, although the correlation was better when restricted to substrates of similar structural type[195]. Such an analysis of the Hammett ρ values in terms of selectivity–reactivity relationships is, however, subject to severe limitations and has recently been criticized[196]. The uncertainty in extrapolating this sort of comparison to substrates of different charge type is typified by the similar ρ values of 4·0 and 4·15, for the coupling reactions to 1-naphthol and its anion respectively, despite the greater reactivity of the latter by a factor of 10^7 [197]. Such a difference in reactivity between a nucleophile in its protonated and unprotonated forms is common to enols, naphthols, pyrazolones, naphthalene sulphonic acids[192], pyrroles[198] and 3-methylindole[199].

3. Reactions with heteronucleophiles

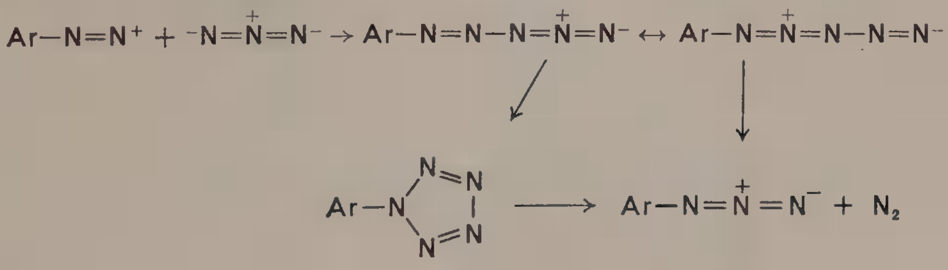
The rate constants for coupling of aromatic diazonium ions with nitrogen in amines appear to decrease in the series *N*-methylaniline[200], dimethylamine[201], aniline[202]. This decrease is not reflected by a systematic change in the values of ρ 3·94, 3·47 and 3·90, respectively. The effect of variation of aromatic substituents on the coupling rate with methylamine is difficult to assess, since electron-donating substituents encourage further reaction of the initially-formed triazene with the diazonium ion to generate a pentazadiene[203].

$$\mathrm{ArN_2^+ + CH_3NH_2 \longrightarrow Ar{-}N{=}N{-}NHCH_3 \rightleftharpoons ArNH{-}N{=}NCH_3} \quad (63)$$

$$\mathrm{ArNH{-}N{=}NCH_3 + ArN_2^+ \longrightarrow ArN{=}N{-}NAr{-}N{=}NCH_3} \quad (64)$$

The kinetic results for this system have so far defied analysis[204].

Coupling with hydroxyl, cyanide, bisulphite and azide ions leads initially to the *cis*-azo compounds, despite the fact that the *trans* isomers are thermodynamically favoured[205]. The *syn* diazohydroxide formed when the nucleophile is hydroxyl ion is extremely rapidly deprotonated to the *syn* diazoate[206, 207] (see Section VII.A). The aryldiazoazide formed with azide ion decomposes into aryl azide and nitrogen, or cyclizes to an arylpentazole, prior to nitrogen evolution[208].



(65)

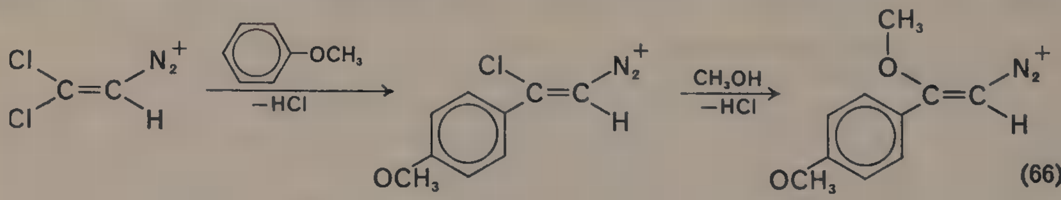
For several solvents the kinetic nucleophilicity of anions is in the order $C_6H_5S^- < N_3^- < CN^-$[209]. An exception to this sequence is provided by the reaction of azide with diazonium ions (other than with *p*-nitrobenzenediazonium) in water[210]. In these particular cases the rate-determining step is assumed to be decomposition of the aryldiazoazide[211]. The above-mentioned reactivity order is maintained towards triarylmethyl and tropylium ions and is regarded as following the relative ease of desolvation of the nucleophiles[209]. Consequently, a considerable part of the activation energy for these rapid reactions is unaffected by the reactivity of the diazonium ions. Hence there does not exist even an approximate relation between Hammett ρ values and overall reactivity as found for azo-coupling reactions. The ρ values in question for $^-OH_{(H_2O)} = 2{\cdot}16$[212], $2{\cdot}1$[213], $^-CN_{(H_2O)} = 2{\cdot}31$[211], $N_{3\,(MeOH)}^- = 2{\cdot}83$[214] are considerably smaller than those for azo-coupling to carbon nucleophiles where $\rho = 4{\cdot}0$, despite the fact that these latter reactions are much more rapid. The coupling rate of 2,6-dichloro-4-nitrobenzenediazonium ion with 1-naphtholate anion is 10^3-times that with hydroxide ion, despite the greater basicity of the latter by a factor of 10^6 [215]. The similarity of the ρ values of azo-coupling to carbon to those of diazonium–diazo equilibria with the above anionic nucleophiles, i.e. $3{\cdot}2 < \rho < 5{\cdot}2$, may indicate that the transition states for these azo-couplings are 'product like' [184]. On the other hand, the smaller ρ values for reaction with anions (after their desolvation) imply a less selective reaction, with 'reactant like' transition state. This reasoning[184] is consistent with formation of *cis* products for 'early transition state' reactions, and direct formation of *trans* products with amines, phenols and aromatic tertiary amines.

B. *Coupling of Aliphatic Diazonium Ions*

1. Stable aliphatic diazonium ions

Stable, isolable aliphatic diazonium salts (i.e. those from which spontaneous nitrogen evolution would lead to very unstable vinyl cations) do not undergo reactions analogous to azo-coupling. This is due to preferred reactions with nucleophiles at alternative sites. Thus olefin diazonium salts undergo substitution at the electrophilic olefin positions rather than addition at the terminal nitrogen[216].

The γ-pyridinyl-substituted diazonium ion (**50**) is deprotonated by triethylamine[217]. The diazonium-substituted acetyl–acetone complex (**51**) normally



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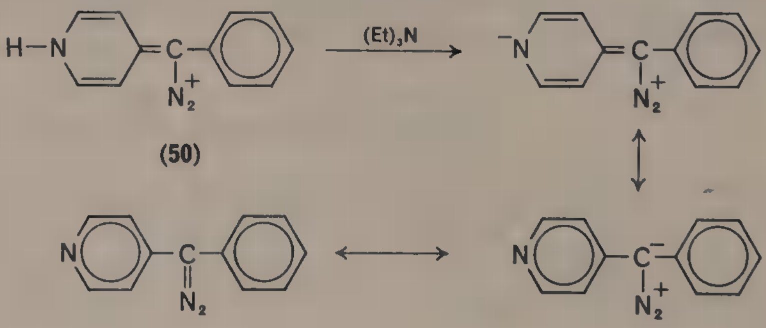

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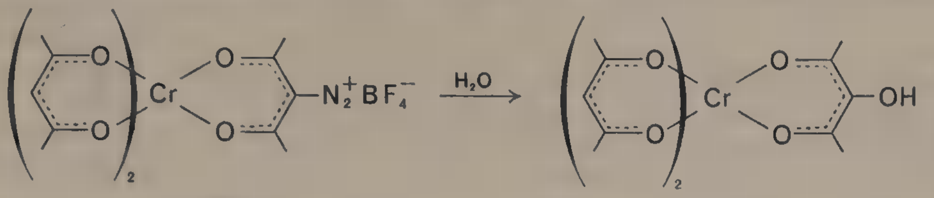
(67)

experiences substitution of the diazonium group by nucleophiles, but does show colouration, indicative of coupling with naphthol[218].

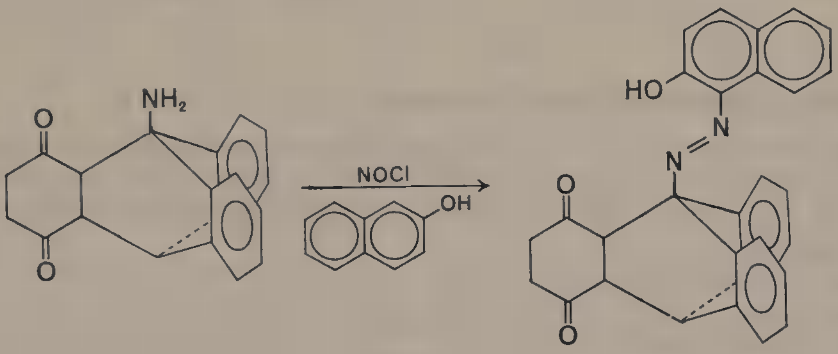


(51)

(68)

2. Trapping of aliphatic diazonium ion intermediates

Coupling products have been isolated from reactions involving aliphatic diazonium ion intermediates. In all cases the ions could be trapped due to nitrogen loss becoming unfavourable, assisted or unassisted, by position either on a bridgehead[219] or on a cyclopropyl ring[70, 220].



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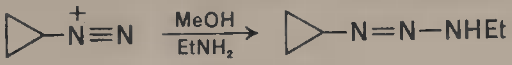


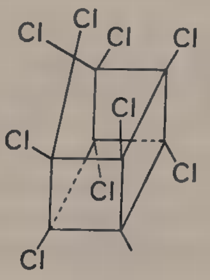
(52) 30%

(70)

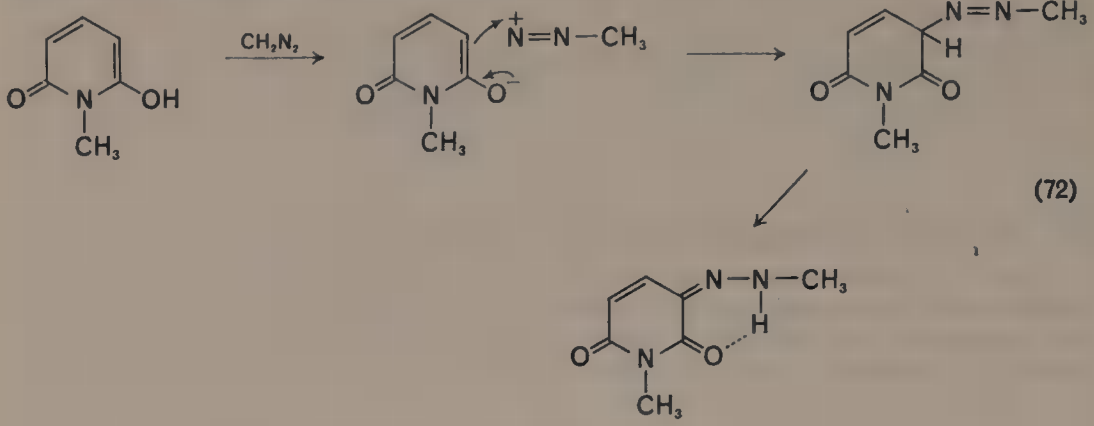
Under the same conditions as the cyclopropyl diazonium ion (**52**) experiences terminal addition, the isobutyl and methyl analogues prefer nitrogen substitution[220]. A bridgehead position is not in itself sufficient to permit diazonium ion trapping. The polychlorinated homocubane diazonium ion (**53**) gave products typical of radical decomposition of an intermediate addition species (**54**), and also coupled with β-naphthol[221]. In contrast, its hydrogenated analogue yielded only normal hydrolysis products in the same reaction conditions[222].

$$\begin{tikzcd}
R{-}NH_2 \arrow[r, "HNO_2"] & \underset{(\mathbf{53})}{R{-}N_2^+} \arrow[r, shift left] & R{-}N{=}N{-}OH \arrow[l, shift left] \arrow[r] & \underset{(\mathbf{54})}{R{-}N{=}N{-}ONO} \arrow[d] \\
 & & & R\cdot + N_2 + \cdot ONO
\end{tikzcd} \qquad (71)$$

R =



The less stabilized methane[223-226] and ethane diazonium[227] ions can be trapped by their counter-ions co-generated in ion pairs.



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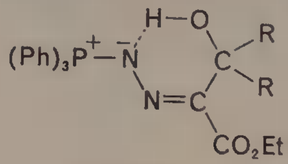
C. *Coupling of Aliphatic Diazo Compounds*

Generally the reactivity of diazoalkanes towards nucleophiles increases with increasing contribution of limiting forms (**1b**) and (**1c**) to their overall electron distribution. Diazoalkanes lacking electron-withdrawing substituents require more reactive nucleophiles.

Trialkyl- or triaryl-phosphines, though more feeble nucleophiles than amines toward many metal ions[228], form, unlike amines, stable addition complexes with most diazoalkanes[229], even diazomethane[230]. This unique reactivity results from the ability of phosphorus to stabilize the betaine thus formed (**55**) by π-acceptance into its empty d orbitals.

$$R_2\bar{C}-N=N^+ + P(Ph)_3 \longrightarrow \underset{\textbf{(55)}}{R_2\bar{C}-N=N-\overset{+}{P}(Ph)_3} \longleftrightarrow R_2C=N-N=P(Ph)_3 \qquad (73)$$

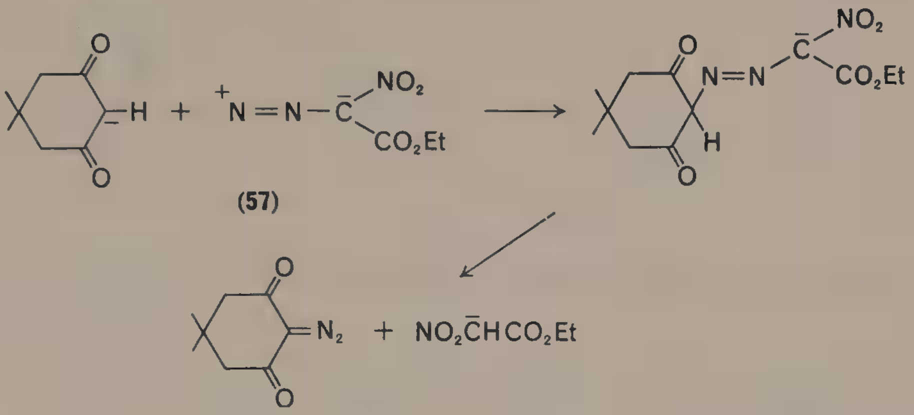
When the delocalization is diminished by hydrogen bonding, for example in the α-hydroxyphosphazine (**56**), the thermal stability of the adduct diminishes correspondingly[172]. In this case dissociation into reactants occurs at 70 °C, whereas normally higher temperatures are required for pyrolysis[231].



(56)

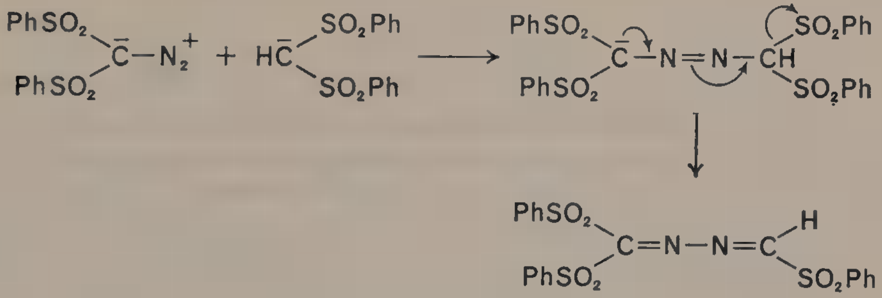
Although the addition reaction is subject to acceleration by electron-releasing substituents in the phosphine aryl groups[232] ($\rho = -1{\cdot}03$), the limitations of the extent of reactions seem to be primarily steric[233]. Thus diazocyclopentadienes substituted with alkyl or aryl groups in both the 2- and 5-positions fail to react with triphenylphosphine. Reaction does proceed with the less hindered and more nucleophilic tri-*n*-butylphosphine, or if the 5-substituent is replaced by a hydrogen, chlorine or nitro group[233]. In the latter two cases the electron-withdrawing substituents would be expected to stabilize both the diazonium reactant and also the product-contributing form **55**. The increased importance of this form has been invoked to explain the more ready hydrolyses of the phosphazines containing these substituents, by nucleophilic attack at phosphorus[233]. Trialkylphosphites also form phosphazine adducts, but examples are scarce[234, 235].

Diazoalkanes disubstituted with strongly electron-withdrawing groups, such as $-CN$[86], $-CF_3$[236], $-SO_2R$[237], react with phosphines or Grignard reagents at or below room temperature. In certain cases such compounds, e.g. α-nitro ethyldiazo acetate (**57**) can also serve as 'diazo-transfer' reagents[238].



(74)

Bisarylsulphonyldiazomethanes also react readily with carbanions[239] (equation 75), and bismethylsulphonyldiazomethanes can experience terminal nucleophilic attack by enamines[240, 241] (equation 76)



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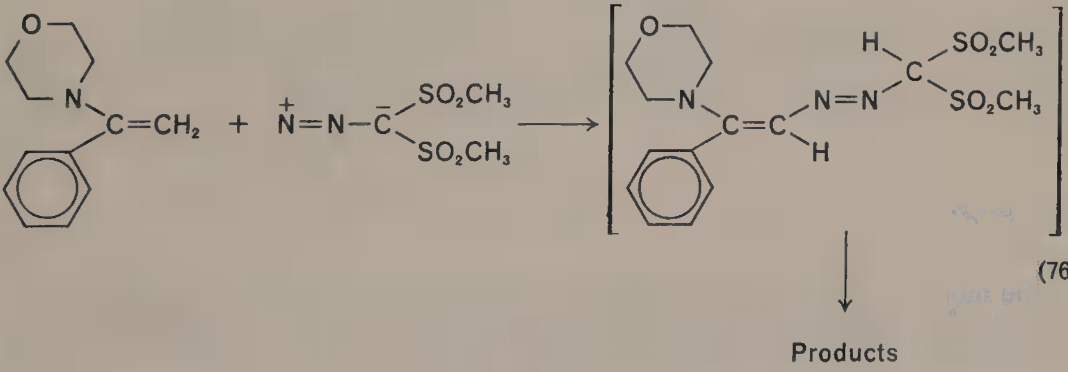

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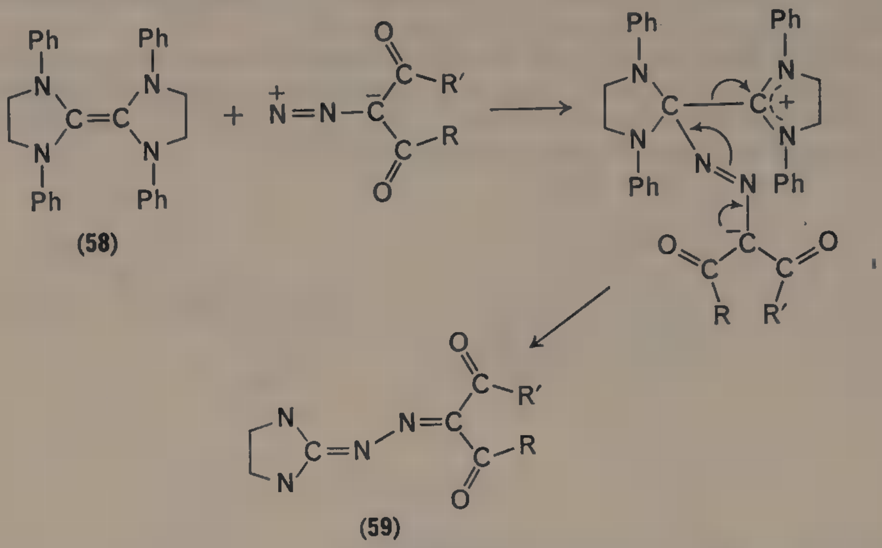
Electron-rich olefins also react with electrophilic α-dicarbonyl diazoalkanes[242] and diazofluorene[243] to form azines.



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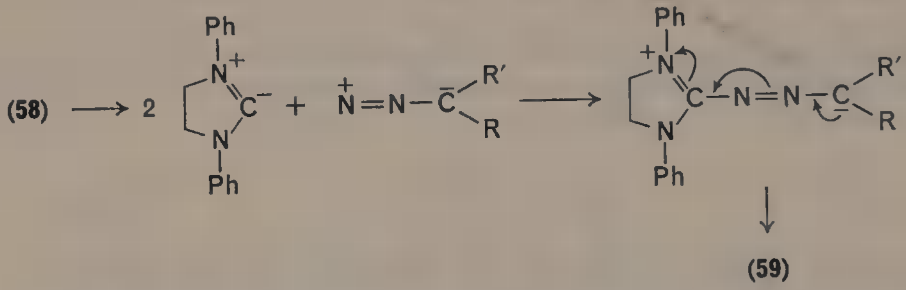
An alternative route to azine products from diazofluorene and **58**, via prior dissociation of the latter to nucleophilic carbenes, has been proposed[244, 245].



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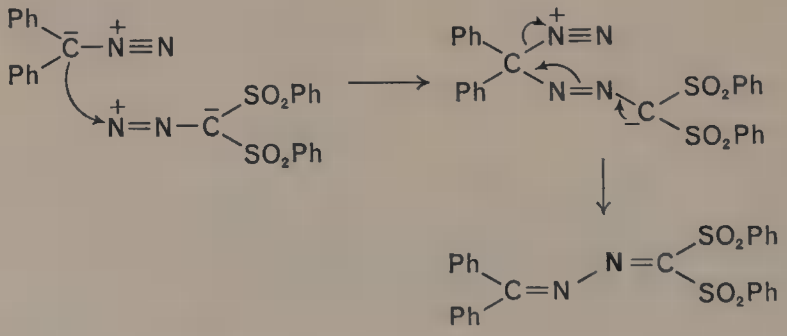
The diazo carbon of diphenyldiazomethane is sufficiently nucleophilic to form azines with stabilized diazoalkanes without passing through a carbene intermediate[86, 246]



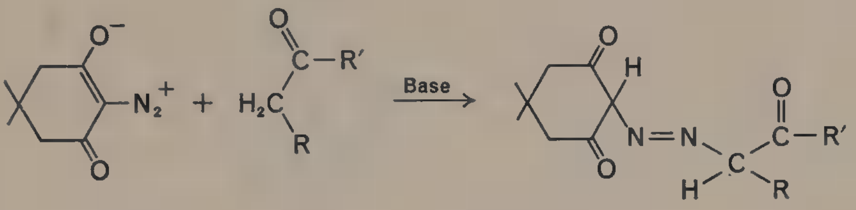
(79)

The more nucleophilic diazoethane carbon reacts similarly with *p*-nitro-ω-diazoacetophenone and less readily with α-diazopropiophenone, whereas diazomethane does not react under the same conditions[247, 248].

The normal course of reaction of diazoketones[174], diazoesters[173] or aryldiazoalkanes[249-251] with carbanions from organometallic reagents[173, 249] leads to a hydrazone after hydrolysis.

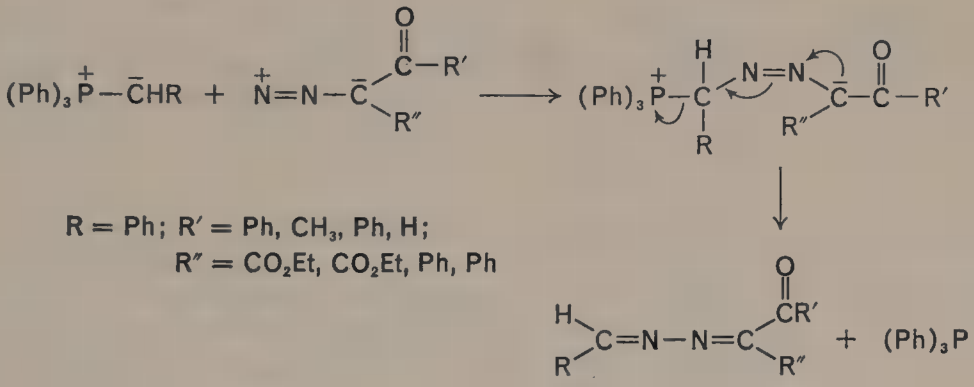
$$\mathrm{Ph_2\bar{C}{-}N{=}N^+ + PhMgBr \longrightarrow Ph_2\bar{C}{-}N{=}N{-}Ph \longrightarrow Ph_2C{=}N{-}\bar{N}{-}Ph \longrightarrow Ph_2C{=}N{-}NHPh} \qquad (80)$$

The initially-formed, azo-coupled products from diazodiketones and enolate ions may be isolated as such[242, 251] or may cyclize to substituted pyrazoles[252].



(81)

The addition products of diazoalkanes and triphenylphosphoranes fragment to form the mixed azine[253].



R = Ph; R′ = Ph, CH$_3$, Ph, H;
R″ = CO$_2$Et, CO$_2$Et, Ph, Ph

(82)

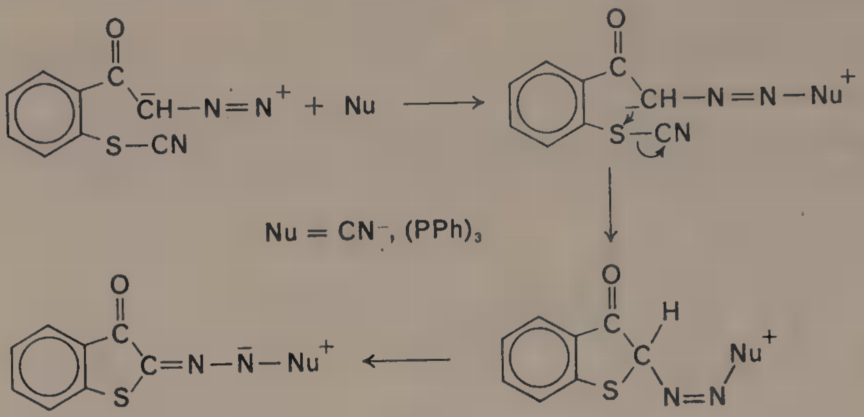
Less-nucleophilic phosphoranes where R = Ac, Bz or CO$_2$Me failed to react.

N-Terminal attack on diazoketones by cyanide and bisulphite anions, and by amino groups, is evident from the isolation of the corresponding addition products[1]. These reactions involving amine and sulphide nucleophiles are usually restricted to intramolecular cyclizations[1], although piperidine forms a linear triazene with the sufficiently reactive 1,1,1,3,3,3-hexafluorodiazo-2-propane[236].

For other nucleophiles the evidence of reaction is less obvious. The extent of hydrogen–deuterium exchange in 2,4,6-trimethyl-ω-diazoacetophenone in deuterated methanol, catalysed by halide salts, depends on the nucleophilicity rather than on the basicity of the catalyst[176]. The proposed exchange mechanism is given in equation (84).

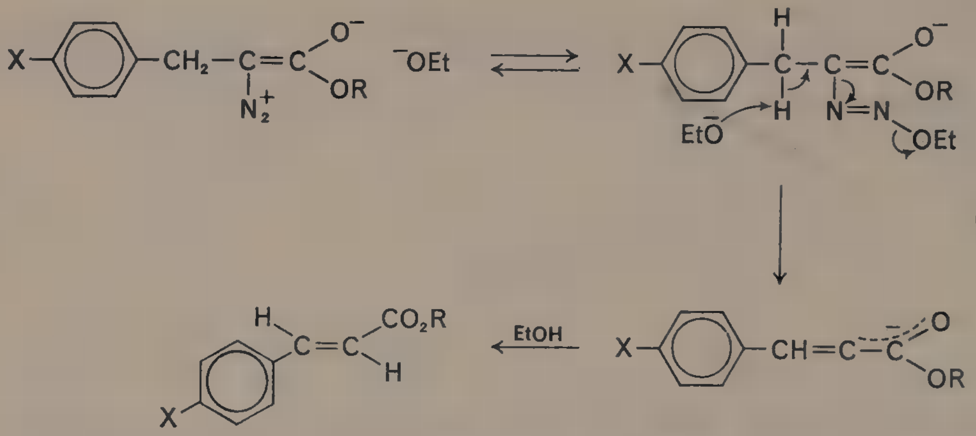
$$\mathrm{RCO\bar{C}H{-}N{=}N{-}B \xrightleftharpoons{R'OD} RCOCHD{-}N{=}N{-}B \xrightleftharpoons{R'O^-} RCO\bar{C}D{-}N{=}N{-}B} \ \text{etc.} \qquad (83)$$

The products of reactions of diazoketones in the presence of hydroxide or alkoxide ions are consistent with intermediates of the above type. Similarly, nucleophilic rather than basic catalysis has been invoked to explain the interaction of diazocarbonyl groups with adjacent electrophilic functions[146].



(84)

The formation of *trans* cinnamic esters from aryl-2-diazopropionic esters in basic ethanol[254] could well involve such an intermediate, instead of the original diazo-ester, as an acidic species.



(85)

On the other hand, the reaction of diazoketones in ethanol–sulphur dioxide mixtures[255] is not necessarily the result of a nucleophilic attack of ethanol on the diazo group. A sufficient increase of acidity of ethanol, due to coordination with the Lewis acid SO_2, to permit protonation, would be an equally acceptable explanation.

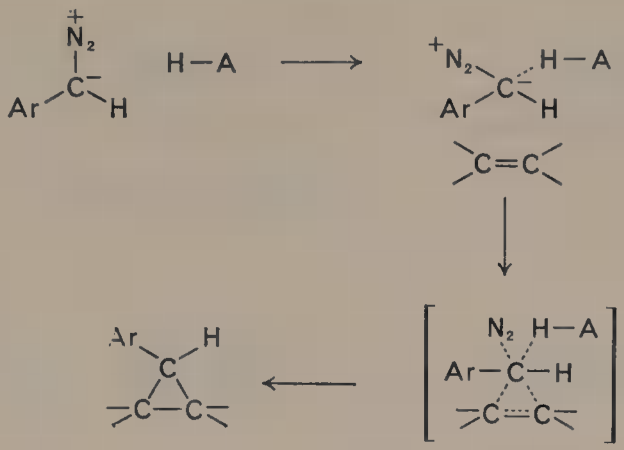
Finally, azo-coupling with aromatic substrates is limited to the very reactive 1,3,5-trihydroxybenzene for diazoketones, ethyl diazoacetate and diazomethane[256], although dicyanodiazomethane couples with the 4-position of *N*,*N*-dimethylaniline[86].

VI. HYDROGEN BONDING

A. *Diazoalkanes as Proton Acceptors*

The formation of a hydrogen bond, between an acid and a diazo carbon atom, has been shown to account for a considerable part of the activation energy of the overall proton transfer (Section II.B.6). In non-polar solvents, complexes so formed may have a lifetime sufficiently long to permit an alternative reaction with the solvent.

Thus Closs[257] has proposed a carbenoid transition state (**59**) for the trifluoroacetic acid-catalysed formation of cyclopropanes from phenyldiazomethane in olefinic solvents.



(**59**)

(86)

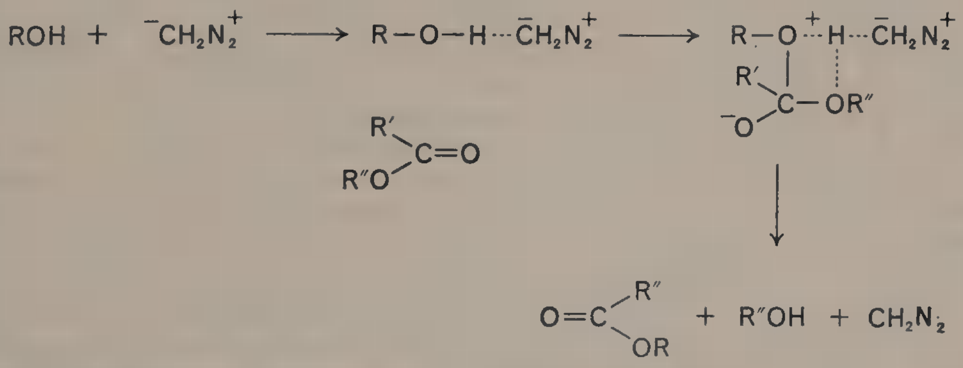
The evidence for such a transition state includes stereospecificity of cyclopropane formation and partial deuterium incorporation from deuterated catalysts, as opposed to monodeuteration of the carbonium-ion-derived products.

A similar hydrogen-bonded intermediate was originally proposed to explain the product distribution in the alkylation of tautomeric acid systems[258].

$$\mathrm{A{-}H + CH_2N_2 \longrightarrow A{-}H \cdots CH_2N_2 \longrightarrow N_2 + A{-}H \cdots CH_2 \longrightarrow A{-}CH_3} \qquad (87)$$

Collapse of intimate or solvent-separated ion pairs would currently be a more acceptable explanation[79, 258].

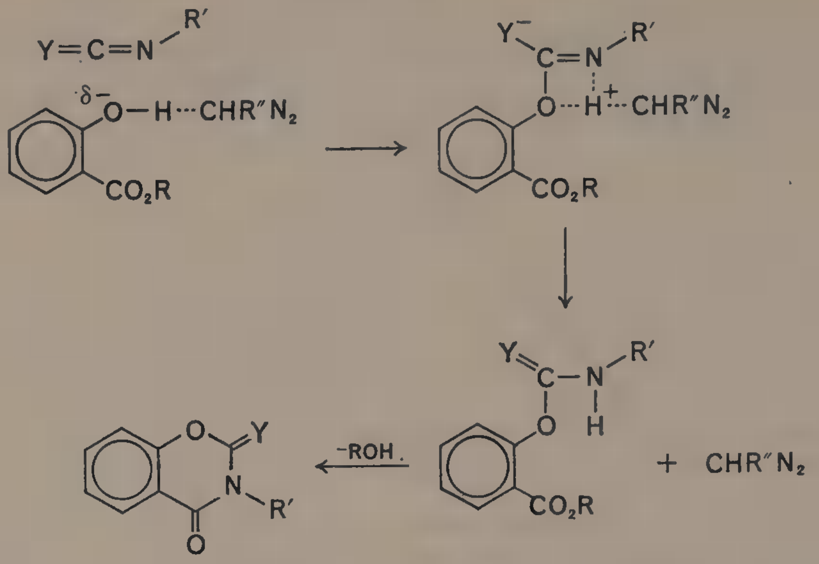
Hydrogen-bond formation to diazoalkanes from alcohols[259] is indicated by the function of the former as transesterification catalysts[260–262]. The nucleophilicity of the alcohol hydroxyl group is sufficiently raised by hydrogen bonding to the weakly basic diazomethane to allow attack on a carboxyl group.



(88)

It is significant in this respect that diethyl oxalate is transesterified under conditions which leave the less electrophilic diethyl malonate unaffected[263]. The catalytic function of diazomethane is supported by the lack of formation of methyl acetate, in the reaction of phenyl acetate with ethanol[260].

Similar mechanisms are proposed for the catalysis by diazoalkanes of the addition of alcohols to electrophilic double bonds[264], and of isocyanates or isothiocyanates to *o*-hydroxybenzoate esters[265] (equation 90).



(89)

Catalytic efficiency for this reaction increases in the order diazoethane, diazomethane, phenyldiazomethane, which is the inverse of the order of their rates of reaction with phenols. For the most efficient catalyst, phenyldiazomethane, 0·1–0·01 molar equivalents are sufficient to ensure complete reaction[265]. The intermediacy of proton-bridged rather than discrete diazonium ion intermediates was demonstrated by the lack of incorporation of deuterium into the products, when molar equivalent quantities of deuterated diazoalkanes were used as catalysts[266, 267].

B. *Diazoalkanes as Proton Donors*

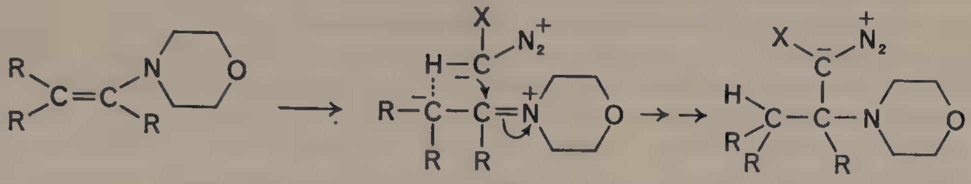
In solution, primary α-diazosulphones[268] and α-diazoketones[269] can function as hydrogen-bond donors, either to themselves or to solvent molecules. This is revealed by a downfield progression of chemical shift of the proton bonded to the diazo group in a series of solvents following the basicity of the solvent. It should be noted that in the solid phase no evidence of hydrogen bonding was to be found in the determination of the crystal structure of 1,4-bisdiazo-2,3-butadione[270].

On the basis of solvent dependence of chemical shift, diazosulphones are apparently better hydrogen-bond donors than are diazoketones. The latter possess, however, a better acceptor site in the carbonyl group as compared to the sulphone group[269].

The difference in hydrogen-bond donor ability between the two classes of compound has been invoked to explain the alkylations of diazosulphones (**60**), but not of diazoketones by enamines[271]. Formation of the hydrogen bond to the enamine apparently increases its immonium ion character (**62**), and hence its susceptibility to attack by the nucleophilic diazo carbon.

A close parallel to the above behaviour exists in the chemistry of diazodiphenyl phosphine oxides (**61**). The p.m.r. spectrum displays a similar, solvent-dependent, chemical shift for the proton attached to the diazo group[272], and furthermore

61 adds electrophilically to enamines in exactly the same manner as do diazosulphones[273].



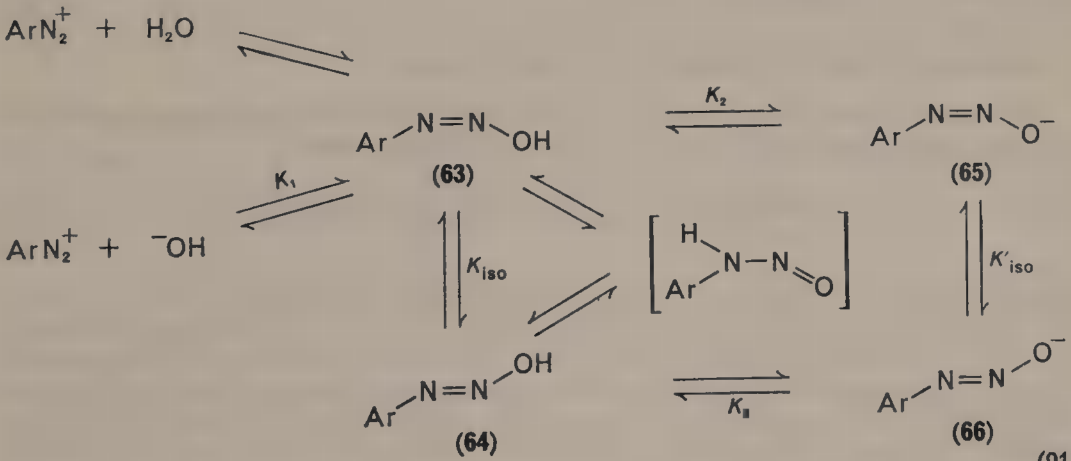
(60) $X = RSO_2-$ (62)
(61) $X = (Ph)_2PO-$

VII. ACIDITY AND BASICITY OF AROMATIC DIAZO COMPOUNDS

A. Diazohydroxides

1. Introduction

The investigations of acid–base equilibria involving diazohydroxides are complicated by two major features. Firstly, both the diazohydroxides and their conjugate bases display geometrical isomerism between the *syn* and the more stable *anti* forms, interconversion of which may be acid catalysed. Secondly the *syn* diazohydroxide is itself a component of a Lewis acid–base equilibrium, with arenediazonium and hydroxide ions. As the equilibrium constant for this reaction is usually much inferior to the dissociation constant of the *syn* diazohydroxide, the latter, when formed from diazonium ions, is almost totally deprotonated by the hydroxide ions present[274]. This behaviour, summarized in equation (91), precludes a direct measure of the acid dissociation constant K_2 from equilibrium concentrations.



(91)

Analysis of kinetic data for conversion of diazonium ions into *syn* and *anti* diazotates (**65**) and (**66**), and *vice versa*, allows separation of dissociation constants (K_2 and K_3) for *syn* and *anti* diazohydroxides (**63**) and (**64**). In some cases, the rates of reaction of **63** and **64** with acids have been determined.

2. Dissociation of *syn* diazohydroxides

2,6-Dichloro-4-nitrobenzenediazohydroxide is exceptional in that, for a certain pH range, it may be present in considerable concentrations in equilibrium with the other species in equation (91)[215]. This is in part due to the instability of the corresponding diazonium ion, which results in an increase in K_1, and also to diminution of the isomerization equilibrium constant K_{iso}. The dissociation constant K_2 was calculated from that of the equilibrium mixture of *syn* and *anti* diazohydroxides and the isomerization constants K_{iso} and K'_{iso}, to be equal to $1{\cdot}55 \times 10^{-5}$. Solutions of *syn* diazotates can be prepared by reaction of hydroxide ion with diazonium ions where substituents are not mesomerically electron withdrawing, and hence do not favour *syn–anti* isomerism[275]. Quenching of these solutions immediately after formation with buffer solutions reforms the benzenediazonium ion with a rate dependent on the concentration of the *syn* diazohydroxide present[276]. Hence, the variation of rate with the pH of the buffer solution employed allows determination of K_2. The Hammett ρ value for the dissociation constants of such a series of diazohydroxides was found to be 1·3.

3. Dissociation of *anti* diazohydroxides

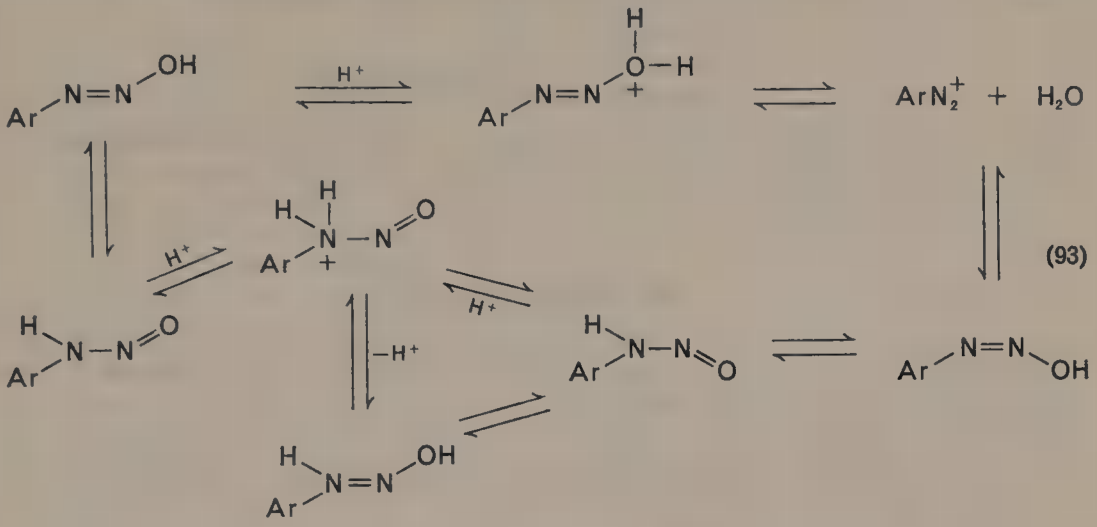
The rates of conversion of *anti* diazotates (**66**) to the corresponding diazonium ions in solutions of high pH (>7) are directly proportional to the equilibrium concentrations of the *anti* diazohydroxides (**64**). Thus the variation of rate with pH readily gives the appropriate dissociation constants K_3 [206]. Such an analysis has been applied to the reactions of pyridine[277], purine[278], mono-[279], di-[280] and trisubstituted[215] *anti* diazotates. The values of pK_a thus established vary from 4·65 for 2,6-dichloro-4-nitrobenzenediazotate to 7·40 for 4-toluenediazotate. In the series of monosubstituted substrates, the dissociation constants give a Hammett correlation with $\rho = 1{\cdot}45$ [279] (or 1·15 [207] as measured by potentiometric titration). The magnitude of these values and those for the *syn* isomers, both being much less than for phenol ionization, exclude, as expected, the possibility of localization of the charge formed on the nitrogen or oxygen.

4. Reaction of *anti* diazohydroxides with acids

The rate of conversion of mono-substituted *anti* diazohydroxides into diazonium ions has a first-order and a second-order component[275, 279]:

$$\frac{-\mathrm{d}[\mathrm{ArN_2OH}]}{\mathrm{d}t} = k_1[\mathrm{ArN_2OH}] + k_2[\mathrm{ArN_2OH}][\mathrm{H_3O^+}] \qquad (92)$$

The first-order component, with rate constant k_1, is a composite of direct dissociation into $\mathrm{ArN_2^+}$ and $\mathrm{OH^-}$ (for which the Hammett $\rho = -2{\cdot}6$) and an uncatalysed (or water-catalysed) isomerization *anti–syn*[279]. The rate constant k_2 of the second-order component represents an acid-catalysed isomerization of *anti–syn* diazohydroxides, and is associated with a ρ value of $-2{\cdot}4$. In the conditions where $k_2[\mathrm{ArN_2OH}][\mathrm{H_3O^+}]$ is significant, generally at pH$\leqslant 4$, the scission of the *syn* diazohydroxide is more rapid than the reverse isomerization. In the pyridine 4-diazohydroxide system a water-catalysed reaction, possibly corresponding to an *anti–syn* isomerization, is significant only at pH<1, in which region the aromatic ring nitrogen is already protonated. Acceleration of the reaction of 2,6-dichloro-4-nitrobenzenediazohydroxide and 2,4-dinitrobenzenediazohydroxide[281] in this region of pH, with increasing acid concentration, can also be ascribed to acid catalysis of the rate-determining *anti–syn* conversion. The existence of such an acid catalysis term does not resolve the question of whether the *anti* diazohydroxides exist as such in solution or are better represented as their *N*-nitrosoamine tautomers[282]. Protonation of either tautomer could facilitate overall conversion to diazonium ion, either by reduction of the isomerization energy barrier or by improving the leaving group in the direct scission reaction.

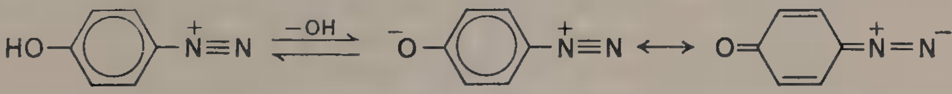

(93)

5. Reaction of *syn* diazohydroxides with acids

Arenediazotates with 2,6-dichloro-4-nitro- and 2,4-dinitro- substituents generate their relatively reactive diazonium ion counterparts by a rate-controlling scission of the *syn* diazohydroxide at pH 4.5. In this pH region, the scissions are general acid catalysed[281]. This was found also to be the case for *syn* diazohydroxides generated by quenching a solution of *syn* diazotates[276]. The Brönsted α values could be measured for the catalysis in both experimental approaches. Those of substrates with the electron-withdrawing substituents were greater (0·34, 0·31 as opposed to 0·19).

B. *Diazophenols*

Arenediazonium ions with *o*- or *p*-hydroxy substituents react with only one equivalent of base to form the corresponding phenolate ion, often named a diazophenol:


(94)

The pK_a value of 3·19 [283] is inferior to that of 2,4-dinitrophenol (4·11) as expected from Hammett substituent constants for the diazonium group.

C. *Triazenes*

A comprehensive review of the acid-catalysed rearrangements of 1,3-diaryltriazenes to *p*-aminoazobenzenes has been given elsewhere[284]. 3-Alkyl-1-aryltriazenes react readily with acids to form the corresponding anilines, nitrogen- and carbonium-ion-derived products[285]. This decomposition prevents direct determination of their basicity. Protonation rates are also inaccessible from the kinetic data accumulated to date. Either there exists a rapid acid–base equilibrium, with rate-determining scission of the conjugate acid in water[286], or the rate-limiting protonation is considered to be coupled with simultaneous departure of a carbonium ion fragment in chloroform[287]. The acid-catalysed scission of 1,5-diphenyl-3-methyl-1,4-pentazadiene in water proceeds by a mechanism comparable to the former[288], with its consequent limitations of evaluation of protonation rate constant.

VIII. ACKNOWLEDGEMENTS

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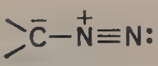
CHAPTER 7

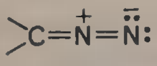
Complex formation

HERMANN M. NIEMEYER
Institute of Organic Chemistry, University of Lausanne,
Lausanne, Switzerland

I. INTRODUCTION

The structure of diazoalkanes may be described in the valence-bond formalism in terms of the canonical structures **1**, **2** and **3**, and their reactions may be classified


(1)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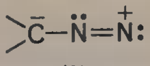
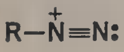

(3)

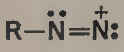
on this basis. Thus diazoalkanes may react as 1,3-dipoles (**3**) or as nucleophiles through carbon (**1**) or through the terminal nitrogen (**2**). In addition, the unsaturated nature of these compounds renders possible the formation of π-type complexes.

Diazonium ions on the other hand may be described as **4** and **5**, and they react normally as electrophiles through the terminal nitrogen (**5**).



$R-\overset{+}{N}\equiv N:$

(4)



$R-\overset{\bullet\bullet}{N}=\overset{+}{N}:$

(5)

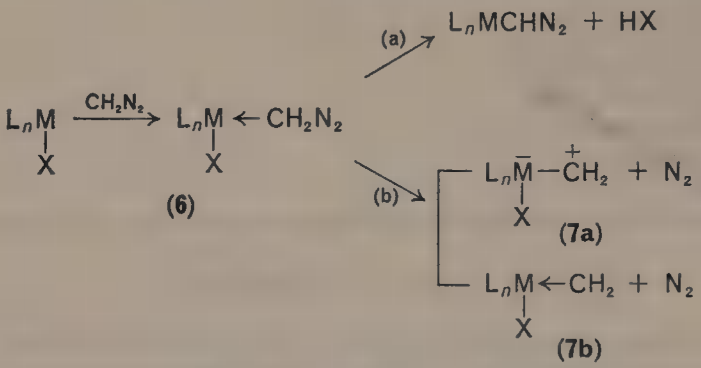
The possibility of certain metal derivatives acting as Lewis acids and bases enables them to form complexes with diazoalkanes and with diazonium ions. Few complexes have been isolated where a diazoalkane molecule as such is present as a ligand, but their presence as reactive intermediates has been invoked in numerous occasions. Consequently most of the evidence presented is of an indirect nature. On the other hand, diazonium ions have yielded numerous stable complexes with transition metal derivatives. While this manuscript was in preparation, an authoritative review appeared in this field[1]. Hence, the emphasis will be on the most recent developments.

II. COMPLEX FORMATION BY DIAZOALKANES

The number of stable complexes of diazoalkanes reported in the literature is severely limited. Nevertheless in the few examples described the metal has been proposed to bind the diazoalkane in three different ways. Hence, metal–carbon, metal–nitrogen and 'side-on' bonding have been suggested.

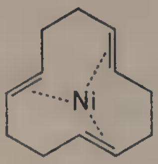
A. Carbon Coordination

There is a wealth of reactions in which diazoalkanes are thought to act towards metal derivatives as nucleophiles through the diazo carbon to give intermediates of type **6** (Scheme 1) but their direct observation has been limited to two reports.

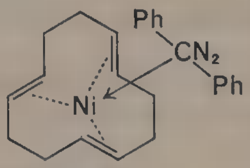


SCHEME 1

Upon treatment of **8** with diphenyl diazomethane at −78 °C the observed colour change from red to brown was attributed to the formation of a complex whose structure has been assigned as **9** on the basis of chemical evidence[2]. Furthermore, the less stable diazomethane apparently forms with **8** an analogous complex at lower temperatures[2].



(8)



(9)

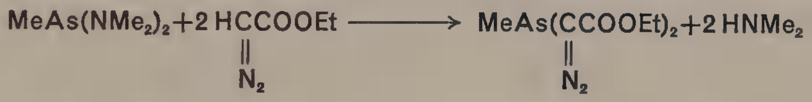
It has been postulated that a similar complex is formed in the reaction of $AlEt_3$ with diazomethane, which at −78 °C yields a colourless solution without nitrogen evolution[3]. Spectroscopic and other methods to probe further into the nature of the bonding in these complexes have not been used.

The intermediate **6** may suffer a variety of reactions which lead to the formation of different types of products. Thus it is often the case that compounds of Groups IVb and Vb which possess a basic or potentially basic group react with diazoalkanes possessing an α proton to give a heterosubstituted diazoalkane as in path (a). Some transition metal derivatives of Groups Ib and IIb have also been shown to react in this fashion but more often these derivatives induce the decomposition of diazoalkanes. Products of formal insertion of the diazo carbon into the bond between the metal and one of its substituents (by loss of nitrogen and 1,2-migration of a metal substituent to the former diazo carbon) are commonly observed with the normal elements and also with transition elements, the intermediacy of species **7a**, an 'inverse' metal ylide, or **7b**, a metal–carbene complex, often being postulated. These species have available other reaction paths such as polymerization via successive attack on **7** by diazoalkane and 1,2-migration of the growing alkyl chain, attack by the terminal nitrogen of another diazoalkane molecule to form an azine, attack by the carbon of another diazoalkane molecule with formation of olefin. In addition it may react with compounds such as olefins to give products of formal carbene insertion and/or of carbonium ion-type rearrangements.

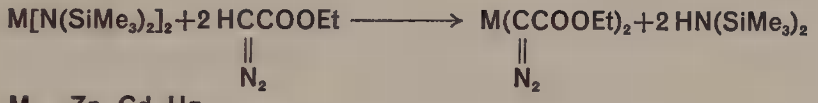
The factors that govern the path chosen by the reaction are not well understood at present. We shall examine some evidence that bears on the question of stability of intermediates **6** and **7**.

Reaction (a) (Scheme 1) has been widely applied in the synthesis of α-heterosubstituted diazoalkanes[4–13], as the examples given below testify.

$$\mathrm{2\,Me_3SnNMe_2 + CH_2N_2 \longrightarrow (Me_3Sn)_2CN_2 + 2\,HNMe_2} \qquad (1)^{14-16}$$

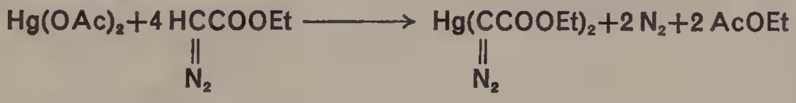


$$\mathrm{MeAs(NMe_2)_2 + 2\,H\underset{\underset{N_2}{\|}}{C}COOEt \longrightarrow MeAs(\underset{\underset{N_2}{\|}}{C}COOEt)_2 + 2\,HNMe_2} \qquad (2)^{17}$$

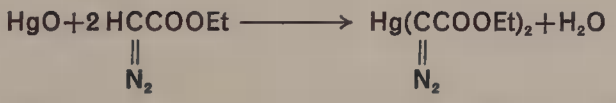


$$\mathrm{M[N(SiMe_3)_2]_2 + 2\,H\underset{\underset{N_2}{\|}}{C}COOEt \longrightarrow M(\underset{\underset{N_2}{\|}}{C}COOEt)_2 + 2\,HN(SiMe_3)_2} \qquad (3)^{18}$$

M = Zn, Cd, Hg



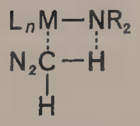
$$\mathrm{Hg(OAc)_2 + 4\,H\underset{\underset{N_2}{\|}}{C}COOEt \longrightarrow Hg(\underset{\underset{N_2}{\|}}{C}COOEt)_2 + 2\,N_2 + 2\,AcOEt} \qquad (4)^{19}$$



$$\mathrm{HgO + 2\,H\underset{\underset{N_2}{\|}}{C}COOEt \longrightarrow Hg(\underset{\underset{N_2}{\|}}{C}COOEt)_2 + H_2O} \qquad (5)^{20}$$

$$\mathrm{2\,AgOAc + 2\,CH_2N_2 \longrightarrow Ag_2CN_2 + 2\,AcOMe + N_2} \qquad (6)^{21}$$

The mechanism of the reaction of metal amide derivatives such as equations (1) and (2), has been the subject of several discussions[16]. A recent proposal[12], appealing in its simplicity, involves a rate-determining nucleophilic attack of the diazo carbon on the metal with formation of a 4-centred transition state of structure **10**, in which interaction also takes place between the diazo hydrogen and a basic ligand in the reactant.

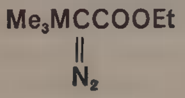


(10)

The reactions of diazoalkanes with transition metal derivatives, such as those shown in equations (4), (5) and (6), have not been studied from a mechanistic viewpoint. In the formation of disilverdiazomethane (equation 6), acetate may be replaced by other anions provided that they give silver salts soluble in the solvent employed. Yields are better with anions deriving from weak acids. Added base helps the reaction, presumably by partially bonding an outgoing proton and/or the terminal nitrogen in the diazoalkane thus rendering the carbon more nucleophilic.

Spectroscopic studies on α-heterosubstituted diazoalkanes provide some basis for judging factors that contribute to their stability. In the i.r. spectrum, these compounds present a band in the region 2150–1950 cm^{-1} attributed to an N—N stretching vibration, sensitive to the nature of the substituent.

For compounds **11**, the $\nu_{(NN)}$ values decrease with progression down the Periodic



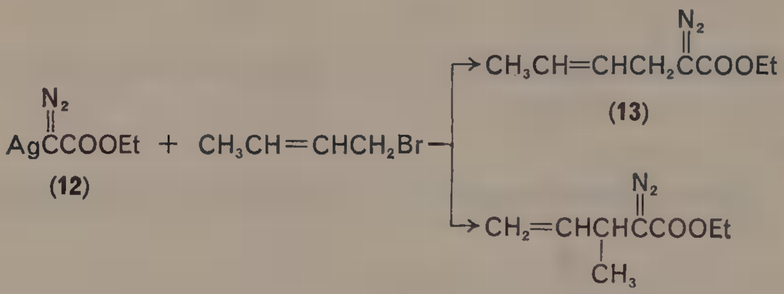
$$\mathrm{Me_3M}\underset{\underset{\displaystyle \mathrm{N_2}}{\|}}{\mathrm{C}}\mathrm{COOEt}$$

M = C, Si, Ge, Sn, Pb

(11)

Table. This trend may be interpreted by invoking the increasing electron-donating effect in the series partially compensated, in particular, in the case of the silicon compound, by p_π–d_π resonance interaction[22].

The possibility of the metal in a metal-substituted diazoalkane expanding its valence shell has also been shown for compound **12**. In its reaction with crotyl bromide, an 85/15 mixture of **13** and **14** is obtained pointing to the intermediacy of an ion pair[23].



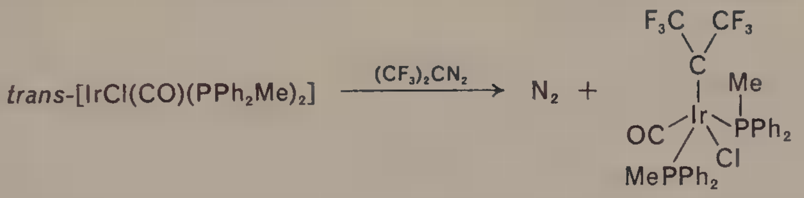
(12) **(13)** **(14)**

The intermediacy of metal–carbene complexes[24, 25] or 'inverse' metal ylides has been invoked in numerous metal derivative-catalysed decompositions of diazoalkanes[26–42]. The nature of the rate-determining step of the reaction has been established by kinetic measurements in only a few cases. In the reaction of diphenyldiazomethane catalysed by $ZnCl_2$ or $ZnBr_2$ to yield, after work up, mixtures of benzophenone and benzophenone azine, the kinetics and product proportions are consistent with rate-limiting formation of the complex $Ph_2\overset{+}{C}\overset{-}{Zn}X_2$ [36]. When $CuBr_2$ is employed as catalyst, a copper complex which may have diphenylmethylene as a ligand is formed in a rapid first step, the further consumption of diazoalkane occurring at a slower rate[32].

Correlations have been found between the rates of decomposition of diazoalkanes and their basicity and the strength as Lewis acid of the metal compound. Thus, while diphenyldiazomethane shows no reaction with $ZnCl_2$ below −15 °C, phenyldiazomethane reacts at −50 °C. The decreased basicity of the former compound may be attributed to inductive electron withdrawal and to the additional steric hindrance of the second phenyl ring[30]. On the other hand, in the presence of the typically strong Lewis acids $AlCl_3$ and $SnCl_4$, 0·1 mmol of diphenyldiazomethane reacts completely in air in less than 1 minute while the reaction takes hours in the presence of the weaker acids $ZnCl_2$ or $SnCl_2$ [30].

In the decomposition of diphenyldiazomethane aided by different metal salts the observation was made that the products were related to the reduction potential of the salt in H_2O [38]. Thus, when $Tl^{III}(OAc)_3$ ($E = +1{\cdot}21$ V) or $Cu^{II}(OAc)_2$ ($E = +0{\cdot}15$ V) was used the products resulted from a two-electron or one-electron transfer with formation of $Tl^{I}OAc$ and $Cu^{I}OAc$ respectively, whereas when $Cr^{III}(OAc)_3$ ($E = -0{\cdot}41$ V) was employed no reduction of the metal ion took place. The mechanism proposed involves internal acetate transfer within a metal–carbene complex[38].

In a very limited number of cases stable metal–carbene complexes have been isolated from the reaction of metal derivatives and diazoalkanes (equations 7 [41], 8 [31] and 9 [43]).

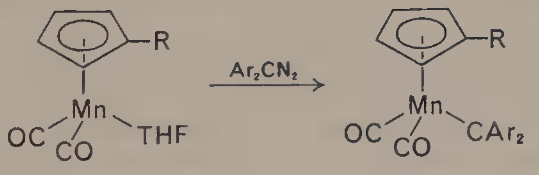


(15)

(7)

$$[Pd(PPh_3)_2(CH_2{=}CH_2)] \xrightarrow{FlN_2} \underset{\textbf{(16)}}{[Pd(PPh_3)_2(Fl)]} + CH_2{=}CH_2 \qquad (8)$$

Fl = 9-Fluorenylidene

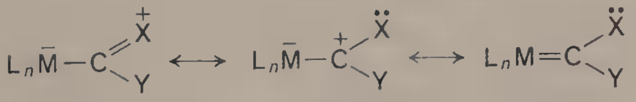


R = H, Me

(17)

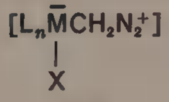
(9)

On the other hand, methods different from path (b) (Scheme 1) have been used to synthesize numerous complexes, most of which possess oxy, thio, seleno or amino substituents on the carbene carbon atom[24, 25]. These complexes may be said to originate from nucleophilic carbenes[44, 45] and their bonding is interpreted in terms of the limiting structures **18**, **19** and **20**. Complexes **15**, **16** and **17** would thus constitute exceptions by being electrophilic carbene complexes. Presumably the electron-withdrawing character of the carbene substituents induces strong π-back donation from the metal and hence produces a strong M—C bond.



(18) **(19)** **(20)**

The methylene insertion reaction has been the subject of several structure-reactivity studies that have confirmed that a nucleophilic attack on the metal is involved in the rate-determining step[46, 47]. The data available do not distinguish either between a stepwise and a concerted process or between a zwitterionic intermediate such as **21a** and an ion pair intermediate such as **21b**.



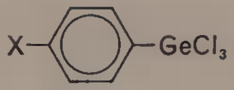
$$[\mathrm{L}_n\underset{\mathrm{X}}{\bar{\mathrm{M}}}\mathrm{CH_2N_2^+}]$$

(21a)

$[\mathrm{L}_n\mathrm{MCH_2N_2^+}]\mathrm{X}^-$

(21b)

In general it is found that organic substitution in the Group IVa halides tends to decrease the reactivity of the M—X bond towards diazomethane. Thus, while $SiCl_4$ reacted rapidly with CH_2N_2 in ether even at −50 °C to give $ClCH_2SiCl_3$, further methylenation was found to be increasingly difficult. Et_3PbCl, on the other hand, did react to give Et_3PbCH_2Cl in high yield[46]. A quantitative study of the substituent influence upon the reaction of **22** with CH_2N_2 has produced a ρ value of 2·3 [46]. These data show that more electrophilic character in the metal favours the reaction.

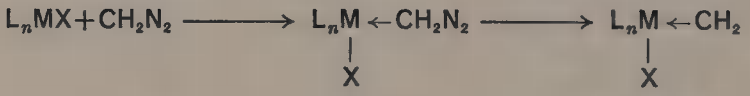


(22)

An initial association of diazoalkanes to the metal has also been proposed for their reaction with Group IIIa derivatives. The adduct reacts further to give either methylenation products[3, 48–52] or/and polymerization of the diazoalkane[3, 53].

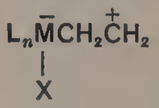
Qualitative experiments have led to the conclusion that the rate of the reaction depends on the Lewis acidity of the metal derivative. Thus, while BEt_3 reacts vigorously with CH_2N_2 at room temperature to give polymethylene, $B(OEt)_3$ requires hours under the same conditions[3].

The fate of the intermediate adduct has been found to depend on the Lewis acidity of the metal derivative as well, weaker acids favouring polymerization over insertion[50]. Thus higher proportions of polymerization over insertion are found for boron derivatives as compared with analogous aluminium ones, for derivatives substituted with OR groups rather than R, H or X, and for reactions in which additional donor molecules have been added[3]. A mechanistic interpretation may be given (equation 10). Intermediate **23** behaves as a strong electrophile and can add further diazomethane to form **24**. However, the stronger the interaction between the metal and the diazo carbon, the more effective will be the competition of M—X bond rupture and migration of X to carbon[54].



$$\mathrm{L}_n\mathrm{MX}+\mathrm{CH_2N_2}\longrightarrow \mathrm{L}_n\underset{\mathrm{X}}{\mathrm{M}}\leftarrow\mathrm{CH_2N_2}\longrightarrow \mathrm{L}_n\underset{\mathrm{X}}{\mathrm{M}}\leftarrow\mathrm{CH_2} \qquad (10)$$

(23)

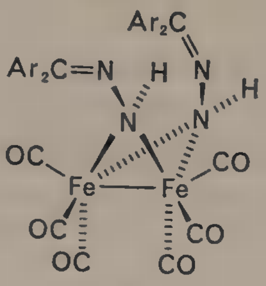


$$\mathrm{L}_n\underset{\mathrm{X}}{\bar{\mathrm{M}}}\mathrm{CH_2}\overset{+}{\mathrm{C}}\mathrm{H_2}$$

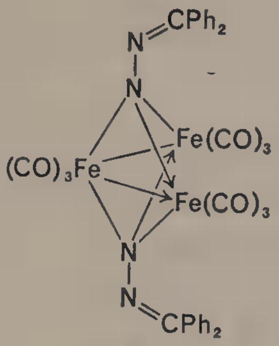
(24)

B. Nitrogen Coordination

The reaction of diphenyldiazomethane with dodecacarbonyltri-iron and also its irradiation in the presence of pentacarbonyliron in benzene leads to two compounds[55, 56], whose structures have been determined by X-ray studies to be **25**[55]



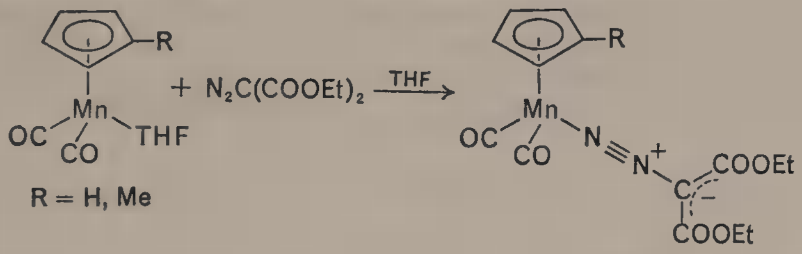
(25)



(26)

and **26**[56]. The N atoms in both complexes show angles characteristic of sp^3 hybridization and the N—Fe bond lengths are close to those found in other complexes known to contain N(sp^3)—Fe bonds.

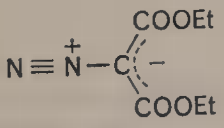
A single case has been reported where a diazo compound as such is bonded to a metal through its terminal nitrogen[57], as shown in equation (11). The product of the reaction is stable up to 80 °C, diamagnetic, and it liberates the diazomalonate ester upon treatment with PPh_3 under irradiation or with CO.



(11)

(27)

The structure proposed may be compared with those determined by X-ray studies for aryldiazenato complexes (see Section III.A), the basis for the comparison being the importance of limiting structure **28** in the ground state of the diazoester.



(28)

Complexes **27** show i.r. absorptions at 2025, 1982 and 1951 cm^{-1} (R = H) and 2022, 1979 and 1948 cm^{-1} (R = Me). By analogy with $[M(\pi\text{-}C_5H_5)(CO)_2(N_2Ar)]$ (M = Cr[58], Mo[59–61] or W[62, 63]), the first two bands may be assigned to $\nu_{(CO)}$ and the last to $\nu_{(NN)}$. The high value of $\nu_{(NN)}$ points to a ligand with an NNC angle close to 180° (see Section III.C.1).

C. ‘Side-on’ Coordination

A series of complexes of Ni and Pd have been synthesized in which a diazoalkane ligand is claimed to be bonded ‘side-on’[31, 64]. They have the general composition $[ML^1L^2(\text{diazoalkane})]$ (**29**) with the ligands being *t*-BuNC, PPh_3 or 1,5-cyclooctadiene and the diazoalkanes, 9-diazofluorene or diphenyldiazomethane. These complexes have been synthesized via addition reactions to $[ML^1L^2]$[65] or ligand substitution reactions with $[ML^1L^2(CH_2{=}CH_2)]$, as shown in the examples (12) and (13).

$$[ML^1L^2] \xrightarrow{R_2CN_2} \underset{\mathbf{(29)}}{[ML^1L^2(R_2CN_2)]}$$

$$[Ni(t\text{-}BuNC)_2] \xrightarrow{Ph_2CN_2} [Ni(t\text{-}BuNC)_2(Ph_2CN_2)] \tag{12}$$

$$[Pd(PPh_3)_2(CH_2{=}CH_2)] \xrightarrow{FlN_2} [Pd(PPh_3)_2(FlN_2)] \tag{13}$$

Fl = 9-Fluorenylidene

The complexes **29** present an i.r. absorption attributed to $\nu_{(NN)}$ between 1550 and 1450 cm^{-1}; a linear end-on coordination involving the terminal nitrogen would presumably show in the region around 2000 cm^{-1} and a coordination through carbon presumably still higher. Furthermore, the trends observed in the i.r. spectra upon changing the metal, the ligands and the diazoalkane parallel the trends found upon similar changes in complexes containing an alkyne ligand, which is known to be bonded ‘side-on’[31].

The structure of the ketenimine complex $[Ni(t\text{-}BuNC)_2\{t\text{-}BuN{=}C{=}C(CN)_2\}]$ has been determined by X-ray studies to involve a ‘side-on’ coordination in which the Ni atom is nearly equidistant to the N and the adjacent C [66]. A similar proposal has been made for the bonding in the diazoalkane complexes, where the orbital picture would involve the donation from an occupied π orbital localized between the nitrogen atoms to the metal and π back donation from the metal into the corresponding unoccupied π^* orbital. ‘Side-on’ coordination has also been suggested for analogous derivatives with dicyanodiazomethane as ligand[66].

III. COMPLEX FORMATION BY DIAZONIUM IONS

Since the first synthesis of an aryldiazenato† complex of a transition metal in 1964 [59], this area of chemistry has been continuously expanding both in the quantity and in the scope of the research carried out in it. Among the transition metals belonging to Groups VIb, VIIb and VIII, there only remain to be isolated complexes of Tc, Ni and Pd. On the other hand, the vast majority of the complexes reported involve the aryldiazenato ligand, only a handful of alkyldiazenato complexes having been characterized.

A. Structure

The terminal aryldiazenato ligand has been observed in two geometrical forms: singly bent and doubly bent. In the first instance the bonding is described as σ-donation from an sp hybrid orbital on the terminal nitrogen with π back donation from d orbitals of the metal into a p orbital on the terminal nitrogen ($N_{(1)}$). A simple valence bond description of this type of complex has been given (structure **30**)[67]. Evidence exists to show that upon reaction of an arenediazonium salt to form a

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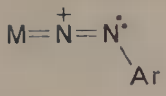
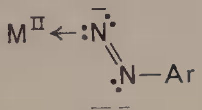
† The following nomenclature will be used[1]: diazene (HN=NH), aryldiazene (ArN=NH), aryldiazenato ($ArN_2{-}$ or $ArN_2{<}$) and arenediazonium (ArN_2^+).

complex where the aryldiazenato ligand is coordinated in this fashion, the oxidation state of the metal suffers no change. Hence, the ligand may formally be regarded as an ArN_2^+ two-electron donor ligand.



(30)

The doubly bent terminal ligand has been described as having a single bond by overlap between an sp^2 orbital on $N_{(1)}$ with a hybrid orbital on the metal, as shown in structure **31** [67]. In this case, the evidence available indicates that when an arenediazonium ion becomes coordinated as a doubly bent ligand, the metal suffers a formal two-electron oxidation. The bonding may hence be formally described as that between a two-electron donor ArN_2^- ligand and a doubly oxidized metal.



(31)

The X-ray studies reported[1, 68, 69] for complexes containing a singly bent ligand[70, 71] show that the NNC angles lie within the range 118–124°, the only exception being $[RuCl_3(PPh_3)_2(p\text{-}N_2C_6H_4Me)]$, with a value of 137°. It has been suggested that slight back donation from the metal into π^* orbitals on the aryldiazenato moiety leaves the N—N bond largely as a triple bond and the NNC angle close to 180° (hypothetical linear terminal diazenato ligand)[1], whereas stronger back donation as described above predicts this angle to be 120°. Intermediate values of the angle might be expected depending upon the relative importance of the linear and singly bent formalisms to the electronic structure or, equivalently, upon the degree of the metal to ligand electron transfer process[67] (see Section III.C.1). Detailed discussions on the electronic structure of the isoelectronic nitrosyl ligand have been reported[72, 73].

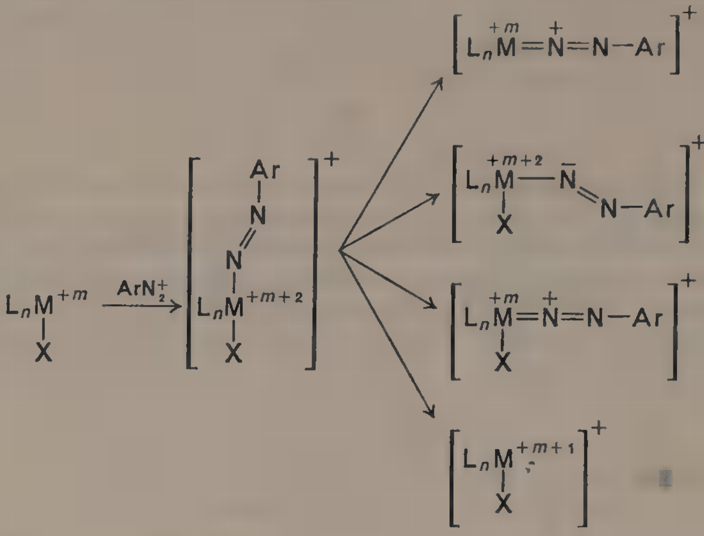
B. Synthesis

The most frequently used reagents for preparing aryldiazenato complexes have been diazonium salts, either as such or as compounds that generate them *in situ*. The complexes are produced via ligand substitution, oxidative addition or Lewis base association reactions[74].

A general mechanism has been proposed[1], which has received additions and partial confirmation from comparative electrochemical studies on nitrosyl and aryldiazenato complexes[75]; it is shown in Scheme 2. The nature of the products has been observed to depend on the metal and its ligand, but with the exception mentioned above[75] no quantitative studies have yet been reported.

Complexes between diazonium ions and transition metal derivatives have been postulated as reactive intermediates in the Sandmeyer[76–79] and related[80] reactions, but structural proofs are not available.

Several other methods have been used to prepare aryldiazenato complexes including[1] apparent insertion of diazonium ions into metal–hydrogen bonds followed by deprotonation of the aryldiazene complex formed[81], reaction of coordinated nitrosyl with aromatic amines, reaction of metal complexes with arylhydrazines[82], organodiazenes or diazoalkanes[83], and modification of complexes already containing an aryldiazenato ligand[81].



SCHEME 2

C. *Spectroscopic Properties*

1. Infrared spectroscopy

Infrared studies have provided a useful tool for examining the interaction of the aryldiazenato ligand with the transition metal to which it is bonded and with other ligands present in the complex. Several studies have shown that although overlap of $\nu_{(NN)}$ with the absorption of other groups in the complex and coupling between the N—N stretching vibration with aryl vibrational modes occur[61, 84, 85], the isolation of $\nu_{(NN)}$ is possible by mathematically decoupling the interacting bands which shift upon ^2H or ^{15}N substitution[85].

The N—N stretching vibration is found within the broad region defined between *c.* 1440 and 2100 cm^{-1}. This wide range is a reflection of the different coordination modes of the aryldiazenato ligand, i.e. **30** and **31**. High values of $\nu_{(NN)}$ ($>c.$ 1650 cm^{-1}) can generally be attributed to the occurrence of complexes of type **30**, whereas low values of $\nu_{(NN)}$ ($<c.$ 1500 cm^{-1}) can be generally identified with complexes of type **31**. With values in the intermediate overlap region, the assignment is not trustworthy.

A method has been proposed[70] which brings the $\nu_{(NN)}$ values to a common scale and reduces the region where the ligand structure assignment is doubtful, the basis of it being the variations expected in $\nu_{(NN)}$ upon changing the nature of the metal and its ligands.

The mutual influence of the aryldiazenato ligand and other ligands present in the same complex can be studied in CO-containing complexes, since $\nu_{(CO)}$ is an easily identifiable absorption. An increase in $\nu_{(CO)}$ implies an increase in the C—O bond order, a consequence of diminished d_π–p_π back donation by the metal[60]. This effect may be induced by substituents in the aryldiazenato ligand. Thus, in complexes **32**,

$$[Fe(PPh_3)_2(CO)_2(p\text{-}N_2C_6H_4X)]^+\ BF_4^- \qquad X = NO_2,\ F,\ Cl,\ H,\ Br,\ OMe,\ OH$$

(32)

the better electron-withdrawing substituents produce the highest $\nu_{(CO)}$ and the lowest $\nu_{(NN)}$ of the series[86], pointing to electron flow from the CO groups to the aryldiazenato ligands.

The complexes of the heavier metals present lower $\nu_{(NN)}$ values (or/and lower $\nu_{(CO)}$ values when appropriate) indicating that they are better electron donors than the lighter ones. Thus for example, $[RuBr_3(PPh_3)_2(p\text{-}N_2C_6H_4Me)]$, $\nu_{(NN)} = 1895\ cm^{-1}$, may be compared with $[OsBr_3(PPh_3)_2(p\text{-}N_2C_6H_4Me)]$, $\nu_{(NN)} = 1855\ cm^{-1}$ [87].

The electronic configuration of the metal influences its capability of back donating electron density, a comparison of the $\nu_{(NN)}$ values for the aryldiazenato complexes reported showing that they exhibit a general trend in which $\nu_{(NN)}$ decreases as the d^n configuration of the metal increases[88]. Since the data available are rather scarce, simultaneous variations in the ligands, the charge and the metal are included in the comparison.

The i.r. spectra of complexes **33** ($\nu_{(NN)} = 1723$, $\nu_{(CO)} = 2030$, $1978\ cm^{-1}$) [89] and **34** ($\nu_{(NN)} = 1689$, $\nu_{(CO)} = 2010$, $1960\ cm^{-1}$) [90], show that a positive charge, which may be assumed to reside mainly on the metal[86], diminishes the electron density available on the latter to share with the ligands.

$[Fe(CO)_2(PPh_3)_2(PhN_2)]^+\ BF_4^-$ **(33)**

$[Co(CO)_2(PPh_3)_2(PhN_2)]$ **(34)**

The nature of the ligands influences the availability of electrons on the metal. In equation (14), replacement of CO by the relatively poorly accepting PPh_3 ligand

$$[Mo(CO)_2(\pi\text{-}C_5H_4PPh_3)(ArN_2)] + PPh_3 \longrightarrow [Mo(CO)(\pi\text{-}C_5H_4PPh_3)(PPh_3)(ArN_2)] \tag{14}$$

$$[Mo(CO)_2(OH)(ArN_2)]_4 + Base \longrightarrow [Mo(CO)_2(OH \leftarrow Base)(ArN_2)]_4 \tag{15}$$

results in an increased electron release from the metal and $\nu_{(NN)}$ and $\nu_{(CO)}$ occur at lower wave numbers in the products[91]. In equation (15) the lower $\nu_{(NN)}$ and $\nu_{(CO)}$ values observed in the adducts[92] may be related to increased electron release from the metal caused by donation of electron density from the Lewis base to the OH ligand through a hydrogen bond.

TABLE 1. Correction parameters to $\nu_{(NN)}$ (cm^{-1})

Metal		Group		Charge		Ligands		Coordination number	
First row	−50	VIb	+100	+2	−140	Third PPh_3	+20	4	+50
Second row	−30	VIIb	+50	+1	−80	Fourth PPh_3	+50	5, 6, 7	0
(Mo, −10)		VIII	0	0	0	$HBPz_3^-$ [a]	−20		
Third row	0			−1	+80	$\pi\text{-}C_5H_4PPh_3$	+60		
				−2	+140	H^-	+20		
				−3	+200				

[a] Pz = 1-Pyrazolyl.

Table 1 collects the suggested correction parameters which should be added (or subtracted) to $\nu_{(NN)}$ [70] to obtain a modified frequency $\nu_{(NN)}$. The magnitudes of the corrections have been chosen so as to give the best agreement with data collected from several hundred known complexes of the isoelectronic nitrosyl ligand.

The number of X-ray structure determinations being very limited, the $\nu_{(NN)}$ values provide a useful tool to predict confidently the type of ligand present in the great majority of aryldiazenato complexes, a value above 1550 cm^{-1} indicating a complex of type **30** and one below 1530 cm^{-1} of type **31**.

A relationship between electron back donation by the metal and i.r. spectra has been demonstrated in complexes containing the *monohapto*-dinitrogen ligand[93, 94], isoelectronic with NO^+ and with ArN_2^+ [95]. In a series of these complexes, X-ray photoelectron spectroscopy studies show that increasing electron density on the N_2 fragment, as measured by the binding energy of its core electrons[96], is coupled with decreasing NN stretching frequencies[97].

2. N.m.r. spectroscopy

Although the ^{1}H-n.m.r. spectra of many of the aryldiazenato complexes reported have been determined, the information they yield is very unspecific and hence they have been utilized as an analytical tool rather than as a probe into the electronic distribution in the complexes. On the other hand, ^{19}F-n.m.r. studies are severely limited in number[61, 98, 99], but they have yielded valuable information on the interaction at the electronic level between metal, aryldiazenato ligand and other ligands in the complex.

The most recent and complete study[61] has applied the technique of Taft[100] and coworkers where the differences in chemical shifts between a *para*- and a *meta*-F substituent are taken as a measure of the electronic effects acting on the ring that holds these substituents. Thus, the more positive the value of $\delta_p - \delta_m$ is, the less shielded the *para*-F is relative to the *meta*-F substituent, and hence the less electron flow into the aryl ring has taken place.

Some results obtained are collected in Table 2. Comparisons among them lead to the same conclusions concerning the influence of the metal and its ligands on the aryldiazenato ligand, as reached on the basis of i.r. spectra.

TABLE 2. ^{19}F-N.m.r. data for aryldiazenato complexes[a]

Complex	$\delta_p - \delta_m$ (p.p.m.)
$[Mo(\pi\text{-}C_5H_5)(CO)(PPh_3)(N_2Ar)]$	−5·02
$[W(HBPz_3)(CO)_2(N_2Ar)]$[b]	−4·54
$[Mo(\pi\text{-}C_5H_4PPh_3)(CO)(PPh_3)(N_2Ar)]^+ BF_4^-$	−3·86
$[Mo(HBPz_3)(CO)_2(N_2Ar)]$[b]	−3·58
$[Mo(\pi\text{-}C_5H_5)(CO)_2(N_2Ar)]$	−2·20
$[Mo(HCPz_3)(CO)_2(N_2Ar)]^+ BF_4^-$	−2·11
$[Mo(\pi\text{-}C_5H_4PPh_3)(CO)_2(N_2Ar)]^+ BF_4^-$	−0·14

[a] Chemical shifts for CH_2Cl_2 solutions and referred to external hexafluorobenzene.

[b] Pz = 1-pyrazolyl.

D. Chemical Properties

No quantitative study on the reactivity of aryldiazenato complexes has yet appeared in the literature. Conclusions concerning the influence of the metal, of the substituents on the aryldiazenato ligand and of the rest of the ligands on the reactivity of the complexes have been based on a reaction failing to produce the expected product or not, or on the total time required for a complex to disappear under given conditions. Some of these data are discussed below.

In general, the reactivity of the complex is very dependent upon the type of bonding between the metal and the aryldiazenato ligand. Complexes possessing structure **30**, which present an M–N bond with a substantial double bond character, are found to be more stable towards N_2 loss than complexes of type **31**, where the M–N bond is essentially single. The N–N bond in complexes **30** presents a partial triple bond character (see Section III.A) and is found to be more difficult to saturate than the corresponding bond in complexes of structure **31**, where it is essentially a double bond. Furthermore, the tendency to react with acids of complexes **30**, which present a ligand impoverished in electrons, is found to be diminished as compared with complexes **31**, where the ligand is rich in electrons.

The nitrogen evolution from complex **35** according to equation (16) is fastest when a NO_2 substituent is present[101], pointing to decreased electron withdrawal

$$\underset{\textbf{(35)}}{[\mathrm{Pt(PPh_3)_3}(p\text{-}\mathrm{N_2C_6H_4X})]^+\,\mathrm{BF_4^-}} \longrightarrow [\mathrm{Pt(PPh_3)_3}(p\text{-}\mathrm{C_6H_4X})]^+\,\mathrm{BF_4^-} + \mathrm{N_2} \qquad (16)$$

$X = NEt_2, NMe_2, OMe, H, Me, F, NO_2$

by Pt^{II} in **35** and hence decreased Pt–N double bond character, when electronegative substituents are present. In accord with this explanation, a negative slope is observed for the correlation between the u.v. absorption corresponding to the n–π^* transition and Hammett's substituent parameters, σ[101]. Furthermore, in the complexes $[Pt(PPh_3)_2(L)(ArN_2)]^+ BF_4^-$ the stability towards the decomposition shown in equation (16) follows the order $NH_3 \simeq \text{pyridine} > PEt_3 \simeq RNC > CO$, thus paralleling the global electron-donating effect of the ligand[102].

The complexes $[M(PPh_3)_2X_3(ArN_2)]$ (M = Ru, Os; X = Cl, Br) exhibit i.r. spectra consistent with structure **30** and are air-stable solids, resistant to protonation or hydrogenation under mild conditions[87]. On the other hand, the complexes $[Rh(PPh_3)_2X_2(ArN_2)]$, presumably of structure **31**, are stable as solids, but when dissolved in organic solvents they yield unstable solutions which react by eliminating nitrogen or, when possible, by abstraction of HCl from the solvent[87].

The complexes $[Os(CO)_2(PPh_3)_2(PhN_2)]^+ PF_6^-$ are very reactive towards protonation, slowly extracting protons from freshly distilled methanol or ethanol, while their ruthenium analogues, although they can be protonated by acids, are stable in the presence of neutral alcohols[87]. A relationship has been established between basicity of a complex and its $\nu_{(NN)}$ frequency. Thus, the following order in basicities has been obtained[81] for the d^6 complexes **36**, **37** and **38**: **36** $[\nu_{(NN)} = 1455\ \mathrm{cm^{-1}}] >$ **37** $[\nu_{(NN)} = 1462\ \mathrm{cm^{-1}}] >$ **38** $[\nu_{(NN)} = 1470\ \mathrm{cm^{-1}}]$.

$[OsCl(CO)_2(PPh_3)_2(PhN_2)]$

(36)

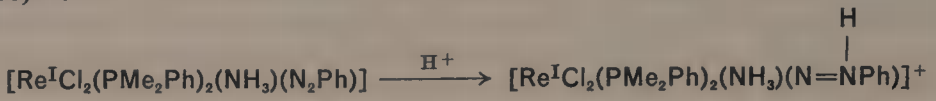
$[RuCl(CO)_2(PPh_3)_2(PhN_2)]$

(37)

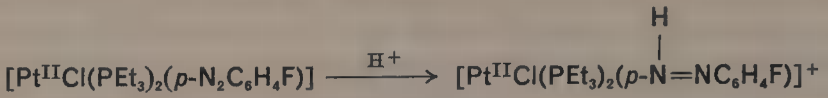
$[IrCl_2(CO)(PPh_3)_2(PhN_2)]$

(38)

Not only the ease of protonation but also the site of protonation varies with the structure of the aryldiazenato complex. Thus complexes **30** are expected to protonate on $N_{(2)}$ while complexes **31** are expected to do so at $N_{(1)}$. These expectations have been confirmed by X-ray studies in the cases of equations (17)[103] and (18)[104].



$$[\mathrm{Re^{I}Cl_2(PMe_2Ph)_2(NH_3)(N_2Ph)}] \xrightarrow{H^+} [\mathrm{Re^{I}Cl_2(PMe_2Ph)_2(NH_3)(N{=}\overset{\overset{\displaystyle H}{|}}{N}Ph)}]^+ \qquad (17)$$



$$[\mathrm{Pt^{II}Cl(PEt_3)_2(\mathit{p}\text{-}N_2C_6H_4F)}] \xrightarrow{H^+} [\mathrm{Pt^{II}Cl(PEt_3)_2(\mathit{p}\text{-}\overset{\overset{\displaystyle H}{|}}{N}{=}NC_6H_4F)}]^+ \qquad (18)$$

Finally, although the discussion has been centred on aryldiazenato complexes, most of it should apply as well to alkyl, acyl and aroyl diazenato complexes. Caution should be exercised however in not extending the generality too far because the stability of the aryldiazenato as ligand is greatly influenced by its capability to accept π electrons from a metal, a characteristic not shared by alkyldiazenato groups[105].

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CHAPTER 8

Synthetic applications of diazonium ions

D. S. Wulfman

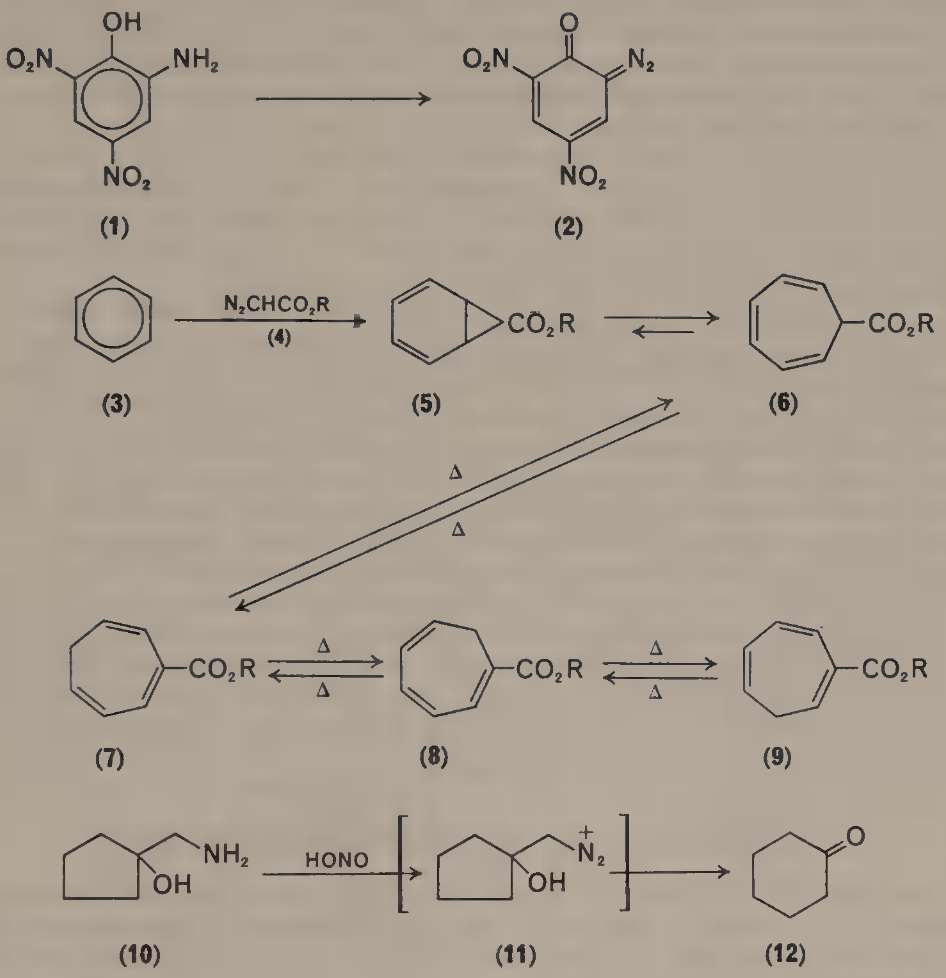
Department of Chemistry, University of Missouri-Rolla, Rolla,
Mo 65401, USA, and
Équipe de Recherche No. 12 du CNRS, Laboratoire de Chimie,
École Normale Supérieure, Paris, France

I. INTRODUCTION

The treatments in this and the following chapter will in many cases be rather selective as a consequence of the sheer volume of material reported on an annual basis and the large number of reviews which have covered various aspects during the past 20 years. (Reviews are marked with an asterisk in the References.) In the areas dealing with the alleged generation of carbenes and carbenoids from diazoalkanes the author has refrained from employing these terms, for as Kirmse has cautioned[655], and the author has recently shown[1309, 1310], the assignment of reactions to these categories rests predominantly on a house-of-cards. In only a very few instances can assignments be made with any degree of rigour.

Numerous examples and studies have probably been overlooked, for the species are sufficiently common and their reactions so frequently employed that the processes have not been abstracted and are not detected by key word searches. In these instances the examples chosen reflect only a bias on the part of the writer for reading literature related to his synthetic and pedagogical needs and not a feeling that a particular worker's contribution is unworthy of enshrinement. The author has tried to cover all literature abstracted through October 1975 and all major journals which were in his hands by that date. In addition he has tried to enlist the aid of many workers who had published in the area during the preceding 2 years. Their responses are too numerous to acknowledge fully but results were made available to him prior to publication by Arackal, Eistert, Doyle, Brokken-Zijp, Carrié, L. and Y. Vo-Quang, Hubert, Woolsey, Marchand, Moss and Rössler. Their kind aid is gratefully acknowledged along with that of S. Julia who made his extensive notes on diazo alkane chemistry available to the author.

The origin of diazo chemistry dates from the initial generation of diazonium succinamic acid from asparagine by Piria[991, 992] in 1849. It had only a transient existence and proceeded to malic acid. Much chemistry has been performed on this class of compounds which furnished one of the major bases for the foundation of the modern chemical industry. Modern synthetic chemistry is normally assumed to begin with the work of Johann Peter Griess[446] in 1858 when he undertook to clarify the observations of Gerland[429] (1853) that a red intermediate was formed in increasingly greater proportion at lower temperatures when aminobenzoic acid was converted to hydroxybenzoic acid by the action of nitrous acid. His studies, like Gerland's, were undertaken at the suggestion of Kolbe and followed the earlier observation by Hunt[226] in 1849 that treatment of aniline with nitrous acid generated phenol. Griess[226] modestly attributed his successes to the fact that he operated at a lower temperature than Hunt of Gerland. He studied the reaction of nitrous acid with picramic acid (1) and obtained the diazoxide (2) which he quickly recognized as belonging to a new class of compounds. He immediately proceeded to subject many other amino compounds to the same treatment. He prepared the first azo coupling product in 1861–62[451, 1328] and by 1865–66 it was being prepared on a large scale by Caro[226].



SCHEME 1

Griess continued his work for 3 years when he was Hofmann's assistant in London and afterwards while working in a brewery for Messrs Allsopp, Burton-on-Trent. He was faced with the need for CHN analyses and overcame the problem by developing a barter system with R. Schmitt in Dresden. Hempel's account is of interest: 'Regelmässig kamen von Burton an den Ufern des Trent die von Greiss dargestellen neuen Körper in kleinen Packeten, um in Dresden an der Elbe analysirt zu werden. Per Fracht kamen dann wohl gleichzeitig als willkommene Beilage Fässer von Allsopp's berühmten Pale Ale in ausgesuchtester Qualität.' Griess's investigations were very thorough and he discovered many of the reactions of aryl diazonium ions which had been observed up until the time of his death in 1891. Thus, by 1908 (50 years after his initial work) chemists had a rather thorough knowledge of the chemistry and structure of aromatic diazonium ions although work still continues in the area. The accuracy of many of the observations is all the more impressive when it is remembered that these progresses were realized without i.r. and n.m.r. spectroscopy, X-ray structure determination and only very crude u.v.[307, 1343] and visible spectra[20] studies.

The first important studies in the aliphatic area after Piria's initial work occurred in 1883 when Curtius prepared diazoacetic ester (**4**)[275, 287]. Diazomethane was prepared by von Pechmann[1247] in 1894. The use of copper salts with aromatic diazonium salts was examined by Sandmeyer[1091, 1346] in 1884, and Gattermann[416] substituted finely divided copper powder for its salts in 1890.

A great resurgence in diazoalkane chemistry occurred in the 1950's when groups led by Alder[11] and Doering[309] reinvestigated the structure of the esters and acids obtained by Buchner[169, 221, 222] from the decomposition of ethyl diazoacetate in benzene(**3**–**9**). Further impetus was gained from the production of 'evidence' that decomposition of diazoalkanes proceeds via 'carbene' intermediates. Additional interest arose from the increasing demand for synthetic pathways for strained hydrocarbons, the study of 1,3-dipolar cycloaddition reactions and studies related to examining the reliability and validity of orbital symmetry calculations.

The chemistry of alkyl diazonium ions has long been the object of a variety of mechanistic and synthetic studies with the synthetic efforts being primarily directed towards exploiting rearrangements of the Tiffeneau–Demjanov type (**10** → **12**) and the replacement of amino functions by various substituents. Most recently, research in this area has been directed towards the generation, isolation and use of diazotates as synthetic intermediates and the continued development of improved means of changing amino functions to other functions.

II. REACTIONS OF ARYL DIAZONIUM IONS

The reactions of aryl diazonium ions have been systematically classified by Saunders[1103]. His classification system with minor changes is adequate and will be used here. It is summarized in the Table of Contents† for this chapter and is used with the permission of the publisher.

The formation of diazonium ions is the subject of another Chapter in this book and will not be dealt with further. Saunders[1103] gives a very detailed discussion of the subject with appropriate references.

The aryl diazonium ions are of varying stability. Their stability is strongly influenced by the pH of the solution, temperature, the anions present, trace contaminants such as transition metal ions and the presence or absence of water[1103].

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† Except for Class C, Group 3 (Reduction products) and Group 5 (S-azo products—diazo-thioethers) which are treated in other sections.

In the solid state some aryl diazonium salts exhibit appreciable stability whereas others are quite brisant explosives. There would appear to be no basic guidelines which predict stability without exceptions but it is possible to make some generalizations. It is highly probable that diazonium salts where the counter-ion is a reasonable oxidizing agent such as nitrate[116], chromate[1103], perchlorate[1103], chlorate[1103], etc. will not exhibit a high degree of stability. Conversely sulphates tend to be more stable as are the chlorides[1103]. However, the behaviour of *p*-diazobenzene sulphonate is notoriously fickle and some workers have found it quite dangerous[110]. Diazonium ions which have a potential leaving group *ortho* to the diazonium function are potentially dangerous because they can form 'benzynes' with the *o*-carboxy and *o*-SO_2^- compounds being at the extreme end of the scale[570]. In these cases fragmentation furnishes two neutral molecules, N_2 and CO_2 or SO_2, all with high heats of formation. There are several diazo derivatives which have been patented as explosives. Thus 4,6-dinitro-2,1-diazoxide[251] has been used as a detonator which is less sensitive to friction than mercury fulminate or lead azide but equal or superior to both as a detonator. One should be suspicious of any

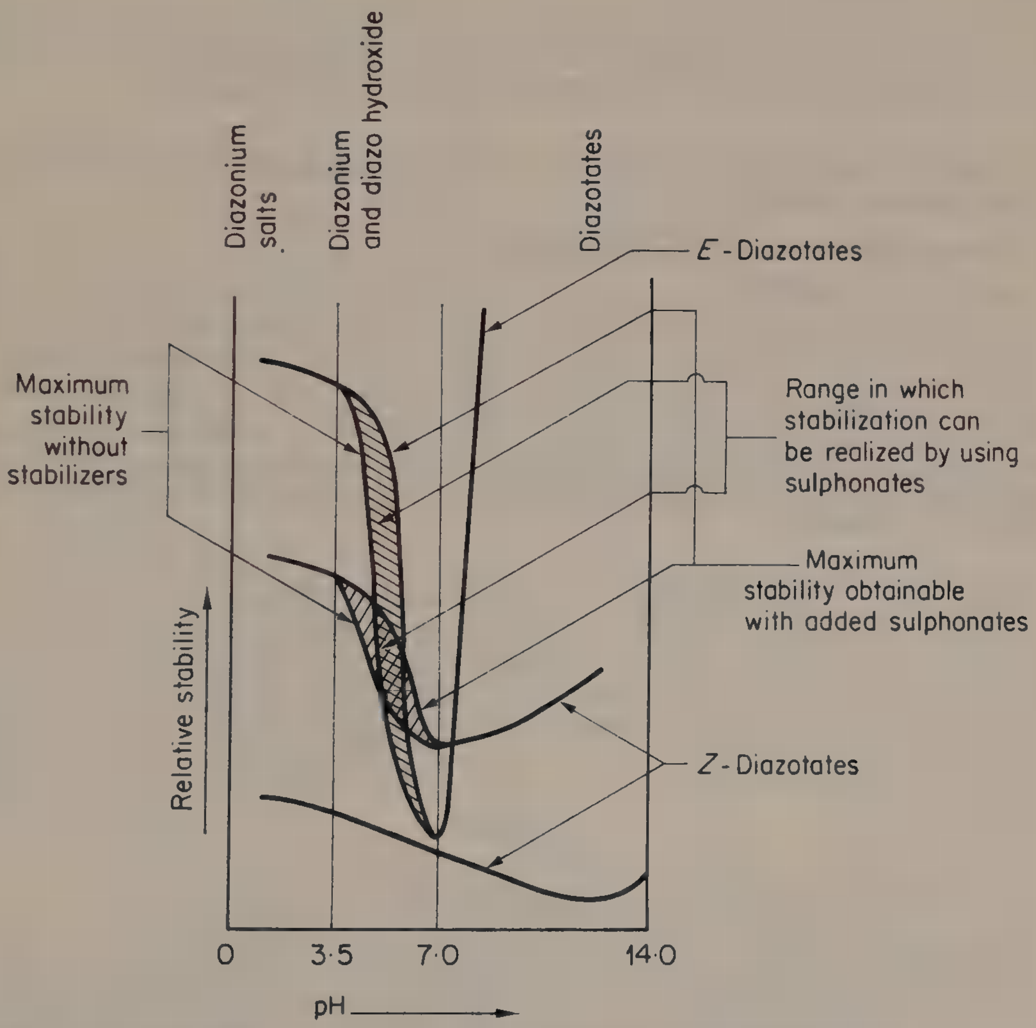


FIGURE 1. Reprinted (with permission) from Saunders, *The Aromatic Diazo Compounds*, 2nd ed., Edward Arnold, London, 1949.

compound having sufficient oxygen to convert more than half of the carbon atoms present into CO and/or a C/N ratio <3. All dry diazonium salts should be considered suspect until clearly demonstrated as being stable and then they should be treated with respect. In aqueous solution decomposition of benzene diazonium ion in strongly acidic media is independent of the anion (Cl^-, Br^-, SO_4^{2-}, NO_3^-)[1129, 1130, 309, 506] and proceeds according to the expression[169, 221, 222], $\ln k = 35{\cdot}6457 - 27025/RT$.

Cain[224] found that the rate of decomposition fell at very high pH values. The overall trend in stability has been summarized by Saunders[1103] in Figure 1. Snow[1160] compiled a list of 32 diazonium chlorides arranged in order of their stability at 20 °C but there appears to be no obvious correlation of structure with stability. It had been claimed that negative substituents increase stability[1103] but the data do not support such a claim[1160].

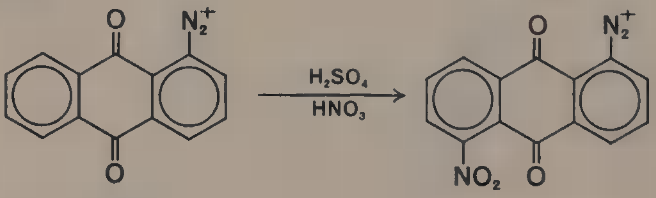
Some metals form double salts with diazonium ions and retard their decomposition. Similar effects occur upon addition of aryl sulphonic acids[760, 810] and on the addition of sodium chloride[506, 1130], borates[1143], tungstates[725] and other neutral salts. Excess nitrite and nitrate is deleterious[675, 1234] as is the presence of colloidal platinum[333], and of copper and its salts[132, 133].

The diazonium ion salts of strong acids are essentially 100% ionized and therefore are comparable to K or Na salts in their degree of hydrolysis, but unlike these metal ions they do form stable covalent bonds with such nucleophiles as RS^-, ^-OH and ^-CN. The resulting products will be discussed under Class B reactions.

A. Class A: Derivatives Formed by Substitution or by Changes in the Substituents of the Aryl Nucleus

1. Group 1: Electrophilic substitution

Although diazonium ions are of only moderate stability it is possible to perform some substitution reactions upon the aryl nucleus. This is facilitated by the fact that the $-N_2^+$ ion is the strongest electron-withdrawing group encountered in organic chemistry and acts both inductively and mesomerically. It is not surprising that in the benzenoid systems the diazonium compounds most prone to electrophilic substitution are the diazooxides which are formally neutral molecules. With polyannulated systems, electrophilic substitution occurs in a ring not bearing the $-N_2^+$ function[1363] (Scheme 2).

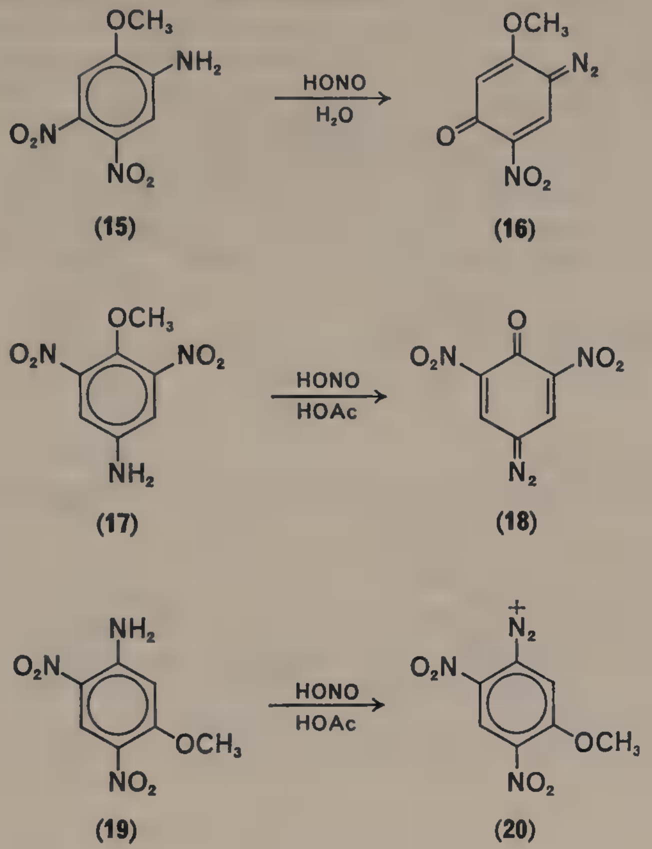


(13) **(14)**

SCHEME 2

2. Group 2: Solvolysis of substituents on the aryl nucleus

When diazotization of an *ortho*- or *para*-substituted amine is carried out, there is always the possibility of the solvent, normally water, replacing a labile substituent to form an *o*- or *p*-diazoxide. This can be prevented by operating in a highly acidic medium where the activity of the water is greatly suppressed by protonation and if the substituent is a chloride or bromide, by using HCl or HBr. Meldola[782] and colleagues examined these processes in great detail and found that normally two electron-withdrawing functions should be present on the initial amine and preferably in an *ortho* and/or *para* relationship to the departing group. Under such conditions



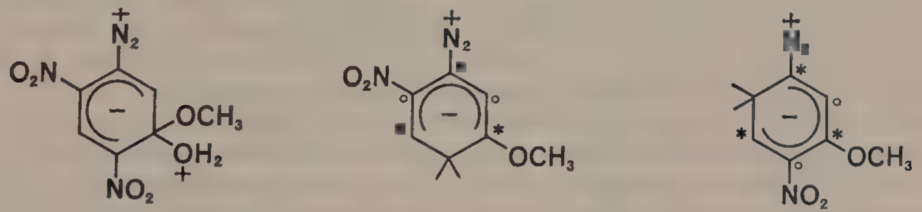
(15) (16)

(17) (18)

(19) (20)

Scheme 3

NO_2 can leave as nitrite ion. Anisoles can even be solvolysed in acetic acid to furnish the diazo oxide. The failure to solvolyse in the last example is to be predicted on the basis that none of the required Wheland intermediates (Scheme 4) for replacement of NO_2 places charge (PMO analysis)[291, 292] upon more than one starred atom bearing an electron-withdrawing substituent. With the replacement of the OCH_3, the required Wheland intermediate places N_2^+ on an unstarred position and the driving force is not present. The rule appears to be that the leaving group must be on a carbon which furnishes a Wheland intermediate where the N_2^+ and one other strong electron-withdrawing substituent are present on starred atoms. Such a treatment is equivalent to the rules of Meldola and Hay[784]. When NO_2 or

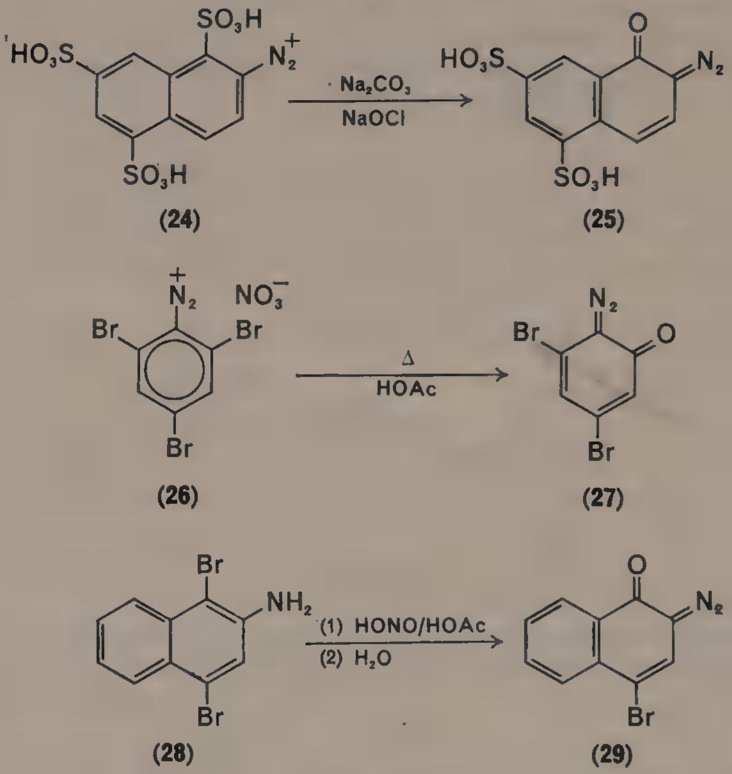


(21) (22) (23)

Scheme 4

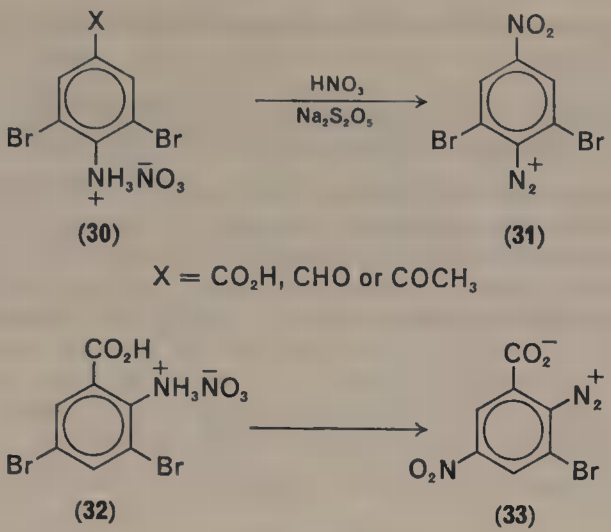
OCH_3 can serve as a leaving group NO_2 is lost[785]. An amusing feature of the displacement of NO_2^- is that once it begins, the amines furnish the HONO needed to carry out the diazotization.

Subsequent to formation of the diazonium ion, it is often possible to replace a labile substituent which has withstood the initial reaction conditions. This can be realized by employing a base such as an alkoxide or hydroxide. In these cases the requirements for positioning electron-withdrawing substituents are not as stringent. The processes are often quite rapid compared with other reactions. The attempted reduction of 1,6-dinitro-2-naphthalenediazonium ion with alcohol under reflux failed and furnished instead the 2,1-diazoxide[783]. Sulphonic acid groups can be replaced[1146] and the yield is improved by oxidizing the resulting sulphite ion to sulphate with hypochlorite[706] or hydrogen peroxide[951–954] (Scheme 5). An extensive investigation was performed by Orton[951–954] who compiled a table of the relative degrees of completion under standard conditions. He found that Br was a better activating and leaving group than Cl, that the replacement of a halogen by NO_2 improves the reaction and the total number of substituents in the 2+4+6 positions should be ⩾2. The data nicely correlate with a simple PMO analysis. The study of the resulting diazooxides from these displacement reactions has received considerable attention because they undergo many coupling reactions to furnish *o*-hydroxy-azo systems capable of forming metal ion complexes.



SCHEME 5

In a few cases it is possible to replace carbon substituents on an aromatic ring in the course of, or immediately subsequent to, diazotization. Elion[326] found that the use of the Witt method of diazotization[1297] led to the replacement of a carbonyl function by a nitro group in a series of 3,5-dibromo-4-aminophenyl carbonyl compounds and that bromine was replaced by nitro in 3,5-dibromo-2-aminobenzoic acid[326] (Scheme 6).



(30) (31)

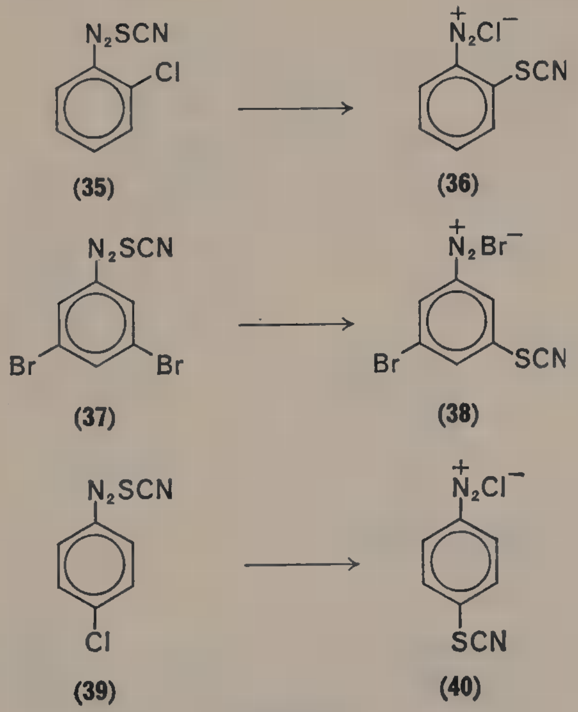
$X = CO_2H$, CHO or $COCH_3$

(32) (33)

SCHEME 6

3. Group 3: Exchange of diazonium anions with substituents of the aryl nucleus

Hantzsch and others[49, 452, 455–457, 492, 498, 501, 505, 543, 1128] found that a few diazonium salts were capable of exchanging anions between the $-N_2$ function and the aryl nucleus. The process was not reversible. As in the case of solvolysis, Br^- was a better leaving group from the aryl nucleus than Cl^- and these are probably only special cases of type A-2 reactions. Although one might write a concerted conversion of **35** to **36**, it is not possible to account for **37** going to **38** in a concerted fashion and a *p*-Claisen mechanism would be required for the transformation **39** to **40**.



(35) (36)

(37) (38)

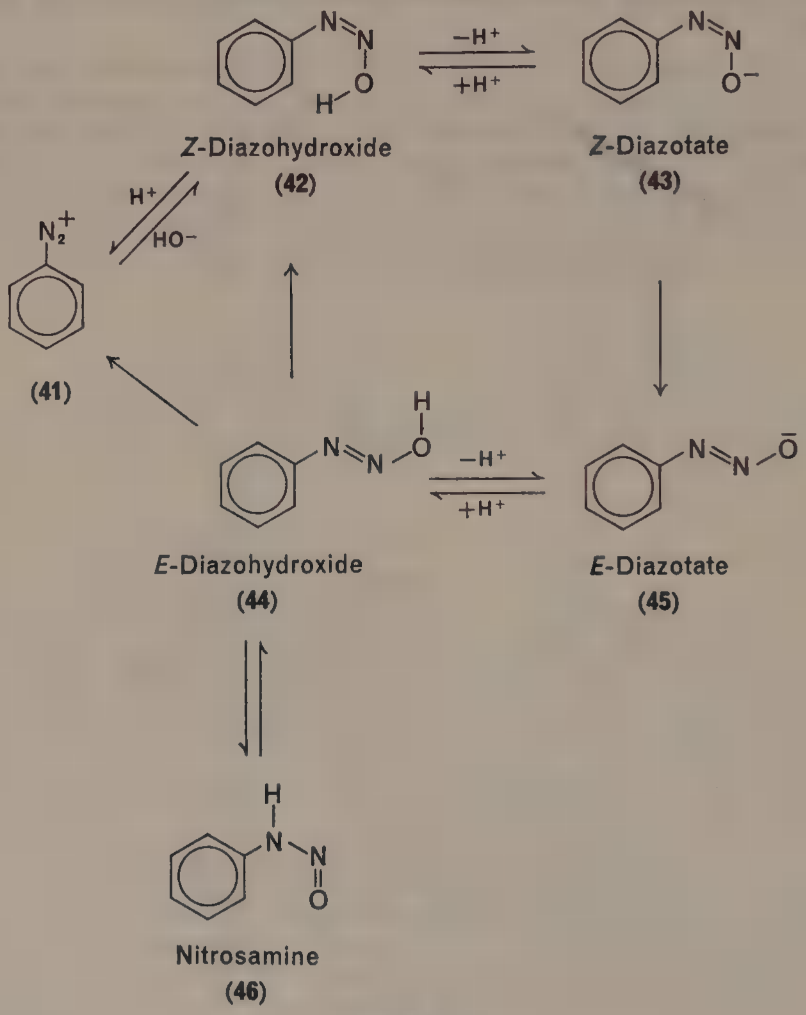
(39) (40)

SCHEME 7

B. Class B: Derivatives in which the Diazo Group is Involved but Remains Functionally Intact

1. Group 1: Metallic diazotates and diazoanhydrides. The use of *iso*-diazotates or nitrosamines as stabilized diazo compounds

The history of diazonium ion chemistry is not lacking in conflicting interpretations of data and as such makes fascinating reading for anyone interested in the development of bonding theory and structure elucidation. Curtius[277] noted in 1890 that an earlier structural assignment of Griess's[41, 42] where he postulated that acidification of $KON_2C_6H_5$ furnished free diazobenzene, $C_6H_5N_2$, was incorrect. The salt was subsequently shown to be the so-called *iso* salt[43] **(45)** which is also known as the stable or *anti* salt. The normal salt **(43)** is also known as the *syn* or labile salt. Their early history is treated by Cain[224] and the modern (i.e. present) interpretation is summarized by Zollinger[1326] and by Laing[709]. The equilibria can be summarized as in Scheme 8. In accordance with current nomenclature the isomers should

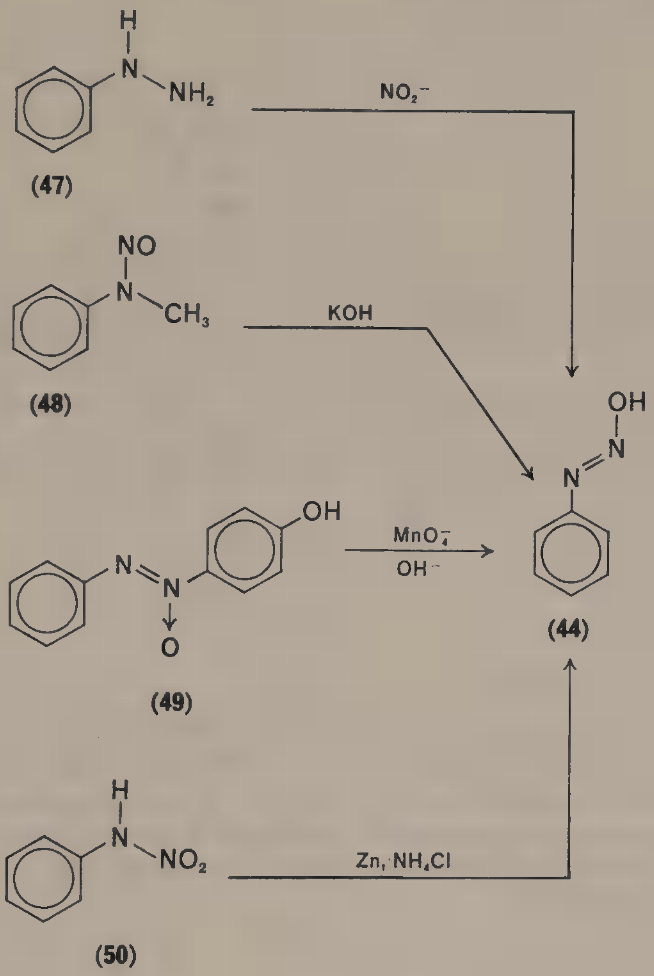


Scheme 8

probably be classified as *Z* for *syn* and *E* for *anti*. The question as to whether the *anti*-diazohydroxide is an azohydroxide or its tautomer, the nitrosamine, has not been adequately answered. There is reason to suspect that some assumed *iso*-diazohydroxides are nitrosamines while others are *anti*-diazohydroxides.

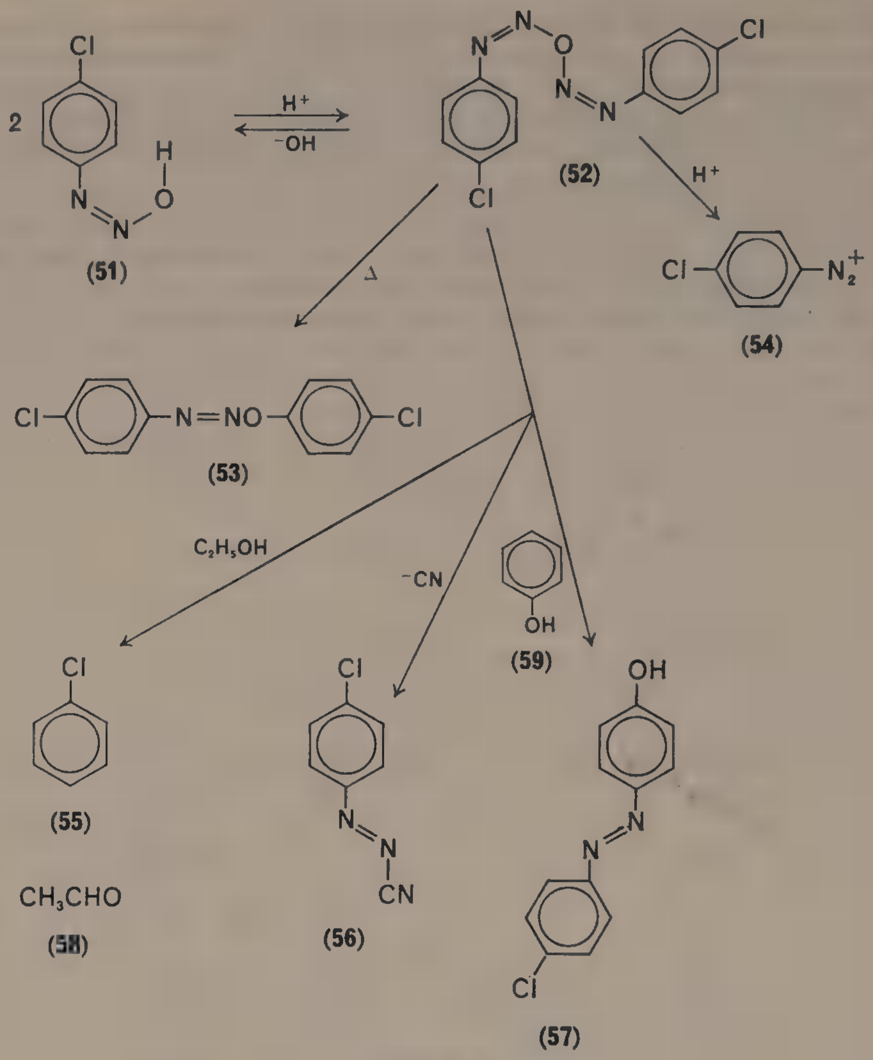
The important synthetic features are: *syn*-diazohydroxides give the same type of coupling reactions as diazonium ions; *anti*-diazohydroxides are stable to coupling but slowly cleave with acid to liberate the free diazonium ion. Clearly the position of equilibria and the structure of the *iso* compounds lie buried under a combination of substituent and steric effects and should be resolvable.

Iso-diazotates are normally formed by one of the methods given in Scheme 9.



SCHEME 9

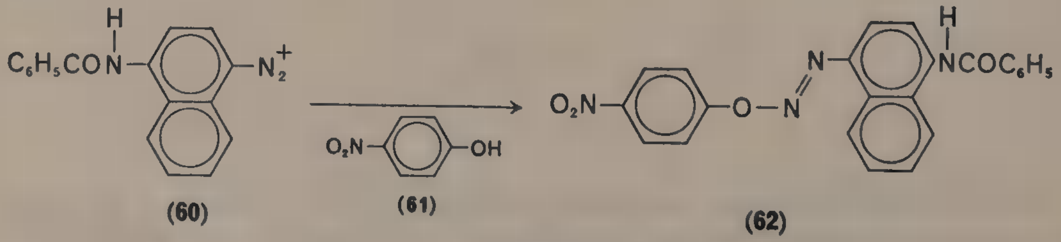
When diazonium salts or *syn*-diazotate solutions are neutralized to a pH range 5·5–7·5 the diazoanhydrides are formed. These are highly explosive, are converted by acids into diazonium ions and by bases into *syn*-diazotates.



Scheme 10

2. Group 2: Diazoethers

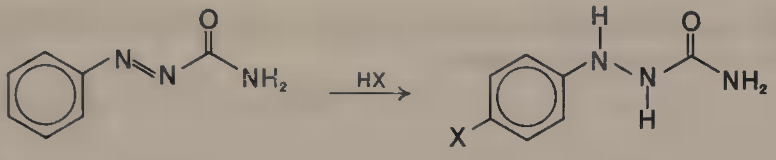
The diazoethers occasionally result from failed coupling reactions[306] but they are normally prepared by alkylation of *syn-* or *anti*-diazotates. Since the ions are ambidentate $[\mathrm{ArN{=}N{-}\bar{O}} \leftrightarrow \mathrm{Ar\bar{N}{=}N{-}O}]$ it is not surprising that aralkylnitrosamines are occasionally formed. The Na and K salts of the *p*-nitro compound furnished the nitrosamide with methyl iodide whereas the Ag salt yields the ether[50, 52, 182, 485, 487, 490, 1249].



Scheme 11

3. Group 3: Diazocyanides, diazocarboxylic acids and related compounds

Two forms of diazocyanides are known, *E* and *Z*, and the structural assignments are probably correct since they are sufficiently stable to permit a variety of transformations. A related isonitrile has been[159, 224, 299, 500, 503, 722, 728, 739, 1175, 1326] prepared by an 'unequivocal' synthesis. The synthesis requires the slow addition of the cyanide solution of the diazo compound in excess acid while the temperature is kept low. The *Z* isomer is formed first and this slowly rearranges to the *E* isomer[499, 500, 503]. In the presence of excess cyanide the formation of an arenediazoniumcyanide–hydrogen cyanide complex occurs[408, 489, 499]. In some cases the isomeric arylazocarbonimidoylcarbonitriles are generated[728].

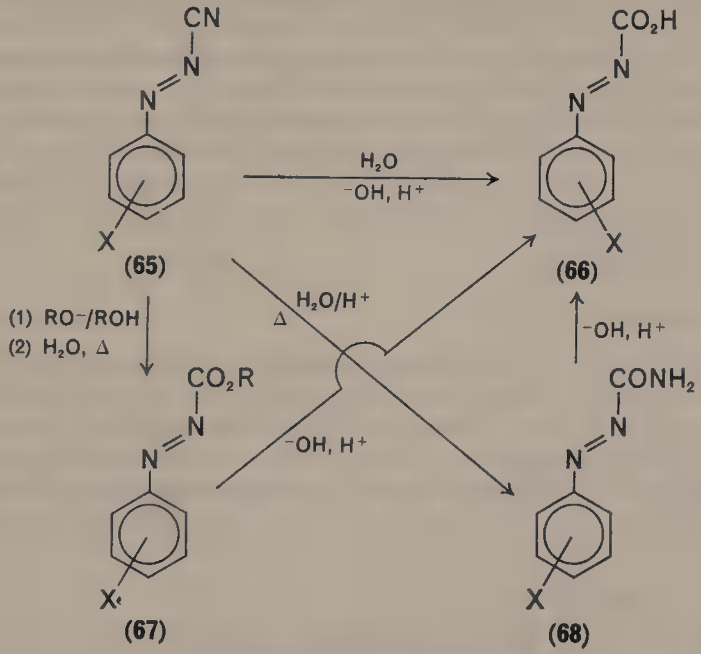


(63) **(64)**

SCHEME 12

The *Z* isomer is normally lower melting than the *E* isomer, both are unionized, coloured and water insoluble. The isomerization to the *E* isomer occurs spontaneously in the melt, in solution or in sunlight. The ease and extent of isomerization are subject to steric and electronic effects. The *Z* isomer couples and in the presence of Cu furnishes the nitrile.

An earlier proposal[558] that one isomer was the isonitrile was disproven[1191, 1192] through the synthesis of the isonitrile by generating it from AgCN and by dehydrating 1-aryl-2-formyl triazenes with pyridine/$SOCl_2$ to form the isonitriles.



SCHEME 13

The *E* nitriles undergo hydrolysis of the CN function to furnish the related acids. The CN function can also be converted into the CO_2R and $CONR_2$ functions[491].

The carbonamides react with H_2O_2 to furnish the azoxy derivatives[18, 984–986] and cleave with alkali to furnish diazotates[1085].

The amides undergo a somewhat general process when treated with cold concentrated hydrogen halide in aqueous media. The halogen enters the *para* position to furnish a *p*-halophenylhydrazidocarbonylamide[1290]. The reaction occurs with other groups of similar electronic character, e.g. 2-pyridyl, 4-pyridyl, 2-pyridyl-*N*-oxide, 4-pyridyl-*N*-oxide, benzoyl, $C(NH_2){=}NOH$, $C(OH){=}NOH$, $C(CH_3){=}NOH$, $C(NH_2){=}NNHBz$, $C(NHPh){=}NPh$ [74, 196, 259, 260, 428, 496, 617, 685, 976, 1029, 1030, 1290] but does not occur with azobenzenes[1290].

4. Group 4: The Diazosulphonates, their preparations, reactions and use as stabilized diazo compounds

Diazonium ions couple with Na_2SO_3 to furnish both labile and stable derivatives of the form ArN_2SO_3Na with bonding through sulphur to the terminal diazo nitrogen[53, 54, 58, 157, 158, 224, 299, 392, 393, 483, 486, 488, 494, 497, 499, 553, 555, 565, 727, 1103, 1115, 1221, 1222]. The reaction involves sulphite ions and not bisulphite[299] and if the pH is too high, diazotates and other undesirable by-products are formed. If the medium is too acidic, reduction occurs[484, 492]. Both the *Z* and *E* isomers can be reduced to the related hydrazines. The stable compounds do not couple but do react with chlorine and bromine to furnish the diazonium halides; they are also cleaved by lead nitrate and silver nitrate. The originally formed labile isomers isomerize extremely rapidly to the stable form but they can be isomerized photochemically to the labile form[616, 1337, 1344, 1347].

In a chemically similar reaction, aryl-sulphinic acids couple with diazonium salts to furnish sulphones ($ArN_2^+ + Ar'SO_2H \rightarrow ArSO_2Ar' + H^+$) [500, 1090]. Diazonium salts also react with alkyl and arylsulphonamides to furnish sulphones[317, 318]; *syn*-diazo cyanides have also been found useful for this type of coupling with sulphinic acids[500].

The mixed alkyl-aryl-diazosulphones decompose by a homolytic path in solvents such as benzene and heterolytically in highly polar media[103]. The product mixtures from the homolytic reactions were SO_2, biphenyl, azobenzene and phenylazobenzene (14 : 32 : 3 : 2). In polar media (acetonitrile) a 71% yield of acetanilide was obtained[638]. When the benzyl derivative was employed in benzene, SO_2, benzaldehyde phenylhydrazone, *N*-benzyl benzaldehydephenylhydrazone and biphenyl were obtained (66 : 55 : 6 : 2)[500]. An earlier study[959] showed that phenyl benzenediazosulphone furnished primarily biphenyl, benzenesulphonic acid and only 5% of the diphenyl sulphone.

5. Group 5: Diazoperhalides

Diazonium halides react with halogens and mixed halogens (e.g. ICl) to furnish compounds of the type $ArN_2XX'X''$ (X = halogen) [1103]. These compounds contain active halogen and are most probably of the form $ArN_2^+X_3^-$; as such, they are reasonable halogenating reagents. When boiled in alcohol they furnish the aryl halide[179]. Treatment of the aryl diazonium perbromides with ammonia offers a route to aryl azides[463].

6. Group 6: Diazosulphides

As a consequence of extensive studies by Brokken-Zijp and her Dutch colleagues[157, 159], much of the chemistry of this class of derivative is now clarified and will probably serve as a foundation and model for studies on related systems. van Beck[1223] has developed a general synthesis for a number of *E* and *Z* diazosulphides. An alkanethiol was allowed to react with an equivalent amount of the diazonium fluoborate in acetone at 0 °C and aqueous sodium hydroxide was added over a period of 1 h. The isomers either crystallized from solution or were extracted with benzene. After 2 h at 90 °C in isooctane, thermal equilibrium between *E* and *Z* isomers was established. The correctness of the structure assignments have been verified for some compounds by Brokken-Zijp[157], who also examined the action of light on both the *E* and *Z* isomers. Operating at 405 nm in methanol, pure *E* or pure *Z* lead to mixtures of both. At 300 nm, *E* isomers and decomposition products (sulphides, disulphides) were obtained. Irradiation of the pure *E* isomer at 300 nm generated only the *Z* isomer. The 4-cyano-, 4-nitro- and 3,5-dichloro-4-dimethylamino benzene diazo-*t*-butyl sulphides and phenyl diazo-*t*-butyl sulphides were studied.

The term 'diazosulphide' as employed by Saunders[1103] was used by him to describe diazothioanhydrides (ArN_2SN_2Ar') and ArN_2SR instead of only the latter as employed in the current literature. The thioanhydrides arise from the reaction of neutral diazonium salts with hydrogen sulphide. The thioanhydrides couple with alkaline β-naphthol[56] and furnish the biaryl upon heating in refluxing benzene[56]. Some of the thiodiazoanhydrides are extremely unstable and even explode under water at 0 °C [334, 561, 852].

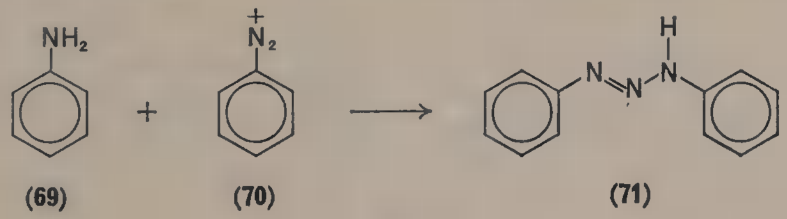
The diazosulphides are more stable than their oxygen analogues and fail to couple or cleave with cold acids or bases. They do decompose thermally via a homolytic process[1225].

If H_2S is passed into acid solutions of aryl diazonium ions, the main product is the aryl-diazoniumthiol hydrosulphide ($ArN_2SH \cdot H_2S$).

C. Class C: Derivatives in which the Diazo Function Disappears but the Diazo Nitrogen Atoms Remain in the New Molecule

1. Group 1: Diazo-amino and -imino compounds or triazenes[224, 1103, 1326]

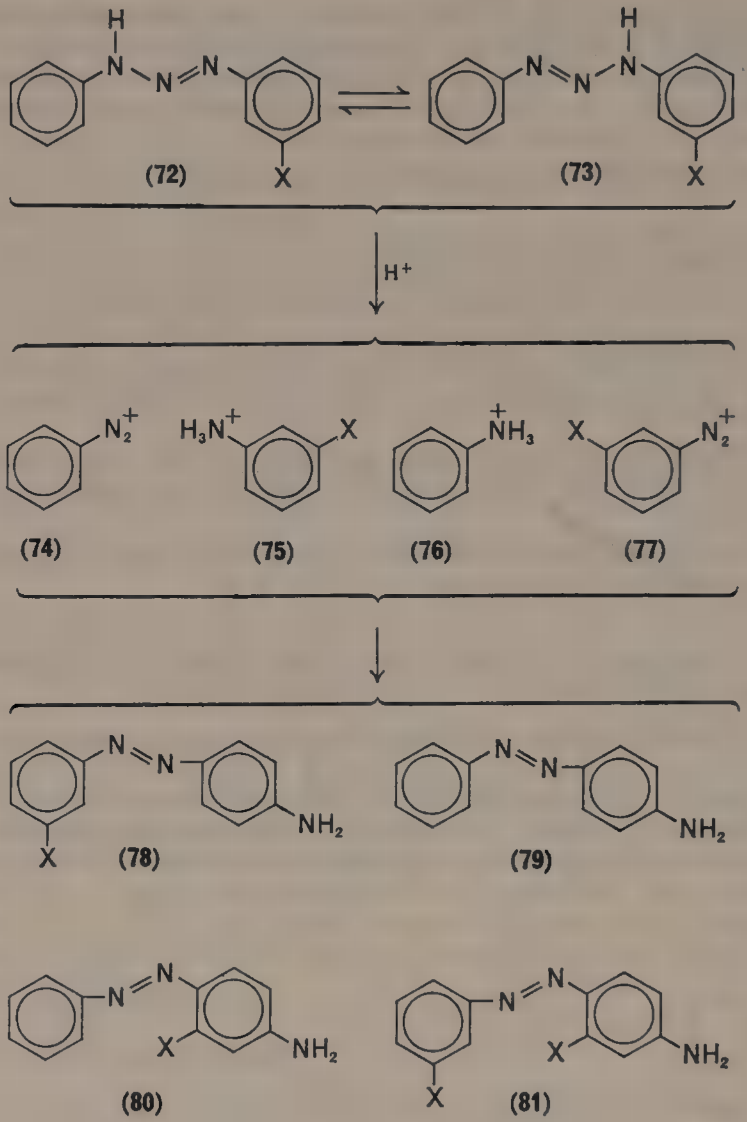
The reactions of arene diazonium ions with amines date from Griess's initial studies[448] where he obtained 1,3-diphenyltriazene by reacting nitrous vapours with an excess of aniline. The process is favoured by neutral conditions and is suitable for reactions with aromatic or aliphatic amines. With aromatic amines in which either aryl unit has a vacant *para* position, treatment with acid leads to coupling with the aromatic nucleus. In addition, equilibration is rapidly reached between both isomers and with acid, cleavage to all possible diazonium and ammonium ions results. Such a situation is simplified by blocking a *para* position.



SCHEME 14

This sensitivity to substituents is sufficiently great that *meta*-toluidine undergoes C substitution rather than N coupling[83].

With primary aliphatic amines, *bis* coupling frequently occurs and 1,5-diaryl-3-alkyl-pentaza-1,4-dienes result. It is possible to generate the aryl alkyl triazenes by adding a cold neutral solution of the diazonium salt to a cold solution of the amine in the presence of sodium carbonate. The resulting triazenes are moderately stable. In the case of the methyl and ethyl *p*-tolyl systems, useful reagents for esterification of carboxylic acids result[301, 435, 764, 993–995, 1281, 1283].

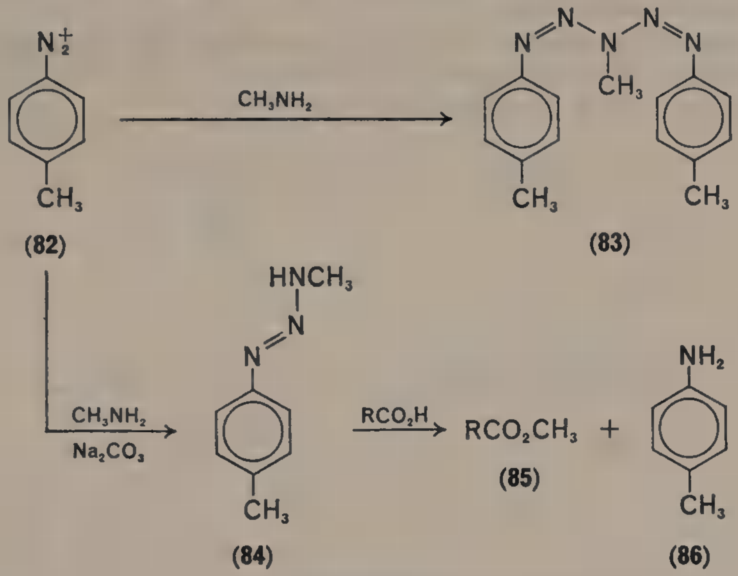


SCHEME 15

This method of esterification offers some advantages over diazoalkanes. Most notable is the ability to generate tertiary esters in modest yields. These are not available from diazoalkanes. With secondary amines, only a very small degree of rearrangement is observed.

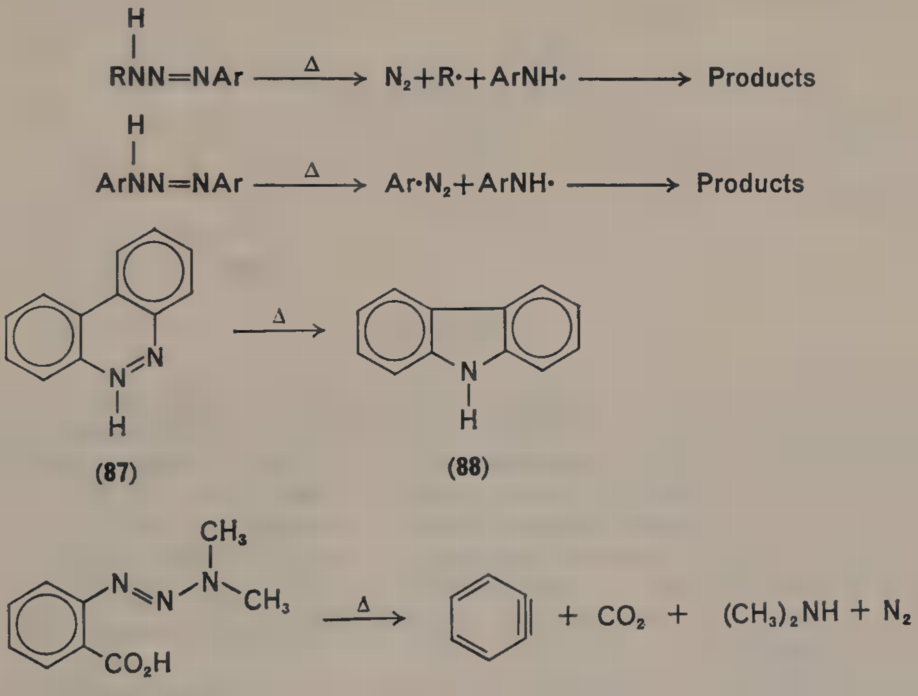
In the course of decomposing the secondary derivatives, extensive alkylation of the aromatic nucleus occurs. The process proceeds with a high degree of stereospecificity and retention of configuration even when the alkyl group is α-phenethyl.

The simple monoaryl triazene, $C_6H_5N_2NH_2$, does not arise by the reaction of the benzene diazonium ion with ammonia but is generated by reduction of phenyl azide with stannous chloride in ether[302]. Griess[458, 462] obtained an explosive substance from ammonia and diazobenzene. Von Pechmann[1251] ran a similar reaction with *p*-toluene diazonium ion and ammonia and obtained $p\text{-}C_7H_7N_2NHN_2C_7H_7\text{-}p$. The structure was verified by methylation which gave the same compound obtained from methylamine. In Griess's original attempts he obtained $C_6H_5N_2C_6H_4NH_2$.



(82) (83) (84) (85) (86)

SCHEME 16



$$R\overset{H}{\underset{|}{N}}N{=}NAr \xrightarrow{\Delta} N_2 + R\cdot + ArNH\cdot \longrightarrow \text{Products}$$

$$Ar\overset{H}{\underset{|}{N}}N{=}NAr \xrightarrow{\Delta} Ar\cdot N_2 + ArNH\cdot \longrightarrow \text{Products}$$

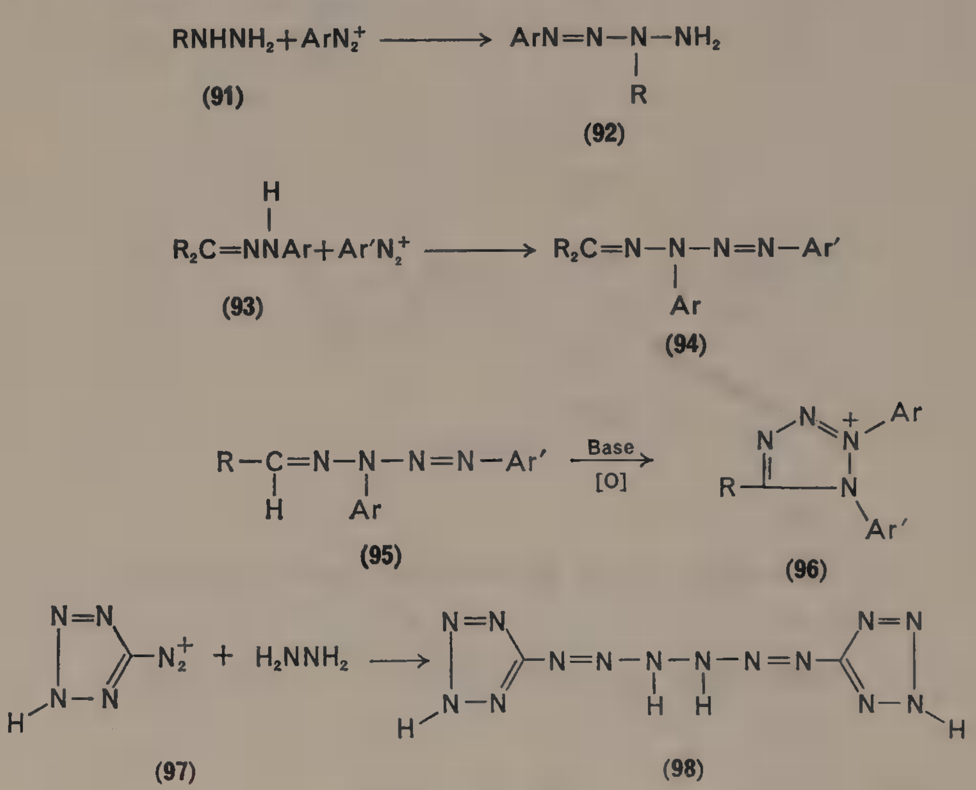
(87) (88) (89) (90)

SCHEME 17

The reaction of the *bis* aryl triazenes with acids furnishes a phenol, nitrogen and an amine. The reaction gives two phenols and two anilines when asymmetric starting materials are employed. In the presence of copper(I) salts and halogen acids, the aryl halide is formed in place or partially in place of the phenol. The amino nitrogen is sufficiently electron poor in *bis* aryl triazenes to render the hydrogens acidic and the sodium salts are known[754]. The systems also are sufficiently good ligands to permit formation of platinum[465], cupric[319], nickel[320], mercury[1271] and palladium[755] complexes.

The *bis* aryl triazenes and alkyl-aryl triazenes decompose thermally by a homolytic process[507, 538, 542, 820, 848, 851, 1024–1026].

The coupling of diazonium salts with hydrazines and hydrazones normally leads to formation of tetrazenes[199, 377, 378, 513, 578, 761, 762, 1113, 1287, 1304]. A variety of other triazene reactions is summarized by Smith[1159].

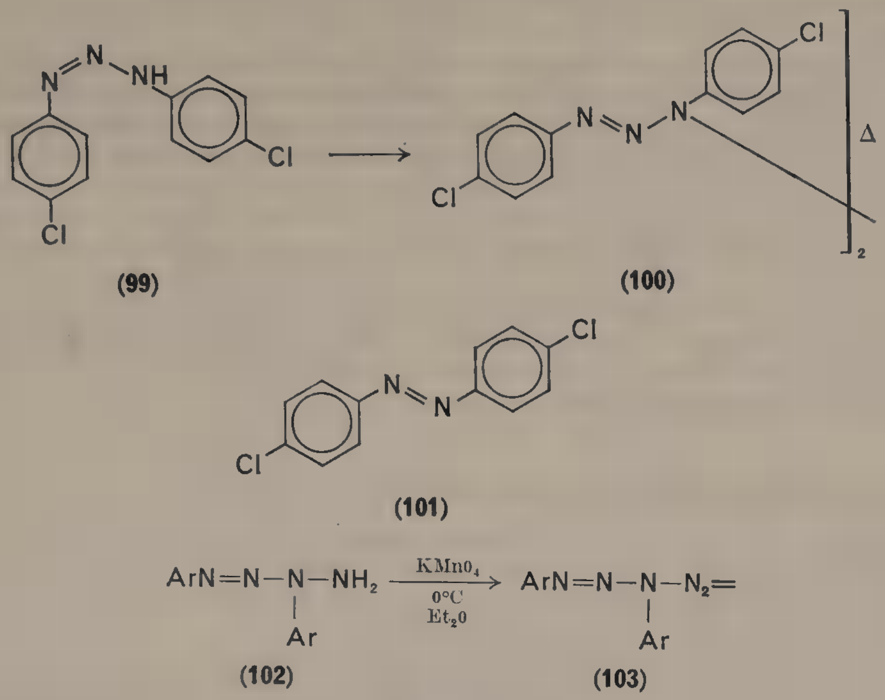


SCHEME 18

The diazo tetrazol (**97**) is reported to couple with hydrazine in a manner not observed with the benzene diazonium ion to form the hexazadiene (**98**)[572, 577]. Tetraryl hexazadienes can be prepared by oxidation of diaryl triazenes. The products undergo slow decomposition to azobenzenes (**99** → **100** → **101**).

When 1,3-diaryl tetrazenes are oxidized with permanganate ion, explosive compounds believed to be octazatrienes are obtained (**102** → **103**)[1305, 1306]. The chemistry of nitrogen chains of three or more N atoms is reviewed in Sidgwick[1113] and in Smith[1159]. Lieber and Smith[730] have discussed poly-aza systems derived from aminoguanidines.

When diazonium ions condense with aryl or alkyl hydroxylamines, triazene oxides or their tautomers the hydroxy triazenes result. These compounds undergo both N and O alkylation.



(99) (100)

(101)

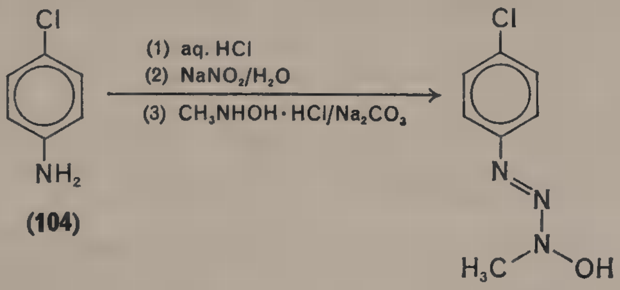
$$\mathrm{ArN{=}N{-}\underset{|}{\overset{}{N}}{-}NH_2}\ \xrightarrow[\mathrm{Et_2O}]{\mathrm{KMnO_4},\ 0\,^\circ\mathrm{C}}\ \mathrm{ArN{=}N{-}\underset{|}{N}{-}N_2{=}}$$

Ar Ar

(102) (103)

SCHEME 19

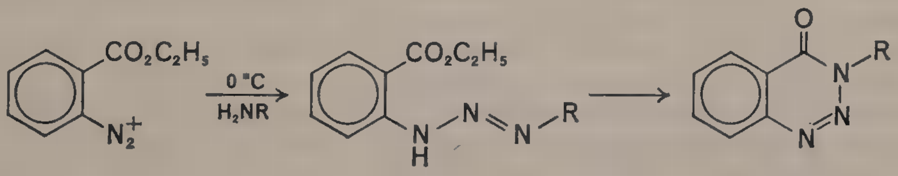
If 4-substituted aryl diazonium salts are treated with methyl hydroxylamine hydrochloride and sodium carbonate at 10 °C, 1-aryl-3-hydroxy-3-methyl triazenes result[393] (**104** → **105**). When ethyl anthranilate is diazotized and treated with



(104) (105)

SCHEME 20

alkylamines, the related triazenes are generated. These in turn are converted smoothly in refluxing ethanol or over basic alumina into 4-oxo-3-alkyl triazenes[715] (**106** → **107** → **108**).



(106) (107) (108)

SCHEME 21

This is in striking contrast with the results with diazotized anthranilic acid (**89** → **90**).

The oxides also result from peracid oxidation of triazenes. This latter approach leads to both possible isomers (1 and 3) when asymmetric triazenes are employed although the presence of an electron-rich aromatic system favours the oxygen ending on the N adjacent to the electron-rich system[55, 60, 61, 68, 69, 79, 134, 136, 314, 327, 805, 806, 1028].

2. Group 2: Oxidation products

In addition to those oxidation processes mentioned in earlier sections the diazonium function can be oxidized. Both *Z* and *E* diazotates undergo oxidation to furnish aryl nitroamines. Ferricyanide, hydrogen peroxide and permanganate have all been used under alkaline conditions[75, 127, 373, 443, 472, 1186, 1203].

3. Group 4: Reactions with nitrogen bases. The formation of aryl azides

Azides have been the subject of a monograph in this series[974]. Diazonium perbromides[459], plumbochlorides[239] and iodochlorides[239] react with ammonia to furnish azides and diazonium salts react with azide ion to furnish aryl azides, presumably via intermediate pentazoles and pentazatrienes.

A route to aryl azides known as the 'Dutt–Warmall Reaction' involves the action of an aryl diazonium ion upon a sulphonamide such as *p*-toluene sulphonamide. The method is theoretically only 50% efficient in aryl diazonium ion since a second molecule couples with the liberated sulphinic acid[154, 317, 318]. The reaction of azide ion with diazonium ions is treated as a Type E process.

4. Group 6: Azo compounds formed by coupling reactions (C coupling)

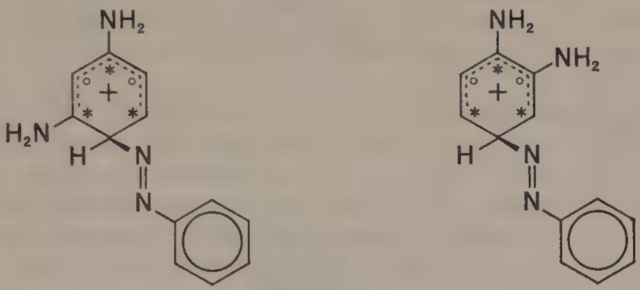
The coupling of aryl diazonium ions with phenols and amines to furnish azo dyes is not a major subject of this review but has been treated with a fair degree of thoroughness in texts by Fieser[370] and by Noller[898a].

We shall therefore limit the treatment here to some of the less well-known coupling processes and a brief treatment of the common coupling reactions.

Coupling to form C-azo derivatives received extensive attention from chemists almost from the time that diazonium salts were discovered and lead to the development of the chemical industry in Germany with a heavy emphasis on the synthesis of dyes. Almost all azo dyes are prepared by the coupling process. The dye-forming reactions are normally performed in aqueous media and the reactions are pH dependent. Many compounds will couple in acidic media as well. The general pH limits are 3·5–7·0 for aryl amine substrate and 5·0–9·0 for phenols. An examination of the stability graph for diazonium ions reveals that this is the same pH range where the stability is at a minimum. In general coupling occurs with phenols, aryl amines and active methylene compounds. Included in this group are such non-classical aromatic phenols as the tropolones and proteins.

The aromatic amines couple in the *para* position when an aniline is involved but otherwise couple in the position of maximum electron density and minimum ΔE_π as predicted by a simple PMO analysis[292]. Thus β-naphthyl amine couples in the 1-position and not the 3-position. Using the PMO analysis (Scheme 22) quickly leads to an explanation of why 1,3-diamino benzenes are more reactive than the 1,2-isomers or the anilines. The same analyses hold for phenols and polyhydric phenols.

The reaction is obviously facilitated by net electron-donating groups (negative Hammett σ values) and hindered by those groups which are net electron withdrawing. Since the anilines couple in the *para* position exclusively, the presence of substituents at that position stops the reaction from occurring unless strong activation of an *ortho* position is operating. With heterocyclic amines such as aminopyridines, coupling is not a very facile process because of the inherent inertness of pyridines to electrophilic attack. The presence of α and α′ amino substituents increases the activity of the γ position towards attack. A PMO analysis would seem to indicate that β substituents should be more effective.



SCHEME 22

The coupling of aminoquinolines has been examined in some detail[1054] with benzenediazonium ion as the electrophile (Table 1).

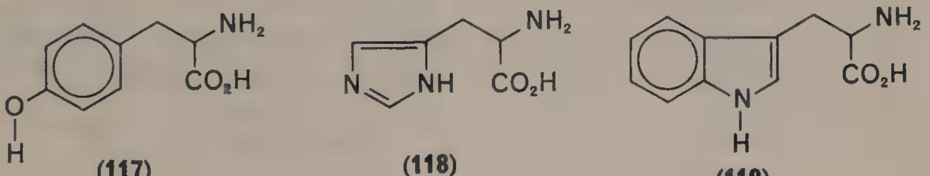
TABLE 1

Coupling at	Triazene[a]	C-4	N.R.[a]	C-6, C-8	C-5	C-8	C-5
Amino function at	C-2	C-3	C-4	C-5	C-6	C-7	C-8

[a] Triazene = coupling with the amino function of the aminoquinoline. N.R. = no reaction.

With aminophenols coupling can, in principle, be controlled by either functional group since the pH dependence of the coupling reaction is different for phenols and anilines. This can often be realized and a number of examples exist[170, 367, 369, 420, 424, 1061].

The coupling with proteins primarily involves the three amino acid units from tyrosine (**117**), histidine (**118**) and tryptophan (**119**). This phenomenon was behind



(117) **(118)** **(119)**

SCHEME 23

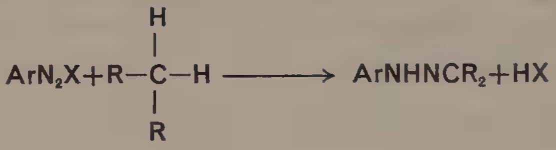
a process employed for dyeing silk. The obvious biochemical applications of the reactions have not been overlooked. Since several amino acids have functionality capable of forming $ArN_2—X—R$ units (where X is an amino or thiol function) coupling is not limited to proteins containing tyrosine histidine, tryptophan or related units.

Unlike the anilines, phenols can couple in the *ortho* position as well as the normally more reactive *para* position. Occasionally the position of coupling in naphthols is dependent upon the diazonium ion employed. Thus 1,5-dihydroxynaphthalene is attacked at the 2-position (counter to the PMO analysis) by diazotized *o*-aminophenolsulphonic acid but at the 4-position by diazotized anthranilic acid[382].

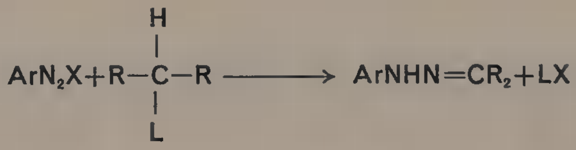
a. *Coupling at active* CH_2 *and CH groups.* There is a large number of compounds which possess active methylene groups and, not surprisingly, a large proportion have been subjected to diazonium-coupling conditions. Some examples include acetoacetic ester[800], nitroethane[797], malonic ester[796], acetone dicarboxylic acid[1244], β-nitroacetophenone[967], glutaconic ester[534], acetophenone-β-sulphonic acid[969], many cyclic ketones[294, 735], pyrazolines[201, 510, 1104, 1232] and the nitroparaffins[48, 71, 78, 361, 798, 799, 801, 1224].

The coupling products frequently exist as the hydrazones if the hydrogen replaced is borne on a $-CH_2-$ or CH_3- unit. This point was the source of considerable controversy[62, 172, 173, 178, 342, 611, 796, 1244], and one should probably treat some of the related literature with a degree of caution. The processes can be exceedingly complex and furnish a variety of products. Thus coupling of phenyl diazonium ion with nitromethane furnishes no fewer than 12 products[249, 335, 362, 1049, 1145], one of which results from rearrangement while recrystallizing from refluxing ethanol[362, 1145].

The overall processes can be conveniently subdivided into those occurring when a hydrogen is replaced in a formal metathesis[1343] and those of the Japp–Klingmann type where a radical is split off such as an acyl or carboxylate function[1344] (equations 1 [971] and 2 [981]). The processes have been well studied and by 1958 over



$$ArN_2X + R-\overset{\displaystyle H}{\underset{\displaystyle R}{C}}-H \longrightarrow ArNHNCR_2 + HX \qquad (1)$$

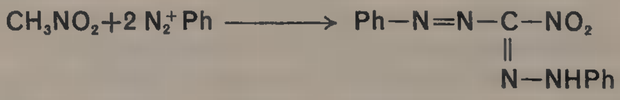


$$ArN_2X + R-\overset{\displaystyle H}{\underset{\displaystyle L}{C}}-R \longrightarrow ArNHN{=}CR_2 + LX \qquad (2)$$

700 pertinent references could be found[971, 981]. The major determinant relative to whether an aryl diazonium species will replace a hydrogen is the activity of the hydrogen and not the nature of the diazonium species.

Normally the reaction will not occur with ketones lacking some additional activating group, and with attack on a methyl group there is a strong tendency to generate a formazyl ketone[40, 47, 1246]. Similar behaviour occurs with nitromethane[592, 1132, 1195].

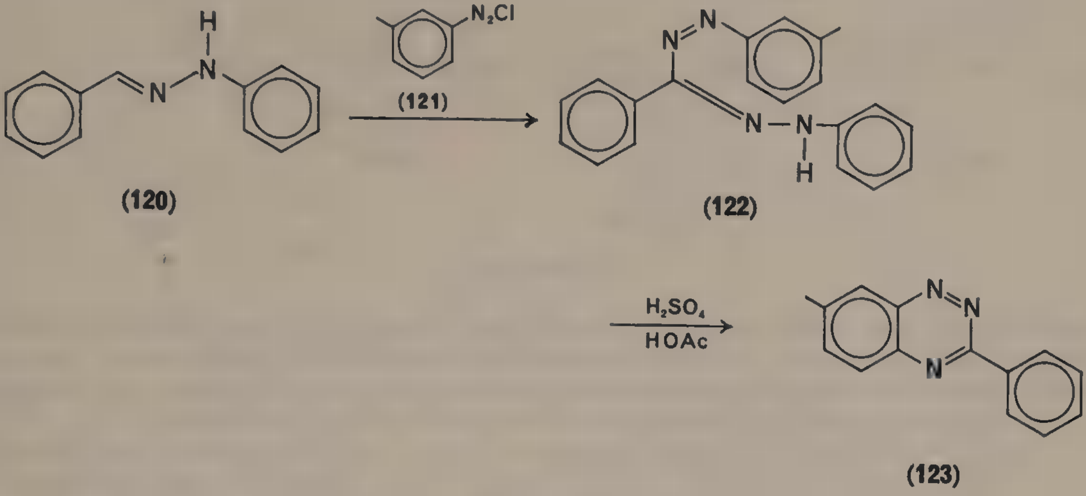
$$CH_3COCH_3 + 2\,N_2^+Ph \longrightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle N_2Ph}{|}}{C}{=}N-NHPh \qquad (3)$$



$$CH_3NO_2 + 2\,N_2^+Ph \longrightarrow Ph-N{=}N-\underset{\underset{\displaystyle N-NHPh}{\|}}{C}-NO_2 \qquad (4)$$

The formazans undergo a fairly general cyclization reaction when treated with strong acids such as sulphuric acid. The process known as the ‘Bamberger Triazene

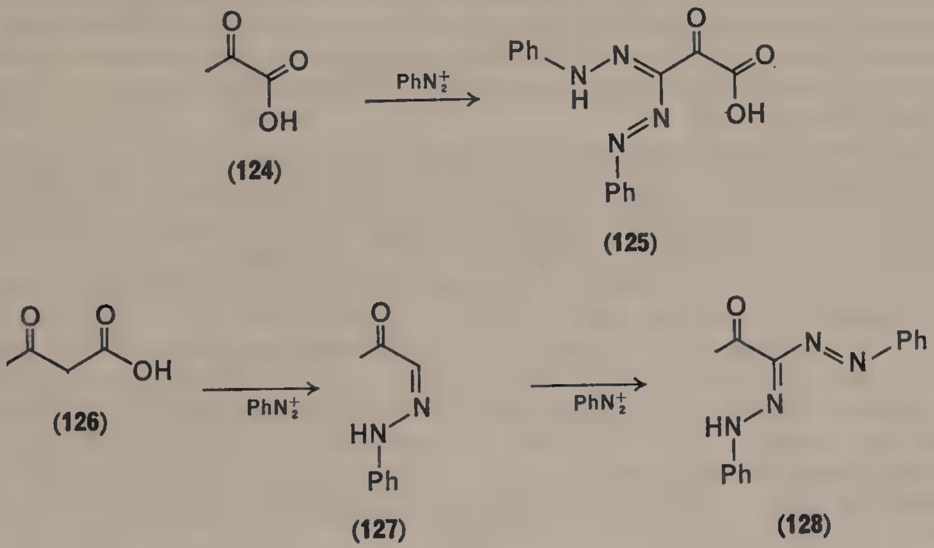
Synthesis' furnishes benzo-1,2,4-triazenes[2, 42, 43, 46, 968]. The chemistry of formazans has been reviewed[1028].



SCHEME 24

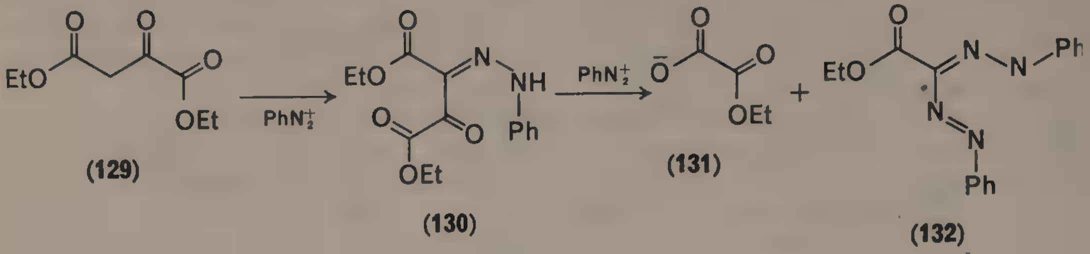
Benzenediazonium chlorides couple with 2-benzoyl-2-cyano-thioacetanilides in aqueous ethyl alcohol to furnish 2-arylhydrazono-3-oxo-3-phenyl propionitriles[312].

(i) Esters, acids and their derivatives. Simple acids do not generally undergo condensation but α-keto acids (e.g. pyruvic) do react. With pyruvic acid two molecules of diazonium salt are consumed[47] in direct analogy with acetone and nitromethane. β-Keto acids undergo loss of carbon dioxide and if an excess of diazonium ion is used a second molecule will react[43, 610, 1055]. Similar results accrue with acetone dicarboxylic acid[1244, 1248].



SCHEME 25

Good yields of the mono hydrazones can be obtained by employing the esters and one equivalent of the diazonium salt but if 2 moles of diazonium salt are employed with acetoacetic esters, a second diazo group enters with loss of the acetyl group[76, 1032, 1033, 1293]. A similar phenomenon occurs with diethyl oxaloacetate[1032, 1033, 1293], where the second mole of diazonium ion leads to ejection of an ethoxyalyl group. According to Parmerter these are the only two groups which are susceptible to loss when attack is on methylene. Other leaving groups are of course encountered with the Japp–Klingemann reaction (*vide infra*). Coupling also occurs with acetacetanilides and malonimides[14–17, 186, 244, 368, 492, 1074, 1139, 1162, 1284].



SCHEME 26

It is not particularly surprising that malonic acid, like nitromethane, is capable of multiple reactions involving 1, 2 or 3 moles of the electrophile with both *mono* and *bis* products resulting from the reaction with equivalent amounts of reagents[195, 1245]; with monosubstituted malonic acids, *bis* substitution readily occurs[405, 1259].

$$\mathrm{CH_2(CO_2H)_2} \longrightarrow \underset{\textbf{(133)}}{\mathrm{ArNHN{=}CHCO_2H}} \longrightarrow \underset{\textbf{(134)}}{\mathrm{ArNHN{=}CH{-}N{=}NAr}}$$

$$\longrightarrow \underset{\textbf{(135)}}{\mathrm{ArNHN{=}C(N_2Ar)_2}}$$

SCHEME 27

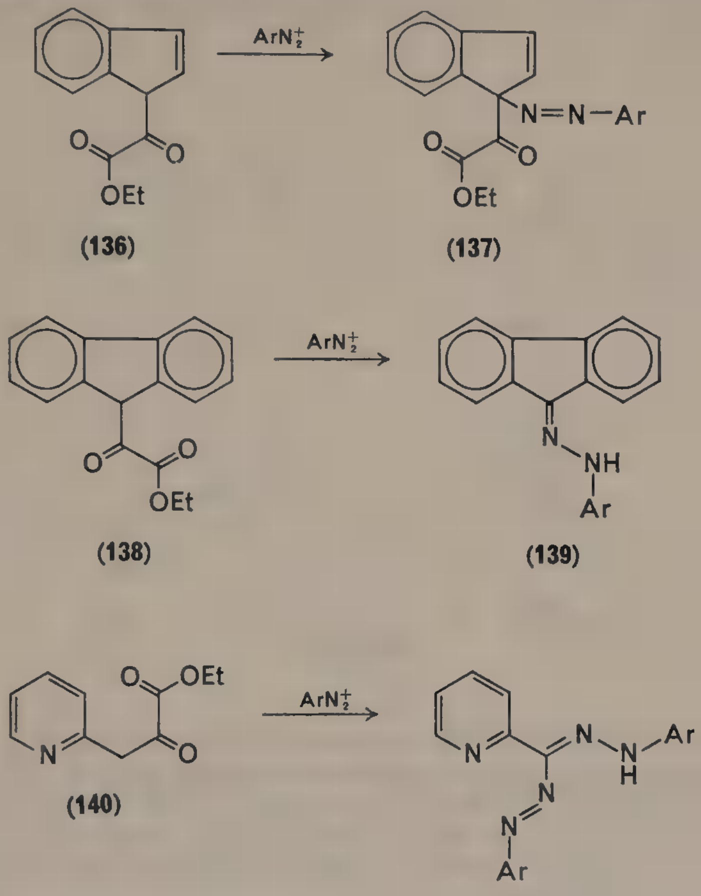
A limited number of reports of arylacetic acids and esters reacting with diazonium ions exists. The reaction goes moderately well with the 2,4-dinitrophenylacetic acid and its derivatives (apparently as a consequence of the highly electron-withdrawing aryl group). The acid reacts twice with loss of CO_2 whereas the ester consumes only 1 mole of diazonium ion.

(ii) Nitriles, nitroparaffins and sulphones. The cyano function also can serve as an activating group and a variety of dinitriles, β-cyano-carbonyl compounds, β-sulphononitriles, β-nitronitriles and β-iminonitriles undergo attack by aryl diazonium ions[143, 145, 250, 273, 338, 344, 346, 384, 705, 738, 741, 1114, 1172, 1173, 1212, 1213, 1240, 1273]. Sulphones[33, 248, 592, 1211, 1213] and nitroparaffins[48, 71, 197, 434, 580, 613, 997–1001] are also quite reactive. Hydrazones are the normal products resulting from attack of a methylene group. Subsequent attack of aldehyde hydrazones derived from activated methyl groups are responsible for the formation of *bis* aryl diazo-derived products. The reactions when carried out as two-step processes are good synthetically and furnish formazans[789–792, 1317, 1318]. The aryl hydrazones of α,β-diketobutyric esters and α-keto-acids undergo attack by a second molecule of aryl diazonium salt in processes formally analogous to the Japp–Klingemann reaction[44, 73, 198, 406, 713, 1034, 1274].

Benzenediazonium chlorides couple with 2-benzoyl-2-cyano-thioacetanilides in aqueous alcohol to furnish 2-arylhydrazono-3-oxo-3-phenylpropionitriles[312].

(iii) Ketones. Aryl diazonium ions attack ketones bearing an electron-withdrawing group to the carbon α to the carbonyl group[100, 101, 120, 141, 241, 281, 297, 342, 599, 600, 703, 706, 731, 783, 787, 1057, 1254, 1292, 1294, 1295]. The reactions are on occasion rather varied.

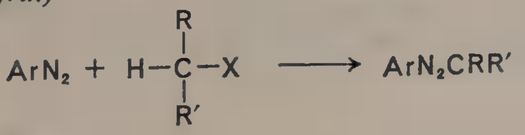
Thus the oxalylindene (**136**) undergoes simple substitution[1295] while its benzo analogue (**138**) undergoes a Japp–Klingemann reaction[706] as does the pyridine derivative (**140**) which furnishes a formazan[1057].



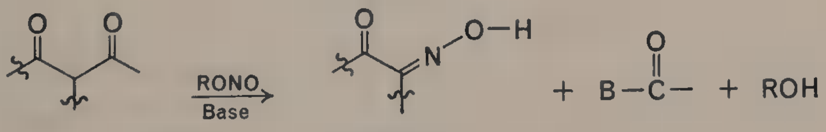
(136) **(137)** **(138)** **(139)** **(140)** **(141)**

SCHEME 28

(iv) The Japp–Klingemann reaction. The Japp–Klingemann reaction[981] has found extensive synthetic application. The processes differ from those discussed above in that only a single active hydrogen is replaced and a functional group attached to the carbon atom being substituted is lost. The reaction strongly resembles formal attack by +NO[1208]. (This parallel occurs in transition metal chemistry as well, *vide infra*.)

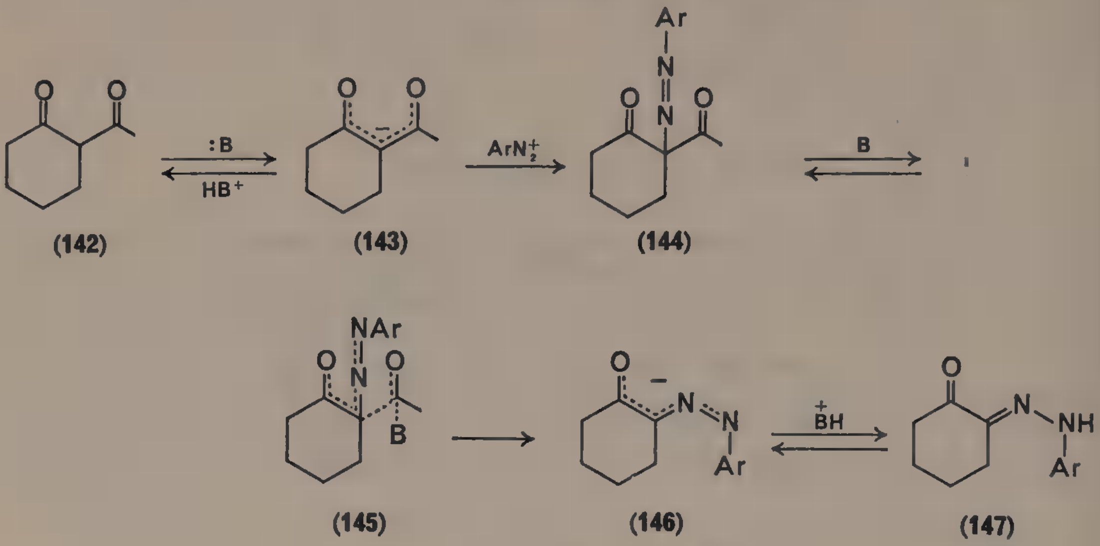


$$ArN_2 + H{-}\overset{\displaystyle R}{\underset{\displaystyle R'}{C}}{-}X \longrightarrow ArN_2CRR'$$



SCHEME 29

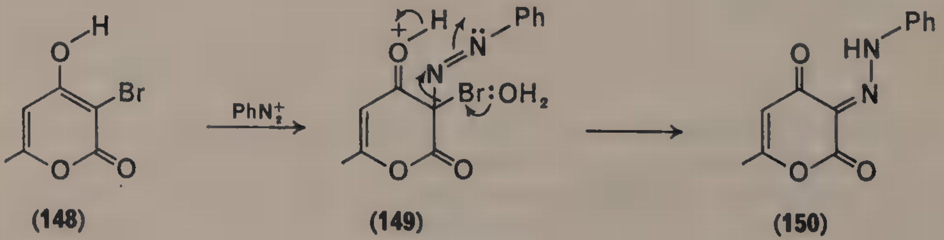
The mechanism of both processes undoubtedly involves initial generation of a stabilized carbanion[510, 1104], then attack by the diazonium ion to furnish a diazo derivative which can then cleave by nucleophilic attack upon the potential leaving group followed by ejection of the product, its tautomeric form or the stabilized anion of the product.



SCHEME 30

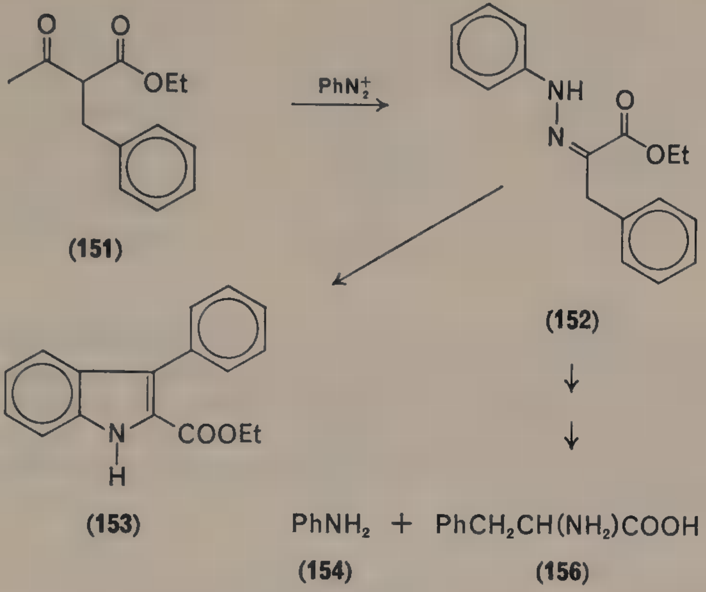
The enhanced stability of both of the final products (the desired product plus the final form of the leaving group) may serve as the driving force for the reaction[117, 177, 199–202, 257, 300, 303–306, 336, 338, 343, 344, 390, 512, 513, 515, 516, 592, 620, 733, 802, 1121, 1123, 1132, 1137, 1140, 1195, 1237, 1238, 1250, 1302]. If we extend this general mechanism to the Japp–Klingemann reaction using a general refinement suggested by Dewar[290] for ester hydrolysis, we obtain Scheme 30.

Normally the Japp–Klingemann reaction requires two or even three electron-withdrawing substituents such as carbonyl, cyano, nitro or sulphonyl groups being present. However, electron-deficient aromatic systems such as fluorene, pyridine, quinoline and dinitrophenyl can serve as activating substituents as can the halogens. Halogen rarely serves as the leaving group. Perhaps this is a consequence of the fact that normally the leaving group is attacked by a nucleophile and with halogens this requires a formally positive halogen. Hence one would predict that the tendency for loss of halogen should be expected to occur in direct parallel with decreasing electronegativity[340, 341]. This interpretation accounts for the apparent anomalous behaviour of 3-bromotriacetic lactone[1288] (148). Acetoacetic esters undergo the



SCHEME 31

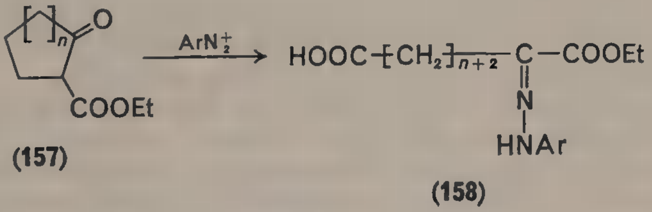
Japp–Klingemann reaction with the loss of the acetyl group and the resulting products are *N*-substituted derivatives of esters of dehydro amino acids. Reduction offers a ready route to the amino acid esters and treatment under Fisher-indole synthesis conditions furnishes indoles[1, 44, 128, 174–176, 180, 321, 347–350, 352–354, 356–360, 525, 584, 610, 611, 683, 734, 1136, 1185, 1260].



SCHEME 32

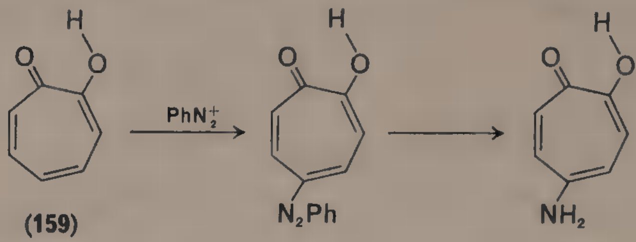
With 1,3-diones, similar behaviour is observed and one has a route to α-amino ketones[298, 339]. This approach is complementary to the use of *p*-tosyl azide in a diazo transfer process which furnishes the α-diazo ketone which can also be reduced to the related amine[39, 337, 1311].

The Japp–Klingemann reaction of 2-carboalkoxycyclanones offers a ready source of ω-carboxy α-amino acids and of 3-(alkyl-ω-carboxy) indoles. Since the starting materials are readily available by a Dieckmann cyclization or by reaction of the cyclanone with dimethyl carbonate, this offers a very ready route to both systems[295, 296, 355, 514, 733]. An interesting variant on this approach employs a 2-acylbutyrolactone. Subsequent ring opening can be performed with a variety of nucleophiles to furnish lactones, esters or hydroxy acids[345, 508, 1161].



SCHEME 33

(v) Coupling with tropolones. The tropolones are prone to coupling with diazonium ions. The reaction is of sufficient reliability to permit its use as a diagnostic tool for the presence of a substituent at C-5. The processes offer ready routes to 5-amino tropolones via subsequent reduction[261, 308, 519–521, 639, 671, 910, 912, [913, 916, 917, 921–925, 928, 930, 931, 934, 937, 939, 1135, 1313]. The reaction is somewhat sensitive to steric effects and both 4-isopropyl and 4-*t*-butyl tropolone fail to couple[919].



(159) (160) (161)

SCHEME 34

The presence of halogens at positions 3 or 3 and 7 greatly decreases[911, 926] the reactivity of the tropolone. For the test to be fully valid, it is necessary to perform the reduction step, for 5-methyl, 5-hydroxy, 5-halo and 5-isopropyl tropolones furnish coloured complexes which are cleaved by reduction without introduction of the amino function[332, 918, 926, 930, 935, 942]. Several other 5-substituted tropolones fail to form complexes[843, 916, 939].

5. Group 7: Complexes of aryl diazonium and alkyl diazonium ions and diazo compounds with transition metals

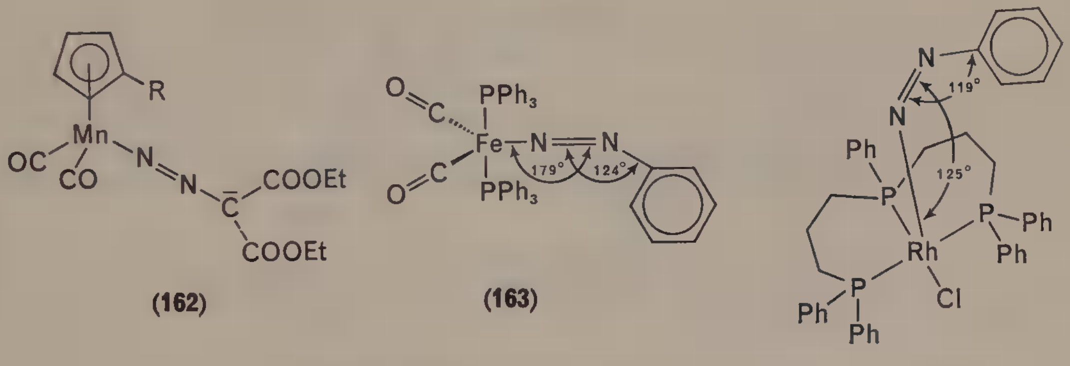
Until relatively recent times one might have dismissed out of hand the possibility of isolating and characterizing transition metal complexes of diazonium ions or of diazo compounds. This was a direct consequence of the fact that many transition metals catalyse the decomposition of both diazo and diazonium ions. There are of course a number of old examples where aryl diazonium salts formed double salts with complex ions of such metals as platinum and mercury, but in those cases the diazonium ion was serving a role similar to that of an alkali metal cation. During the past 11 years a sufficient number of aryl diazonium–transition metal complexes have been isolated and characterized to warrant a review with over 100 references[1193]. With diazo compounds, the number of examples is somewhat more limited, but in both cases well-documented examples now exist where the $-N_2$ function serves as a ligand with bonding to the metal occurring through the terminal nitrogen. The fact that bonding occurs through the nitrogen is probably the cause of their stability. There is reason to believe that the loss of nitrogen from diazo alkanes in the presence of metal catalysts proceeds via attack on the diazo carbon[1312].

The nomenclature which has been used to describe these complexes in the literature is not uniform. Thus the terms 'arylazo', 'aryldiazo'[865, 867, 868] have been employed for the aryl complexes although the compounds can be named as derivatives of diimine[523], diimide[602] or diazene[385, 699]. Some workers have employed the terms 'hydrazido dianion'[523] and 'phenyl hydrazido dianion'[765] to describe the protonated complexes. It is perhaps unfortunate that ultimately the arrogance[404] of *Chemical Abstracts* will probably dominate[1193] and the *diazene* nomenclature will be employed and the I.U.P.A.C. proposed term, *aryl diazenato* will not become fixed in the literature. The use of *diazonato* (aryl or alkyl) would appear even more logical and consistent with the fact that the term *diazo* has been used for 111 years.

This term has been in use for at least a hundred years before the American Chemical Society took upon themselves the role of final arbitrator for Chemical Nomenclature[311, 404, 960].

The complexes appear to fall into two basic classes: those in which the $-N_2$ function formally furnishes three electrons to the metal to satisfy the 18-electron requirement of filling the valence shell, and those which formally furnish a single electron to satisfy the 18-electron requirement. These groups can be identified by X-ray crystallographic analysis of the M—N—N bond angle. The three-electron donor situation leads to angles in the range 170–179° [29, 234, 313, 596, 742, 765] and the one-electron donor system leads to a bond angle of 125·1° [426]. Sutton[1193] has discussed the bonding theory which leads to predictions of 180° and 120°.

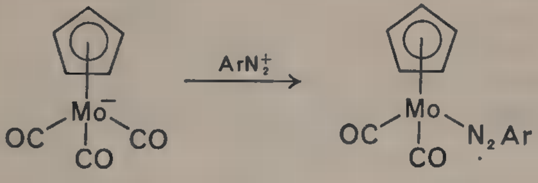
There is a very limited number of alkyl-diazonato complexes and structural analysis by X-ray is lacking. The spectroscopic parameters presented are totally consistent with the claimed structures.



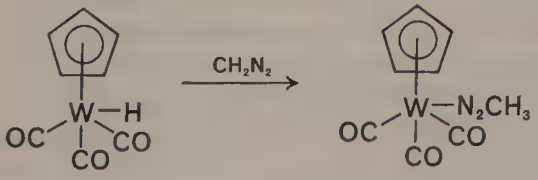
(162) (163) (164)

SCHEME 35

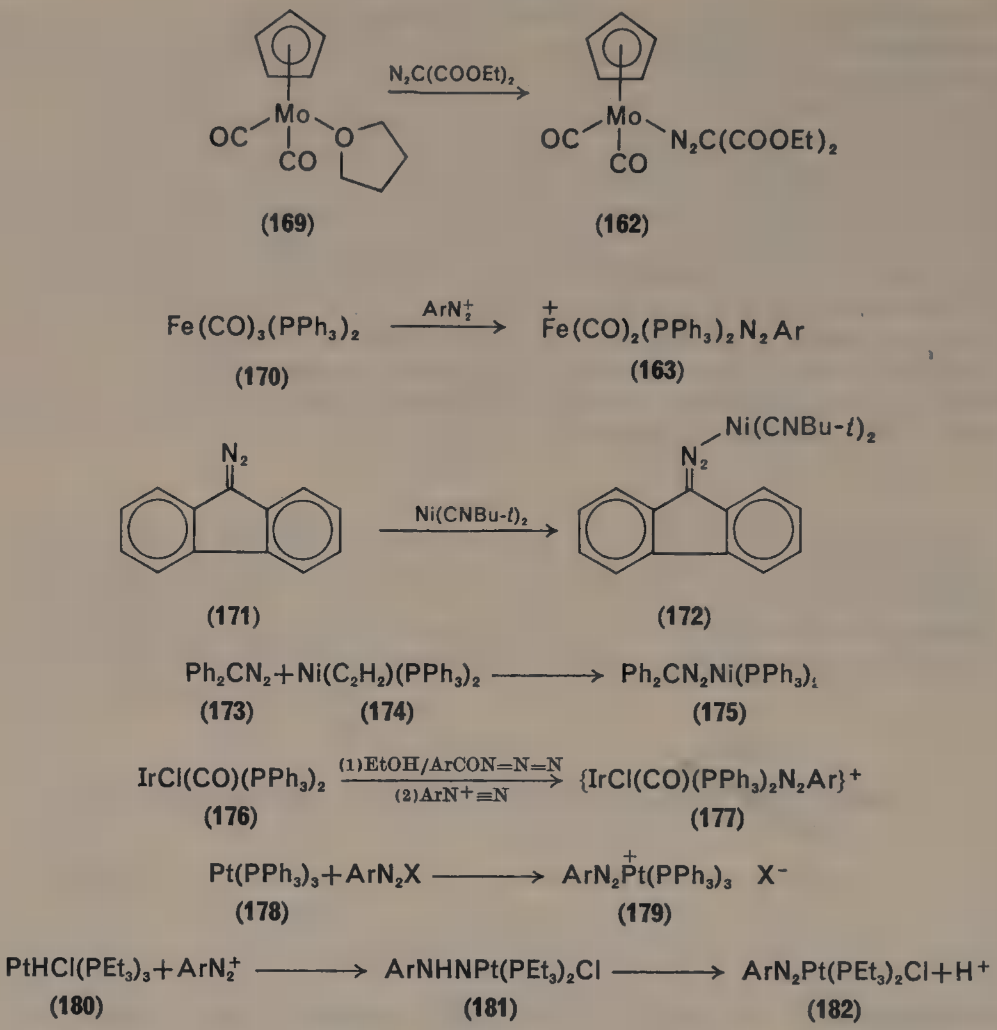
The formation of the diazonato complexes is most commonly realized by direct reaction of the diazo compound or the diazonium salt with a complex (ionic or neutral) with or without the displacement of an existing ligand.



(165) (166)



(167) (168)



SCHEME 36

The number of diazoalkane complexes with transition metals is small. For a summary of the aryl diazonium based complexes readers should see Sutton[1193].

The aryl-diazonato complexes tend to be basic at the nitrogen adjacent to the metal atom[1193] and undergo protonation on nitrogen. However, since they are prepared as ends rather than intermediates, their chemistry is not well characterized.

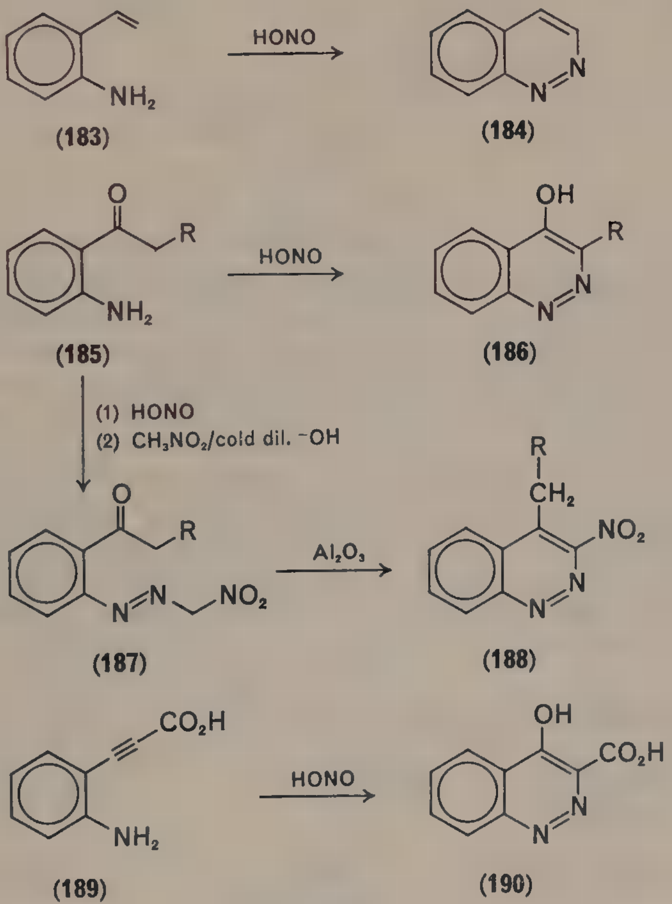
D. *Class D: Type B Ring Compounds in which the Diazo Nitrogen has been lost. The Pschorr Type Syntheses*

Detailed discussions of several of these classes of heterocycles have appeared in the form of monographs and as such will be described only in terms of their syntheses unless there exist additional diazo- or diazonium-type reactions. These reactions are treated below. The chemistry of the members of groups in which the nitrogen is lost are not of concern here and we shall only treat their generation from diazonium compounds. There are obviously other means of obtaining many of the products which do not involve diazo or diazonium chemistry and standard references and reviews cover most, if not all, alternate methods.

In recent years the chemistry of aromatic systems has increasingly been relegated to the briefest of treatments in standard textbooks. This is perhaps a reflection of the amount of research activity in the area or the simple increase in the total amount of material covered. As a direct consequence the chemistries of diazonium ions normally discussed in beginning texts are the reactions in Class E and coupling with an occasional reminder that certain *ortho*-substituted anilines are not suitable for diazonium reactions. The chemical reason behind this becomes evident when one notes that the so-called 'forbidden' groups are potential nucleophiles ideally located adjacent to electrophilic diazonium groups. This proximity effect means that systems incapable of bimolecular reactions may well be capable of unimolecular cyclization. The *ortho* function need not of itself be a nucleophile or have nucleophilic character if the conditions of the reaction can cause the substituent to generate a transient intermediate capable of serving in that role. Thus an enolizable ketone can readily fulfil the role of an ethylene.

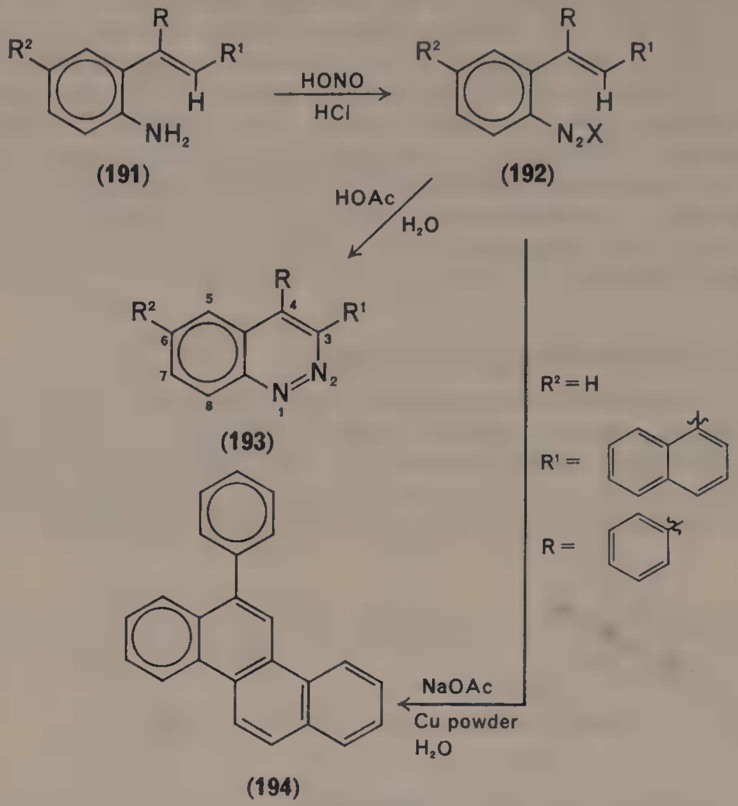
I. Subclass a: Diazo nitrogen retained

a. *Group 1: Cinnolines.* The presence of a vinyl group in the *ortho* position of an aniline or other aromatic primary amine may lead to the formation of a cinnoline[376, 964, 1252, 1276] upon diazotization. The configuration around the vinyl group need not be *cis* for both *cis* and *trans* 1,2-disubstituted ethylenes can participate[1285]. The basic reaction shown in Scheme 37 has some limitations which



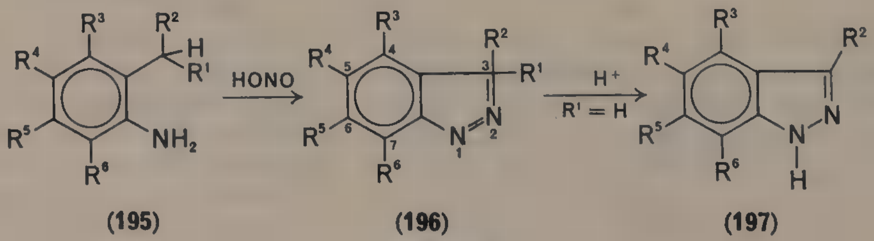
SCHEME 37

have been detailed by Simpson[1285]. He has concluded that when R = H or CO_2H and R′ = aryl, the reaction does not occur. If R = aryl, R′ can be aryl also. When R′ = aryl, there is a possibility that a Pschorr condensation will compete[30, 48, 250, 289, 603, 621] (Scheme 38). This process is discussed in detail under Group E, Class 5, reactions. The synthesis of cinnolines from *o*-vinyl diazonium ions is known as the Widman–Stoermer synthesis[12, 25, 117, 161, 162, 479, 723, 944, 965, 1120, 1123, 1147, 1148, 1150, 1179, 1285]; from *o*-acyl diazonium ions as the Borsch synthesis[13, 26, 634–636, 683, 724, 945, 1117, 1122], and from *o*-alkynyl diazonium ions as the Richter synthesis[603, 1116, 1121, 1153, 1252]. Baumgarten[90] has modified the Borsch synthesis as shown (**185** → **187** → **188**).



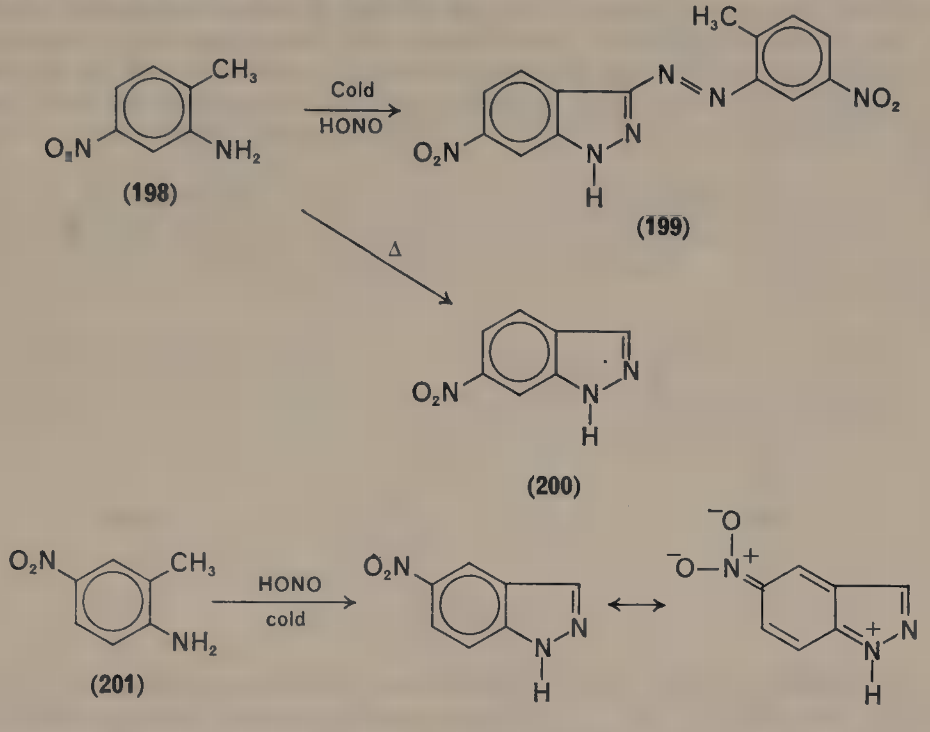
SCHEME 38

b. *Group 2: Indazoles.* In certain cases a methyl, methylene or methine group is rendered sufficiently acidic by substituents to make it a potential C acid. When this occurs adjacent to a potential diazonium ion, cyclization may occur to furnish 3-*H*-benzpyrazole which may if a hydrogen is at C-3 rearrange to furnish the 1-*H*-benzpyrazole (indazole) (Scheme 39). The presence of electron-withdrawing



SCHEME 39

groups as R^1, R^2, R^3, R^5 will facilitate the reaction[65, 409, 803, 817, 818, 906, 1296]. However, there exists the possibility that the resulting indazole will be coupled to unreacted diazonium compound if there is an electron-withdrawing group at C-6 (R^5) or C-4 (R^3) but not at C-5 or C-7 (e.g. Scheme 40).

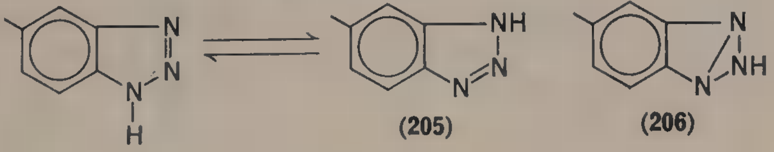


(198) (199) (200) (201) (202) (203)

Scheme 40

The difference between the two substrates would appear to be a consequence of the 6-nitrobenzpyrazole having a more basic C-3 due to contributions from the anilino nitrogen. This would be strongly suppressed by electron-withdrawing groups in the 5- or 7-positions.

c. *Group 3: Benztriazoles. Bis*-diazotization of *ortho*-diamino systems is extremely difficult, and under a wide range of diazotization conditions they afford triazoles[7, 148, 330, 339, 468–470, 567, 632, 708, 814, 815, 903, 1078, 1103, 1127, 1219, 1257, 1321, 1323, 1325]. The reaction was discovered by Hofmann in 1860 when he worked with nitro-*o*-phenylenediamine[567]. The driving force is sufficiently great that acetylation of one nitrogen does not prevent the reaction and mono-alkylation has no effect. Asymmetrically substituted *o*-phenylene diamines may lead to two isomeric triazoles. At the time of their discovery, a debate as to structure occurred between Griess and his adherents and Kekule and his. Much research was directed towards preparing and isolating both isomers. Kekule's[632] structure (**204** and **205**) would lead to two products, Griess's to one (**206**)[469, 470].

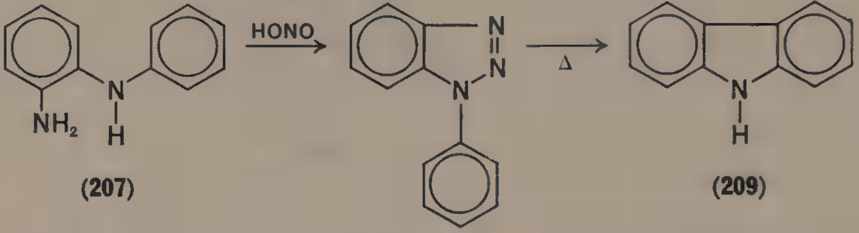


(204) (205) (206)

Scheme 41

Finally, Morgan and colleagues[814, 815, 1321] prepared the two *N*-acetyl derivatives of **(204)** and **(205)**. The former was known as the α-isomeride and the latter the β-isomeride. Unequivocal syntheses were employed and the argument was closed by their hydrolyses to furnish the same 'compound' (mixture) which on reacetylation furnished a mixture of the α and β acetyl derivatives with the α-isomeride being predominant. They claimed that they were able to separate the two triazoles which had slightly different absorption spectra and did not equilibrate in organic solvents. The question of which tautomer is dominant in these systems has been extensively examined using modern instrumental techniques[625, 704, 808, 957, 1003, 1163].

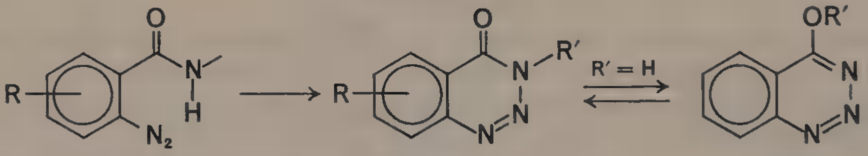
When *ortho*-amino diphenylamines are submitted to diazotization conditions, they readily undergo conversion to benzotriazoles. The triazoles were shown to be thermally unstable by Graebe and Ullmann and to offer a ready route to carbazoles[103, 229, 442].



(207) **(208)** **(209)**

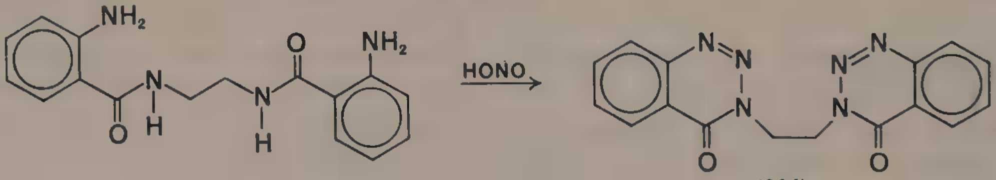
Scheme 42

d. *Group 4: Benztriazines.* Normally diazonium ions will not couple with an amide to furnish a triazene but the intramolecular process occurs with great facility[371, 601, 700, 1103, 1202, 1270] (Scheme 43) and with a wide range of substituents for



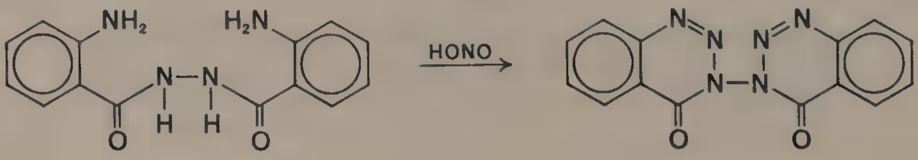
(210) **(211)** **(212)**

Scheme 43



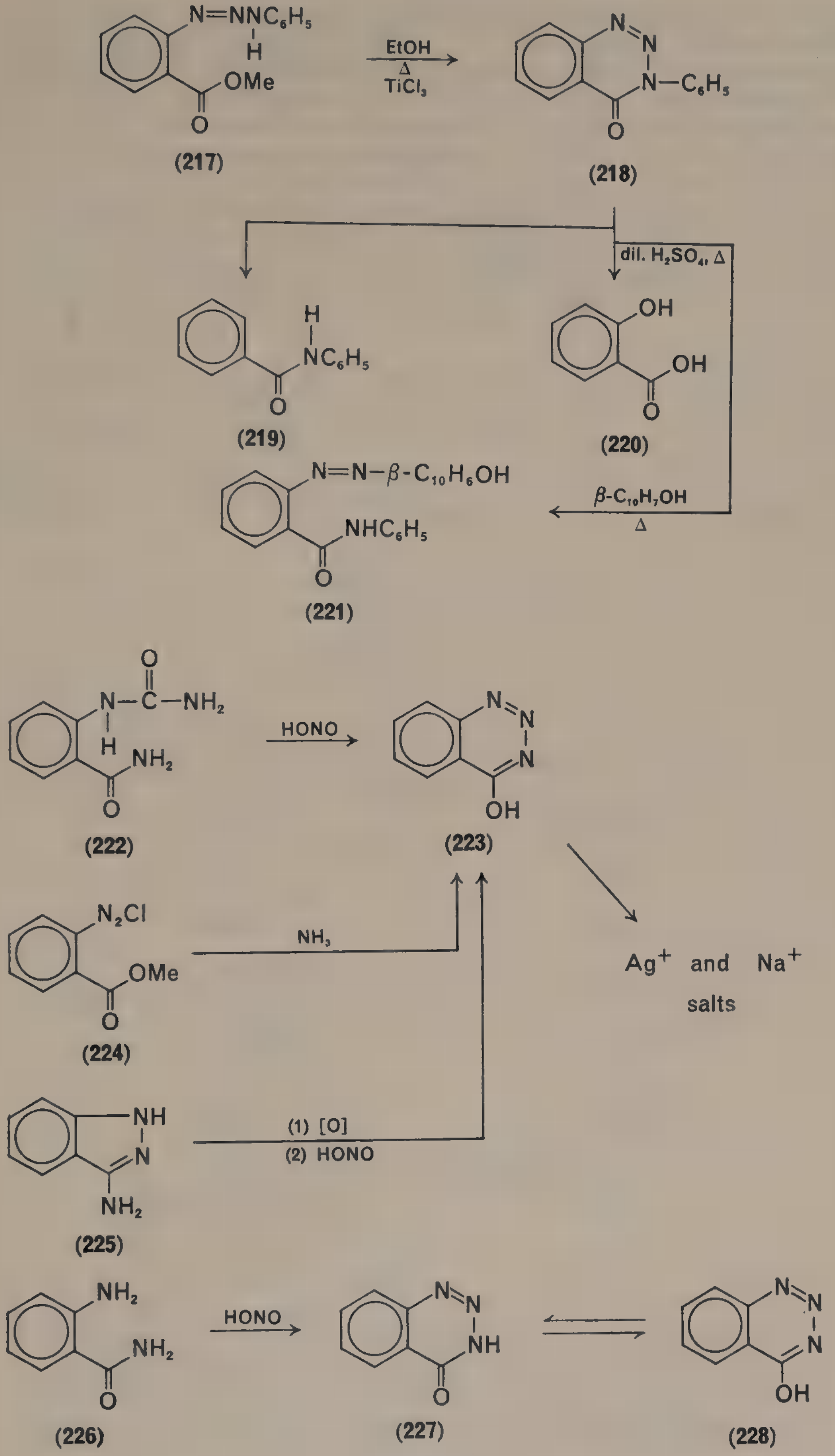
(213) **(214)**

Scheme 44



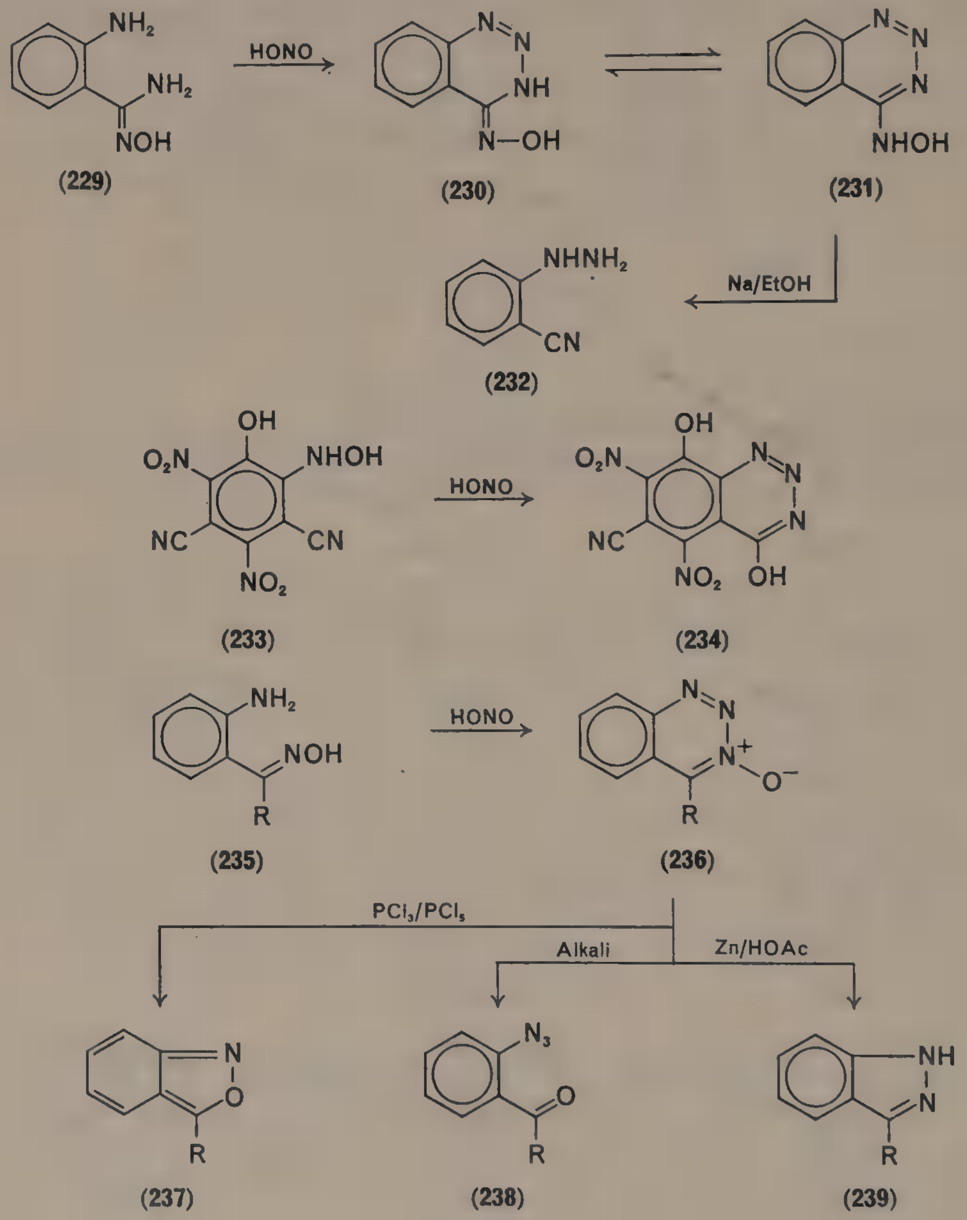
(215) **(216)**

Scheme 45

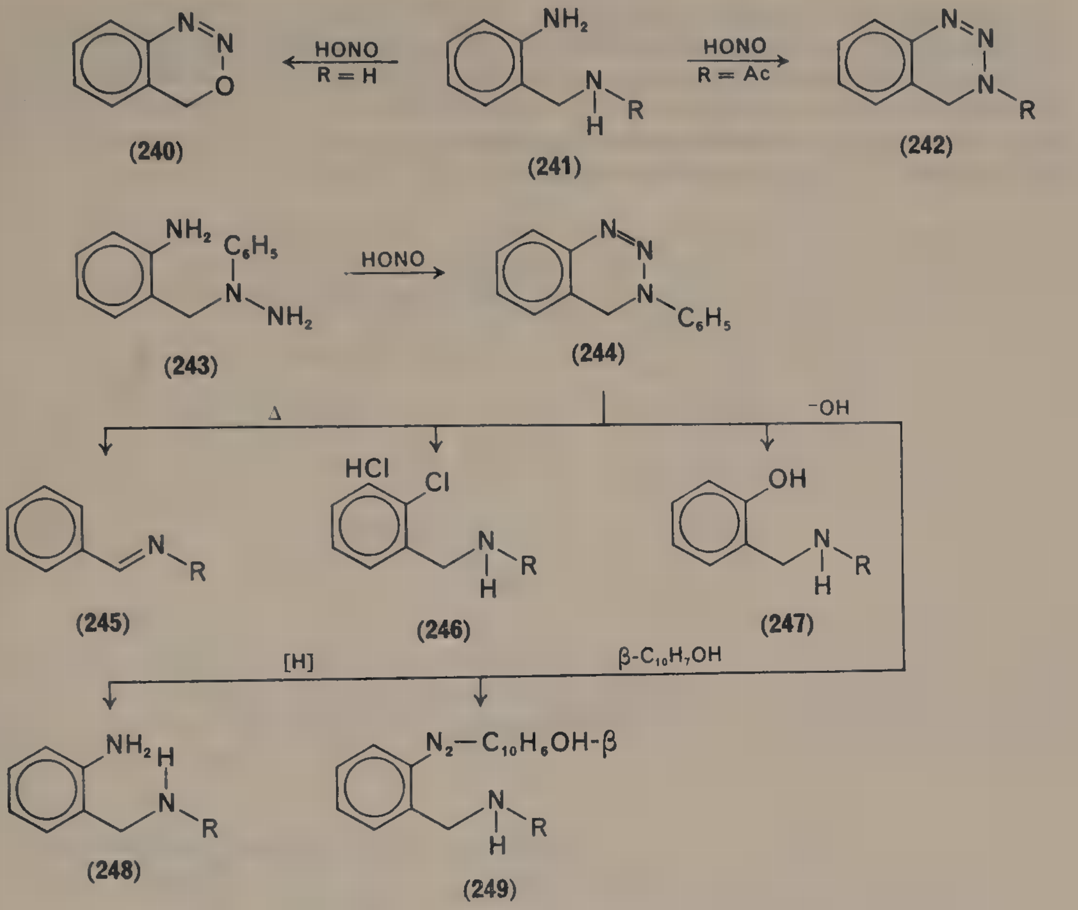

(217)
EtOH
Δ
$TiCl_3$
(218)
dil. H_2SO_4, Δ
(219)
(220)
β-$C_{10}H_7OH$
Δ
(221)
(222)
HONO
(223)
Ag+ and Na+ salts
(224)
NH_3
(225)
(1) [O]
(2) HONO
(226)
HONO
(227)
(228)

SCHEME 46

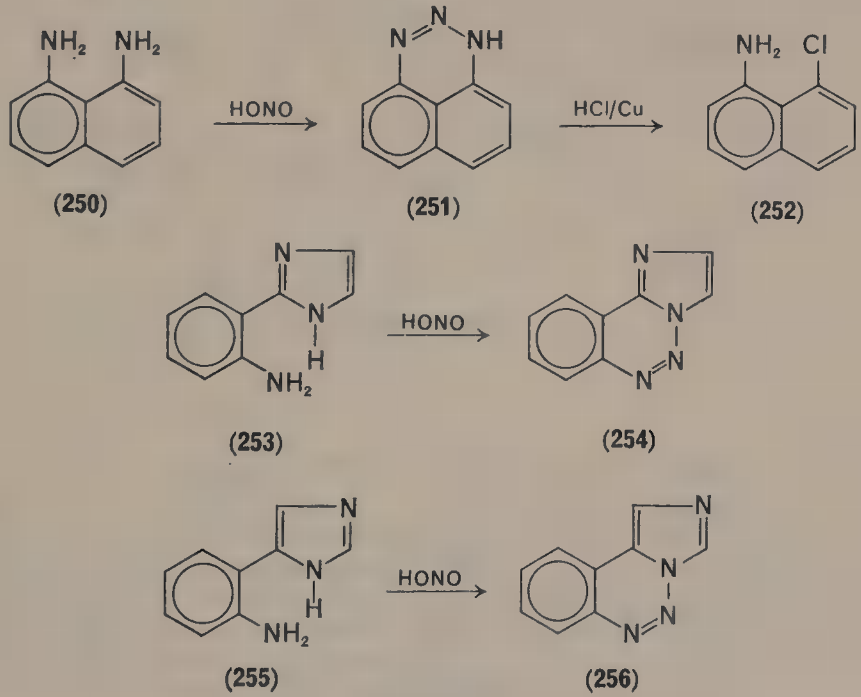
R and R′ to furnish 1,2,3-benzotriazines. Examples are known employing *bis* acyl hydrazides as well as diamides[371, 372, 531, 700, 770, 795, 982, 983] (Schemes 44 and 45); diazoamine esters[240, 770] (Scheme 46) ureas[601]; diazonium salt esters (Scheme 46)[1316], amino benzpyrazoles[63, 66, 67, 446, 655, 1272, 1309, 1310] (Scheme 46); amino benzamide oximes (Scheme 49)[410, 990]; cyano hydroxylamines (Scheme 47)[63, 66, 67, 1202]; amino oximes (Scheme 47)[64, 72, 778, 1189]; amino benzyl aryl hydrazines (Scheme 48)[188]; amino benzyl amides (Scheme 48)[188, 190–193, 1047, 1253]; amino thioamides[1050], 1,8-diamino naphthalenes (Scheme 49)[7, 329, 1086, 1124, 1258, 1349, 1355]; heterocyclic amino carboxamides[618]; amino *ortho*-2-pyrazoles and amino *ortho*-5-pyrazoles, their benzopyrazole analogues[1241, 1242] (Scheme 49); rearrangement of a benzpyrazolodiazene[987] (Scheme 50). Additional leads to 1,2,3-triazines are given in References



Scheme 47

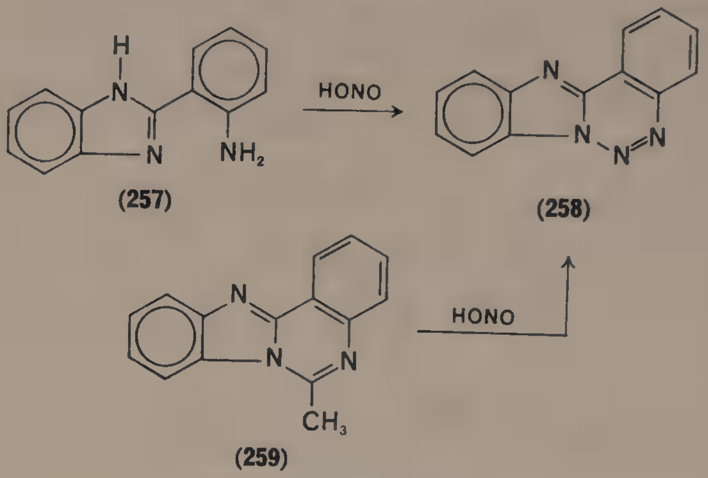


SCHEME 48

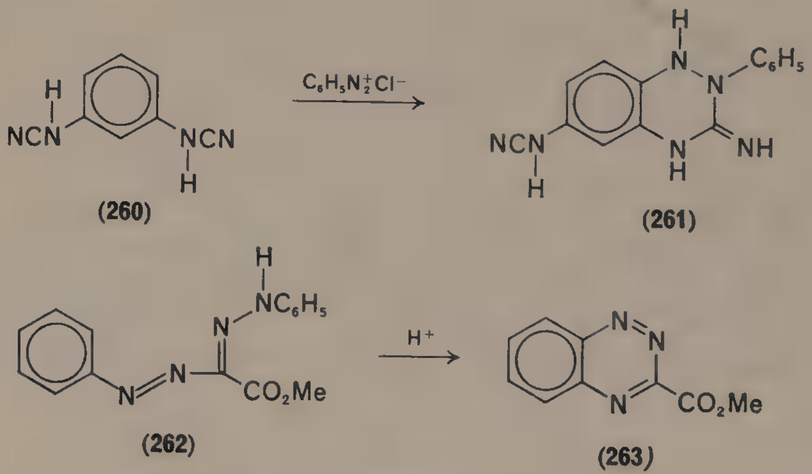


SCHEME 49

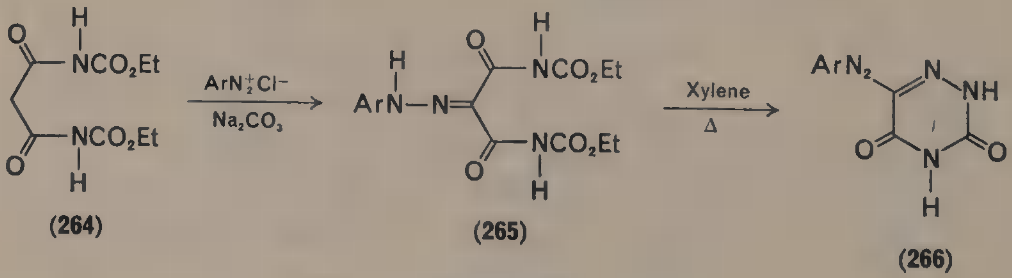
37, 138, 366, 403, 527–530, 640, 687, 811–813, 901, 1087, 1352 and 1353 and for 1,2,4-triazenes see References 364, 842, 905, 966, 977, 1284, 1286 and 1307. The reaction of a diazonium ion with a cyanamide (Scheme 51)[987] or 1-aryl diazo aryl hydrazines[42, 43, 46, 73, 77, 268, 363, 436, 437, 779–781, 853–866, 1350, 1370, 1380] (Schemes 51 and 52) offer a route to 1,2,4-benzotetrazines. Syntheses with aryl diazo aryl diazonium ions open routes to 1,2,3,4-benzotetrazines[97, 533, 1320, 1322, 1324].



SCHEME 50



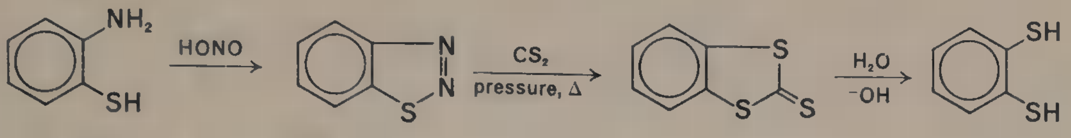
SCHEME 51



SCHEME 52

The products of the type **244** are not aromatic in the heterocyclic system and undergo coupling with β-naphthol and other phenols. As such they can serve as disguised and stabilized diazonium intermediates. In general, substituents on N-3 render the triazine ring systems susceptible to use as diazonium ions at elevated temperatures. A number of syntheses depend upon the triazines and triazine *N*-oxides as intermediates.

e. *Group 5: Benzothiadiazoles.* When *p*-amino thiophenols are subjected to diazotization conditions they couple through sulphur to furnish the 4,4′-bis-(aminophenyl)disulphides[1380]. When the *ortho* isomers are subjected to the same conditions, cyclization to furnish benzothiadiazoles results[445, 566, 593, 605, 606]. These compounds participate in some processes characteristic of diazonium ions. Hence the nitrogen can be replaced by treatment with carbon disulphide[593] and as such offers a route to aryl 1,2-dithiols.



(267) (268) (269) (270)

SCHEME 53

2. Subclass b: The diazo nitrogen is lost

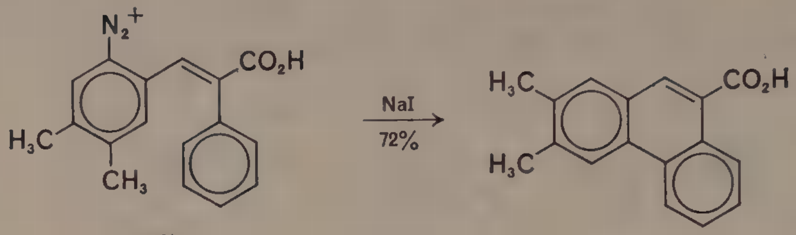
a. *Group 6: The Pschorr type synthesis and its heterocyclic analogues.* Although Saunders[1103] breaks down the various processes into subgroups, many of the reactions in the group are formally identical to the Pschorr Phenanthrene synthesis[288]. The reaction proceeds well with a variety of groups X, e.g. CH=CH [1007–1023], —CH_2—CH_2— [1081], —S— [269a], —O— [289], —NR— [539a], —CO— [441], —CH_2— [381], —Se— [1019], —SO_2— [289], —SO_3— [1105a]. The processes are probably mechanistically very similar. A possible exception is the bis-diazotizaton of 2,2′-diaminobiphenyls[1007, 1017, 1277].

(271) (272)

SCHEME 54

The nature of the intermediate had been the subject of some speculation but quite probably involves a bis(benzo)triazapine which readily loses nitrogen[412]. Saunders[1103] had proposed that the reaction involved the tetra-azotized system losing hydrazoic acid from a partially reduced system but this seems unlikely on thermodynamic and electronic grounds. Chauncy and Gehlert have successfully replaced the copper catalyst in the Pschorr synthesis with NaI[243].

Although the Pschorr syntheses formally resemble the Gomberg–Bachmann–Hey syntheses, they differ in terms of experimental conditions. The former are normally carried out in acidic media whereas the latter are invariably performed in basic media. The Pschorr processes are homogeneous because the attacking species is part of the substrate whereas the Gomberg–Bachmann–Hey reactions are heterogeneous. Thus the Pschorr syntheses possess the inherent advantage of decreased entropy requirement.



(273) **(274)**

Scheme 55

When a rigid bridge is incorporated, the configuration must be *cis* for closure to occur. DeTar has suggested that the ethylenic bridge is perhaps the best bridge available as a consequence of its rigidity[288]; with *trans* bridging other processes occur[1082]. He also noted that electronic factors seem to be of secondary importance[288]. With the presence of *o*-hydroxy and *p*-hydroxy substituents, difficulties occur which lead to the formation of diazooxides. The presence of ether or amine functions in the *ortho* position can lead to extensive tar formation[1217]. When substituents are present at the 3′- and 5′-positions, two possible modes of attack operate unless one of the 2′- (6′)-positions is blocked. Since the processes exhibit only a small degree of sensitivity to electronic effects, one will invariably obtain mixtures of products when the possibility exists. However, when appreciably different $\Delta E\pi$ values are to be expected, the PMO analyses will correctly predict the product to be generated.

E. *Class E: Derivatives Formed by Replacement of the Diazo Group*

With the possible exception of the coupling of diazonium ions with aryl amines and phenols, Class E represents the most widely known class of aryl diazonium reactions and is very sketchily presented in nearly every basic text on organic chemistry. The emphasis is normally placed upon replacement by hydrogen and the four halogens and is usually limited to the Mai–Kornblum reduction, the Sandmeyer reactions and the Balz–Schiemann reaction. Many other replacement processes are known which are of great synthetic utility and have been the subjects of chapters in *Organic Reactions* and a variety of reviews. Copper and its salts are encountered with a large number of the replacement reactions described in this section. Each valence state has associated with it a name, Cu(0) Gattermann, Cu(I) Sandmeyer and Cu(II) Korner–Contardi. It seems quite likely that in this case a single valence state is actually involved. The Merck Index groups all of the processes under the name Sandmeyer reactions[1168].

1. Group 1: Replacement of the diazo group by hydrogen

Classically, diazonium ions were reduced with ethanol and Griess[453] made the original observation in 1864 when he obtained benzene, dinitrophenol and acetaldehyde from the reaction of ethanol with benzenediazonium nitrate.

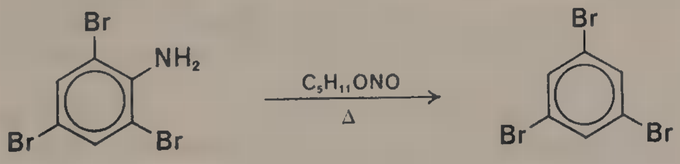
The processes are relatively sensitive to conditions and reduction is favoured by the presence of water, use of the diazotate rather than diazonium ion and the presence of electron-withdrawing substituents in the *ortho* position such as nitro or halogens or hydroxy. Hodgson[549] had suggested that the greater the positive character of the diazonium carbon, the greater the ease of replacement by hydrogen. The validity of such a statement might appear questionable in the light of current theory since the substituents included above encompass $+E$, $-E$ and $-I$ but all are capable of stabilizing homolytic processes. The reaction is often accompanied by the formation of appreciable quantities of the aryl alkyl ether which is in direct parallel with the formation of phenols from water. When diazonium halides are employed, aryl halides can become important products. This problem was overcome by Chamberlain[238] who employed alkaline conditions which generated diazohydroxides or diazotates which furnished no ethers. Unfortunately, even this improvement frequently leads to only moderate yields of the hydrocarbon. Parsons and Bailor[973] found that copper bronze improved the reduction of 4-methylazobenzene-4′-diazonium sulphate and other workers have successfully employed Cu(0) prepared in a variety of ways to facilitate reduction by alcohols[545, 552, 1206].

Under the best of conditions, reduction with alcohols is not a good reliable method and this led to a search for alternative reducing agents. Friedlander[398], Bamberger and Meimberg[45], Eibner[325], and Hantzsch and Vock[504] investigated the use of sodium stannite in aqueous media and found it effective. The *E* diazotates do not reduce with sodium stannite[504]. As noted previously, acid reduction with tin furnishes the hydrazine. Surprisingly, diazotized ethylamino gallate is reduced by stannous chloride to ethyl gallate[1004]. Two rarely used reduction techniques which may actually have promise are alkaline sodium pyrosulphite[444] and hydroquinone[956]. Brewster[153] avoided the ether formation process and obtained good yields in the naphthalene series. Other methods include the use of aluminium[597, 816, 919] in ethanol solution and cuprous oxide in alcohol or formaldehyde solutions[548, 550, 746, 1079].

The most widely accepted reduction technique, the use of hypophosphorous acid, is due to Mai[746] and has been rated by Adams and Kornblum[3] as the preferred method. Yields range as high as 80% whereas other methods rarely reach 60% and are dependent to a large extent upon the ratio of diazonium salt to hypophosphorous acid. Difficult reductions require as much as a 15-fold excess of reducing agent even though the apparent process involves oxidation of 1 mole of reductant to phosphorous acid.

$$\mathrm{ArN_2^+ + H_3PO_2 + H_2O \longrightarrow ArH + H_3PO_3 + H^+ + N_2} \qquad (5)$$

Cadogan[217] has successfully replaced the amino function on a number of anilines in a one-pot process involving treatment of the amine with excess pentylnitrite in refluxing THF or dioxan.



(285) (286)

SCHEME 56

2. Group 2: Replacement of the diazo group by halogens including astatine

The replacement of the diazonium group by a halogen has been known since 1860[447] when Griess heated diazoaminobenzoic acid with concentrated hydrogen halides to obtain halobenzoic acids. Griess[454] later extended his studies to prepare

$$HO_2C{-}ArN_2 \xrightarrow{HX} HO_2CArX + N_2 + R_2N{-}ArCO_2H + R_2NH_2X \qquad (6)$$

representatives of all of the halogens by adding diazonium sulphates to concentrated solutions of the hydrogen halide using *meta*-carboxybenzenediazonium sulphate; he found that the yield was improved by increasing the halogen concentration[471]. This point was pursued further by others who added halide salts to furnish increased halide concentrations[414, 559]. Cupric chloride was the additive of choice for preparing *p*-chloronitrobenzene. Although the reactions are normally run in concentrated acidic solutions, Griess[454, 471] did observe that thermal decomposition of solid salts such as the chloroplatinate and hexachlorostannate furnished the chlorides. The most common solid salt decomposition is due to Schiemann and Balz[40, 331, 1106, 1109, 1190] which, with the improvements of Schwecten[1131], provides a moderate scale route to aryl fluorides. The most widely known halogen and pseudohalogen replacement processes were developed by Sandmeyer[1091–1100]. Sandmeyer had been attempting to prepare phenylacetylene from copper acetylide and benzenediazonium chloride and obtained some chlorobenzene. He was able to show this had arisen from reaction with copper(I) chloride. Subsequently, Gattermann[416, 419] found that freshly prepared copper powder ($CuSO_4 + Zn$) brought about the formation of chlorobenzene from benzenediazonium chloride. Ullmann[1216] found that commercial copper bronze could also be employed.

The use of copper salts is not needed for preparing aryl iodides and can be accomplished by adding an alkali iodide to a diazonium sulphate or by using HI[270, 454, 466, 467, 581, 626, 763, 1110, 1212, 1291].

a. *Replacement by fluorine*. Although the generally preferred method for introducing fluorine is the Balz–Schiemann reaction and normally good to excellent yields are obtained, it is not free from difficulties[1190]. Some of these difficulties are not surprising, e.g. inadvertent replacement of functional groups during the diazotization step. A common problem when solubilizing substituents such as OH are present is difficulty in isolating the fluoroborate salt. To overcome this, other perfluoro inorganic acids have been examined and the hexafluorophosphates have shown some promise because they are extremely insoluble and PF_5 is a very weak acid[1083, 1084]. Thus the isolation of *p*-hydroxybenzenediazonium fluoroborate is not realized while the fluorophosphate is obtained in over 75% yield. Unfortunately, the thermal decomposition to furnish the fluoride is seldom better than the Balz–Schiemann approach. Attempts to improve the decomposition of diazonium fluoroborates have not been overly successful. There is at least one report of tetramethylurea serving as the solvent of choice for decomposing diazonium hexafluorophosphates[1084].

Additives have been employed for a variety of reasons. Decompositions of nitro-aryldiazonium fluoroborates are often difficult to control and neutral diluents such as sand or even sodium chloride are often employed[720, 1063, 1106]. Clearly the use of salts with nucleophilic anions is a risky approach since much of the decomposition occurs via heterolytic mechanisms. The use of alkali fluorides can overcome the problem of additional nucleophiles but tends simultaneously to change the mechanism from heterolytic to homolytic by interchange of anions[98].

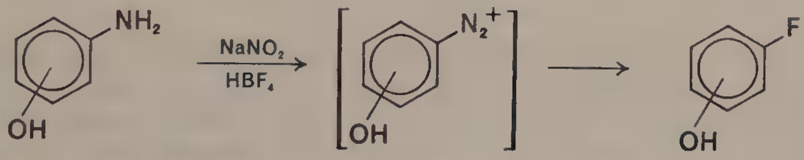
$$\left.\begin{array}{r} PhN_2BF_4+MF \rightleftharpoons PhN_2F+MBF_4 \\ PhN_2F \longrightarrow Ar\cdot+F\cdot+N_2 \longrightarrow \text{Products} \end{array}\right\} \qquad (7)$$

The use of transition metal catalysts has also been claimed to lead to homolytic processes. Copper(I) fluoride and chloride have been used with some success when there are no highly polar substituents such as NO_2, OH, CO_2H. These are some of the same substituents which lead to difficulties with uncatalysed reactions[110, 111]. Apparently the use of copper(II) fluoroborate has not been examined even though it should be free from many of the objectionable characteristics of other systems.

The use of various solvents has been examined and the results are frequently consistent with a heterolytic process[747–750, 879, 947], e.g. halobenzenes, nitrobenzene, benzonitrile, diphenyl ether, trifluoromethyl benzene, acetophenone and methyl benzoate. When benzenediazonium fluoroborate was decomposed in pyridine solutions, the formation of 2- and 4-phenylpyridines were the dominant arylation processes observed. These are most consistent with a homolytic process. In those cases where homolytic processes appear to be occurring, the yields of fluorides are always low.

When the Balz–Schiemann reaction is applied to diazonium ions to furnish fluorides which are highly susceptible to nucleophilic attack, problems can arise in workup. If a nucleophilic centre is already present, as in many nitrogen heterocycles, the reaction can fail totally[98, 1064, 1065]. On occasion Pschorr-type cyclizations cause considerable difficulties[386].

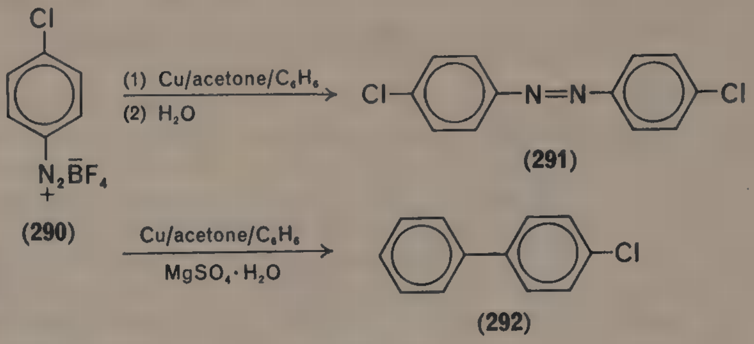
Danek, Snoble and Nouzova[280] succeeded in preparing the *o*-, *m*- and *p*-fluorophenols by diazotizing the aminophenols in 40% fluoroboric acid at −10 °C. With the *o*- and *p*-diazonium salts the fluoroborates could be isolated in good yield and decomposed thermally as the dry salts, whereas the *m*-diazonium ion was destroyed in solution (Scheme 57).



(287) (288) (289)

SCHEME 57

b. *Replacement of the diazo group by chlorine and bromine.* The most frequently employed method used to replace a diazo group by chlorine or bromine is due to Sandmeyer and involves the diazotization of the related anilinium halide and addition to the cuprous halide. There appears to be no general trend in conditions required and it is therefore necessary to optimize temperature and concentration for the process under consideration[21]. The best results are obtained when the diazonium ion solution is run into the cuprous halide solution. This tends to minimize formation of phenol and hydrocarbon coupling reactions. The diazonium ion appears initially to form a complex with the copper salt which then loses nitrogen. The reaction with cuprous chloride almost invariably gives excellent results when the conditions have been optimized. A large number of other metal chlorides have been investigated as alternative sources of halide ion and catalytic activity[554, 563] but copper appears to occupy a unique position in diazonium chemistry. Waters[1269] has ascribed this to the oxidation potential of copper(I).



Scheme 58

With bromine, the Sandmeyer processes are complemented by the use of a complex double salt such as $(ArN_2)_2HgBr_4$ [884, 885, 1131], which is thermally decomposed, by hydrogen bromide decomposition of the diazonium bromide with or without copper or its salts being present, and by the decomposition of the diazonium perbromides. Various copper(I) complexes and salts have been used when troubles have been encountered[266, 271, 272].

Schwechten's[1131] double salt pyrolysis is an extension of Griess's earlier work and has been used to some advantage by Newman[884, 885] who recommends employing twice as much mercury salt as employed by Schwechten.

Griess used the perbromides[454, 464] to prepare the aryl bromides. The diazonium perbromides were used with sodium carbonate and the products were distilled from the mixtures. In some cases no diluent is needed[179]. Newman[885] has diazotized the anilinium bromide in hydrobromic acid solution by adding nitrogen trioxide until the solution remained dark coloured, and then heated until nitrogen was no longer evolved.

c. *Replacement of the diazo group by iodine and astatine.* Griess[454, 466, 467] discovered that replacement of the diazonium group by iodine was extremely facile either in hydroiodic acid or upon addition of an alkali iodide. Waters[1262, 1269] ascribes the ease of the reaction to the fact that the redox potential is near that of copper(I) and that the process involves generation of I_3^+. Normally the reaction is mild although 2-diazodiphenyl has proceeded explosively[581].

The element astatine can be introduced into an aromatic nucleus via the diazonium astinide. Thus, at −5 °C, *o*-halobenzenediazonium ions form complexes with astinide ion which are subsequently decomposed at 80 °C to furnish, as the major radioactive product, the corresponding 1-halo-2-astinobenzene[794].

3. Group 3: Replacement of the diazo group by nitrogen-containing functions through formations of a new C—N bond

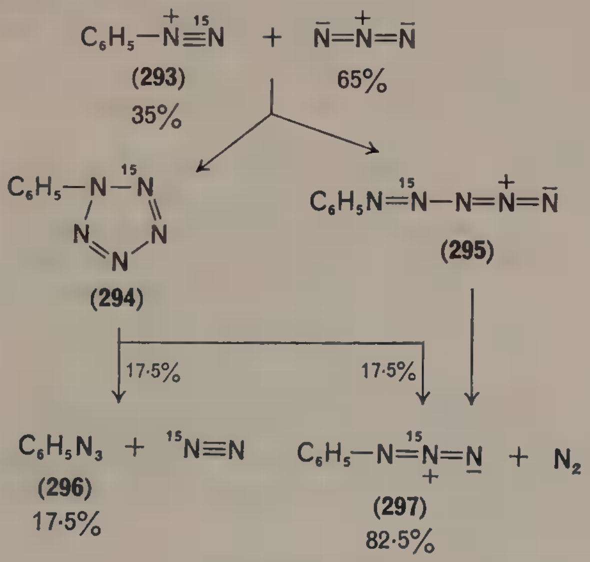
It is possible to replace the diazonium group by a number of groups which result in new C—N bonds but the only ones of wide synthetic utility are the introduction of the NO_2 and N_3 functions. It is only of academic interest to convert an arylamine into itself by generating the diazonium ion and then allowing it to react with hydroxylamine to furnish a mixture of azide and aniline[745]. In some cases this can be accomplished by reaction with ammonia, presumably via the diazoamines which undergo prototropy to furnish the aniline plus nitrogen[474, 1255, 1266]. It appears that neither reaction has any promise as a route for introducing labelled nitrogen. A possibly more promising way of introducing labelled nitrogen is via the replacement of the diazonium group by NCO in the presence of copper salts[417, 418]. Synthetically this offers no special advantage over treating the amine with phosgene if labelling is not desired.

a. *The formation of nitro compounds.* The replacement by NO_2 can be realized by several paths including the Sandmeyer reaction, and the Korner–Contardi reaction and the Griess replacement.

A number of copper derivatives have been employed including Cu_2O, finely divided copper powder[89, 1166, 1233], copper(II) sulphate in conjunction with cobalt nitrite complexes[555], cupric chloride[694–698] and cuprocupric sulphite[502], all in the presence of excess nitrite. In a number of cases the diazonium fluoroborate has been decomposed with a copper salt in the presence of nitrite salts[777, 1167].

Double mercury salts of the type $(ArN_2)_2Hg(NO_2)_2(NO_3)_2$ [502] have been decomposed in the presence of copper derivatives. In line with Newman's observations on the double salts with mercury halides[884, 885], one might suspect that the use of the diazonium nitrite with an additional equivalent of mercury salt would prove a more useful process.

In a number of cases, the generation of diazonium ions in the presence of large excesses of nitrite ion leads to formation of the nitro compound directly. This is most readily realized if the aryl group possesses electron-attracting substituents in the *ortho* and/or *para* positions. The substituents can be electron donating in the mesomeric sense, thus bromo and nitro substituents are both effective[167, 168, 955, 1098, 1207].



SCHEME 59

b. *The formation of azides.* The aryl azides were known as azoimino compounds well into the 20th century and as such have appeared in the literature since 1864 when Griess[449, 450] reported that benzenediazonium perbromide reacted with ammonia to generate phenylazoimine.

$$PhN_2^+Br_3^- + 4\,NH_3 \longrightarrow PhN_3 + 3\,NH_4 + 3Br^- \qquad (8)$$

The same compound results when benzenediazonium sulphate is treated with hydroxylamine[374, 745], by diazotization of phenylhydrazine[576, 732] or reaction of hydrazine with benzenediazonium sulphate.

$$\left.\begin{aligned} \mathrm{PhN_2^+\bar{H}SO_4 + NH_2OH} &\longrightarrow \mathrm{PhN_3 + H_2O + H_2SO_4} \\ \mathrm{PhNHNH_2 + HONO} &\longrightarrow \mathrm{PhN_3 + 2\,H_2O} \end{aligned}\right\} \qquad (9)$$

A very general synthesis is known which proceeds in part via the unstable pentazole which loses nitrogen to furnish the azide. The synthesis was developed by Noelting and Michel[904] in 1893 but it was not until 1954 that evidence was obtained indicating the formation of an intermediate pentazole along with a diazonium azide[254, 587, 1215].

The pentazoles are extremely unstable substances and their chemistry has been reviewed by Ugi[1215a] (see Scheme 59 above).

4. Group 4: Replacement of the diazo group by oxygen. Formation of phenols, phenol ethers and phenol esters

One of the earliest reactions observed with diazonium ions was replacement by —OR (R = H, alkyl, acyl). The formation of alcohols is a common reaction of alkyl diazonium ions and is often an annoying side-reaction when aryl diazonium ions are formed.

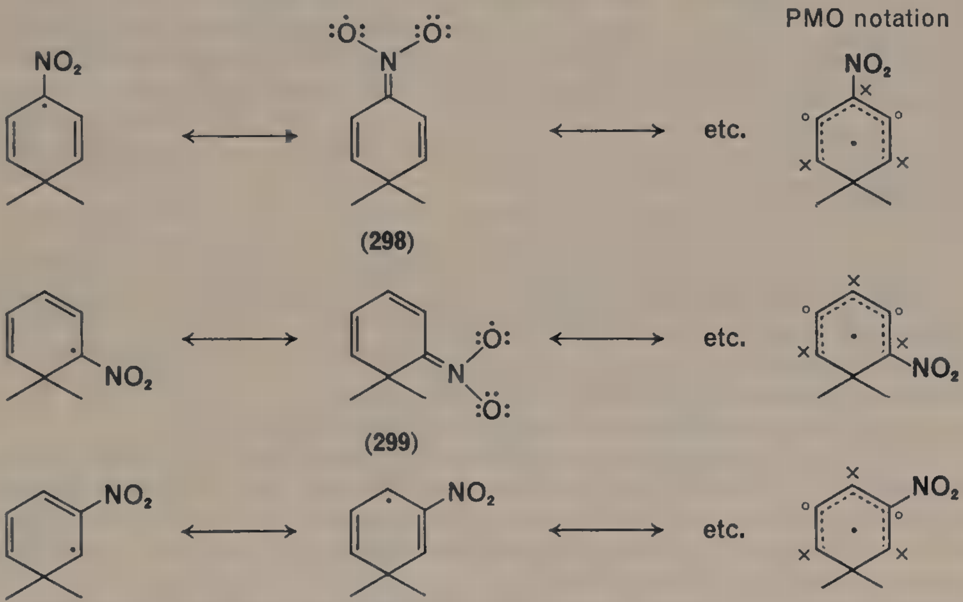
The alkyl diazonium reaction was noted by Piria[991, 992] in 1848 when he treated asparagine and aspartic acid with nitrous acid and obtained malic acid. The formation of phenol by heating an aqueous solution of benzenediazonium sulphate was reported by Griess in 1866[460]. The reaction was employed by Fisher in 1878 to help elucidate the structure of the triphenylmethane dye, rosaniline, which has three amino groups which he replaced with hydroxyls[375]. The reaction is generally successful and works well with tetrazotized biphenyls. Substituents do affect the ease with which the reaction occurs[171, 223, 225, 526, 541, 896, 907, 1329, 1335, 1348, 1365]. Care must be taken to avoid an excess of nitrous acid or nitrate ion since under the acidic conditions of the process, the resulting phenols are often prone to nitrosation or nitration[902, 1230].

The formation of ethers from alcohols and diazonium ions is in direct parallel with the reaction with water. The reaction is frequently accompanied by reduction to the hydrocarbon. The two reactions compete effectively and often prevent one from obtaining a good yield of the desired product unless care is taken to employ the anhydrous diazonium salt. (There is however some divergence of opinion on this matter. Thus in at least one case, 15% water was found permissible[1053].) When this is done, the ethers are often obtained in excellent yields. The reactions are usually performed in refluxing alcohol[793, 950, 970, 1051–1053, 1141] but operating in a pressure vessel to permit an increase in temperature has been efficacious in several instances[793, 950, 970, 1050, 1052, 1053, 1041]. The reaction does not work well with phenols where yields of less than 20% are common and they are accompanied by large quantities of arylated phenols[242, 571].

5. Group 5: Replacement of the diazo group with formation of a C—C bond

a. *Formation of aryl cyanides.* In Section II.B.3 we have discussed the formation of diazocyanides and their reactions. Sandmeyer[402, 1093] demonstrated that treatment of a diazonium salt with KCN–CuCN furnished aryl cyanides. Subsequently a large number of aryl nitriles have been prepared in this fashion and the reaction is now recognized as a simple variant of the Sandmeyer reaction with halides[8, 691, 989, 1075, 1080, 1094, 1125, 1218, 1354, 1362]. The yields are often only moderate because the initially formed 'labile' diazocyanides rapidly isomerize to the 'stable' isomers which do not decompose to furnish the nitrile. Unlike the Sandmeyer reaction with halogens, other metal complexes can be used, in particular tetracyanatonickel(II). A claim has been made that its use is to be preferred over biscyanato copper(I)[402, 691]. Potassium tetracyanatoammine copper(II) has also been employed to avoid the potential hazard of generating cyanogen[1369].

b. *Formation of symmetrical and asymmetrical biaryls.* Diazonium hydroxides decompose in aromatic solvents to furnish biaryls. The reaction, known as the Gomberg–Bachmann reaction[32], proceeds by a free radical mechanism and is strongly paralleled by the related Grieve–Hey–Heilbron syntheses using aromatic nitrosamides which are decomposed in the substrate aromatic solvent[32, 284, 328, 438, 539, 1103, 1326]. Both provide a route to unsymmetrical biaryls (Scheme 60) and are mechanistically similar. The reactions have been reviewed. These processes offer one of the best routes to unsymmetrically substituted biaryls and furnish ready access to *meta*-substituted biphenyl when substituents are to be in only one ring; the related substituted aniline is employed along with the aromatic hydrocarbon. Unlike electrophilic substitution, the products from substrates such as nitrobenzene are *para* substituted. This is not particularly surprising if one remembers that the corresponding Wheland intermediates (**298**, **299**) will be more highly delocalized with *para* or *ortho* attack than with *meta* (**300**). With substrates such as pyridine all possible isomers result. The related unimolecular process involving the formation of phenanthrene and fluorenes is known as a Pschorr synthesis and has been treated in Section D.2.b. The Gomberg–Bachmann reaction furnishes yields in the poor to good range (60+% but infrequently higher). The Pschorr reaction (actually discovered previously by Graebe and Ullmann[441, 442] and Fischer and Schmidt[381])



(298)

(299)

(300)

Scheme 60

being an intramolecular process can be expected to furnish good yields, 70–90% not being unusual. It should not surprise anyone to find that isomer mixtures result when the non-diazonium ring system is asymmetrically substituted. Obviously the presence of an *ortho* ethylene bridge causes the molecules to undergo some or even dominant closure to cinnolines and related heterocycles. Thus all three of these related reactions are subject to the same limitations as are other *o*-substituted diazonium ions.

A fundamental limitation of both the Gomberg–Bachmann and the Grieve–Hey–Heilbron syntheses is the need to employ the substrate hydrocarbon in the liquid state. When this is combined with the desirability of having the substrate molecule as the most symmetrical portion of the biaryl to be synthesized, very strong limitations in scope arise. Since the reactions are normally run below 30 °C, many formal processes are just not practicable in the laboratory. The use of solvents is not particularly encouraging since the aryl radicals generated can attack the solvent as well. Thus when chloroform or carbon tetrachloride are used, appreciable quantities of the aryl diazonium compound end up as aryl chlorides[474]. With substrates such as pyridine, the dry diazonium salt can be added to the pyridine[807] or by the reaction of the sodium diazotate with pyridine–acetic anhydride[389]. Alternatively the nitrosoacetyl derivative can be heated in pyridine solution[517, 518].

Cadogan[215] has smoothly converted aryl diazonium fluoborates to dihalodiazobenzenes by decomposing the diazonium salt in 10% acetone 90% benzene at room temperature using copper powder. If 2 mol of water are present, the biphenyls result (Scheme 58).

c. *Arylated quinones and other unsaturated species including hetero aromatics and non-classical aromatic systems. The Meerwein reactions.* It is possible to arylate quinones, α,β-unsaturated carbonyl compounds, vinyl nitriles and styrene using aryl diazonium ions. In the case of quinones and quinone oximes they are frequently dissolved in acetic acid or alcohol and the diazonium salt is added at room temperature. The evolution of nitrogen is normally complete in 24 h[22, 137, 139, 707, 759, 1071, 1103]. When olefins are used as substrates, copper salts are normally employed as catalysts[767, 1330]. This process has become known as the Meerwein reaction[1071]. With many substrates two possible products can arise in principle, but a simple analysis on the basis of which intermediate radical will be most stable usually suffices to predict the correct product.

A large variety of olefinic substrates can be used and these include, vinyl halides[269, 679, 844], acrylonitriles[163, 293, 425, 679–682, 717, 751, 752, 1332], phenylacetylenes[766], phenylpropiolic acid[767], acetylene[844], coumarin[394, 767, 1332], cinnamaldehydes[767], cinnamyl esters[684, 767], acrylic acids[702, 844, 1036], butadienes[152, 265, 476, 844, 1072, 1073], styrenes[164, 279, 679, 680, 1039], vinyl ketones[753, 844, 847], maleic acids[1035], maleic and fumaric esters[767, 1196, 1235], maleimides[1068, 1070], furans[160, 395, 396, 717, 946] and nitrostyrenes[109].

Most of these reactions are straightforward but in some cases addition of aryl halogen across the double bond occurs[152, 265, 269, 293, 425, 476, 679, 680, 682, 712, 751, 752, 767, 844, 847, 1068, 1070, 1072, 1073, 1196, 1235]. This is in part influenced by the reaction conditions. Cinnamic acids and maleic acids are often accompanied by decarboxylation with the aryl group formally replacing the $-\mathrm{CO_2H}$[106–108, 286, 407, 622, 716, 767, 771, 772, 1035]. This is somewhat dependent upon reaction conditions, with very low pH apparently favouring retention of the carboxyl function[622].

The variety of less common unsaturated substrates also undergo the Meerwein reaction. These include oximes[94, 95, 140, 622, 623, 980], malonic ester[480], nitromethane[1214], ferrocene[155, 880–882, 1275] and γ-pyridines[1031].

There seem to be few limitations upon the aryl diazonium compound used except that at very low pH values some lose nitrogen to form aryl halides which is facilitated by the copper catalysts normally used. At higher pH resin formation can create problems.

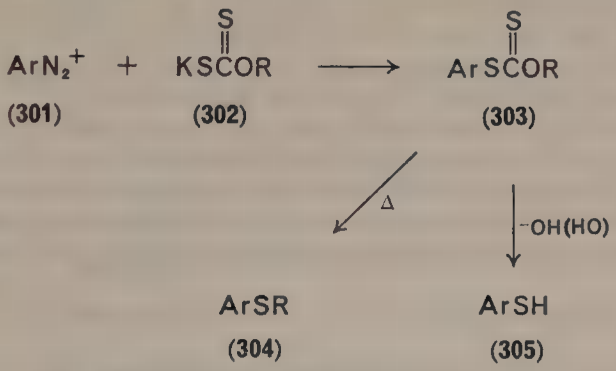
6. Group 6: Replacement by groups in which attachment occurs through sulphur, selenium or tellurium

Many of the aryl diazo-sulphur derivatives mentioned previously are of extremely limited stability and lose nitrogen explosively to furnish aryl-S derivatives. Griess[440, 461] prepared diphenyl sulphide by reacting benzenediazonium salt with solutions of potassium sulphide. The same product occurred when the silver or gold salts obtained from the diazonium hydroxide were treated with hydrogen sulphide. Even in extremely small runs of these reactions, explosions occurred. The use of cupric sulphide in analogy with a Sandmeyer-type process fails and furnishes only tars[132]. The reaction with elemental sulphur furnishes phenyl sulphide and, in a similar fashion, reaction with selenium furnishes the selenide[1270]. With tellurium one obtains the diaryl dihalotelluride[1270].

When the hydrogen sulphide is replaced by alkyl mercaptans, the resulting aryl diazonium alkyl sulphides can be readily (often explosively) decomposed into the aryl alkyl sulphide[710, 1164].

Clearly this approach does not offer much attraction to cautious chemists and approaches employing the sulphur atom in modified form are more desirable.

The safe generation of thiophenols and of aryl thioethers from diazonium salts can be realized by the Leukart thiophenol reaction where the diazonium salt is allowed to react with a potassium xanthate. If the ether is desired it is pyrolysed; if the thiophenol is wanted it is subjected to alkaline hydrolysis[726].

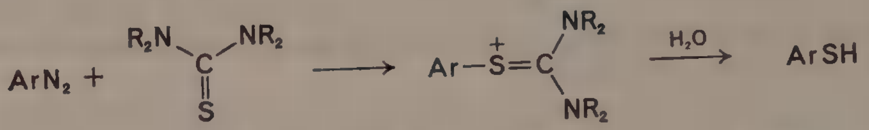


SCHEME 61

This process along with the somewhat similar approaches of Lustig[740] and Clifford and Lichty[252] have fairly general applicability[252, 574, 594, 1271, 1340].

When aryl diazonium salts are added to solution of calcium or sodium polysulphides, the bis(aryl) disulphides are generated and these can be subsequently converted to the thiophenols[1270, 1351, 1338].

The reaction of aryl diazonium ions with thioureas generates aryl thioronium salts which hydrolyse to furnish the thiophenols[203]. When the thiourea is unsubstituted, troubles can arise. Thus a diazonium anthrone furnishes the thiol[1338] while thiophenol was not isolated from the reaction with benzene diazonium ion[203]. Forrester and Wardell list only the Leukart synthesis for thiophenols[388] amongst the various syntheses given. The sulphides can also be prepared from the reaction of a dialkyl sulphide with benzyne and diaryl sulphides with differing substituents can be obtained by copper-catalysed decomposition of the aryl diazonium aryl sulphides[540, 690].



$$ArN_2 + (R_2N)_2C{=}S \longrightarrow Ar{-}\overset{+}{S}{=}C(NR_2)_2 \xrightarrow{H_2O} ArSH \qquad (12)$$

Aryl diazonium ions react with thiocyanate and selenocyanate ions to furnish the related aryl thiocyanate or aryl selenocyanate[124, 355, 415, 421–423, 688, 846]. Subsequent hydrolysis furnishes the corresponding phenol analogues. A large number of metal and metal salt catalysts were examined in the thiocyanate case with ferric chloride being the superior catalyst for conversion of *o*-nitrobenzenediazonium chloride at 15–20 °C (76%) and tungsten hexachloride being the best catalyst at 60–70 °C (69%)[690]. With *meta*-nitrobenzenediazonium chloride, ferric ion was found to be the best catalyst (80%)[689].

The aryl selenocyanides are convenient intermediates in aryl selenium chemistry[598].

7. Group 7: Replacement of the diazo group by arsenic, antimony and bismuth

In a footnote to a paper, Koenigs[686] noted in 1890 that the benzenediazonium ion gave a cherry-red colour with arsenite. This is a characteristic phenomenon observed when aryl arsonic acids are prepared by the Bart reaction which was described in 1910 in the German, English and French patent literature[1331, 1342, 1356].

Prior to that time arsenite had been employed as a reducing agent in strongly alkaline solution. The Bart reaction is of general utility[482, 963] furnishing the aryl arsonic acids in fair to excellent yields[87, 88, 91, 387, 604, 619, 624, 729, 883, 909, 948, 1111, 1263, 1357–1359, 1366]. It has been used to prepare heterocyclic[38, 125, 230, 979, 1155, 1366] and polycyclic[151, 1088, 1102, 1174] arsonic acids. The reaction is strongly dependent upon pH and is catalysed by silver-, copper- and nickel-based catalysts. A modification, known as the Scheller reaction, proceeds through the copper-catalysed decomposition of the aryl diazonium tetrachloroarsenite which furnishes an intermediate which decomposes in hot water to furnish the aryl arsonic acid[126, 1364, 1367].

$$ArN_2OH + Na_2HAsO_3 \longrightarrow ArAsO_3Na_2 + N_2 + H_2O$$

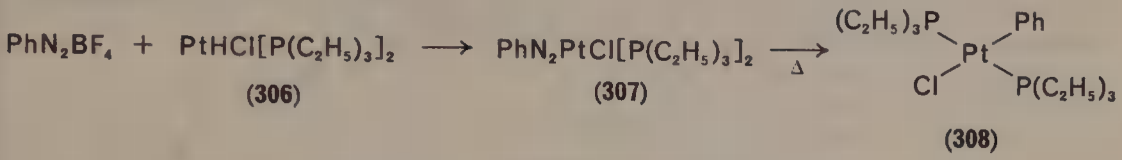
Elemental arsenic[1265, 1267] and elemental antimony[1267] are attacked by aryl diazonium salts when warmed in acetone and furnish the triaryl antimony dichlorides or triarylarsenic dichlorides.

$$ArN_2Cl + Sb \longrightarrow Ar_3SbCl_2$$

The aryl stibonic acids are formed by treating a strongly alkaline solution of the diazo compound with an alkali antimonate[1112, 1333, 1360, 1361]. A modification employs the aryl diazonium chloride–zinc chloride double salt (e.g. May's double salt). This is decomposed in the presence of copper of copper(I) salts[1112, 1339, 1341] or zinc dust[878]. Aryl bismuth compounds are generated by decomposing the diazonium–bismuth chloride double salt in a solvent such as acetone. Mono-, di- and triaryl bismuths are formed in moderate yields[431, 432].

8. Group 8: Replacement of the diazo group by metals

The aryl diazonium ions form a large number of double salts with a variety of heavy metals. The decompositions of some of these offer routes to aryl metal systems where a metal–carbon bond results. There is apparently only one example involving a transition metal (Pt)[1024].



SCHEME 62

This fact is rather surprising since a large number of aryl diazonium metal complexes are known[1193] and many metals are capable of forming aryl–metal bonds. One might expect to form aryl–metal bonds in some of the cases where the decompositions of aryl diazonium ions are catalysed by transition metals and their derivatives. The absence of such products may be a consequence of oversight rather than thermodynamics.

With mercury, tin and lead it is possible to prepare the aryl derivative from aryl diazonium ions. Nesmeyanov and coworkers have prepared a number of arylmercurichlorides from the aryl diazonium chloride–mercuric chloride double salts in the presence of copper[867–877]. Alternatively, one can react the diazonium salt while strongly agitating the mercury cathode[315, 744].

$$\mathrm{ArN_2Cl\cdot HgCl_2} \xrightarrow{\mathrm{Cu}} \mathrm{2\,CuCl + N_2 + ArHgCl}$$

Stannic halides also form double salts with aryl diazonium ions and these, when reduced with zinc, copper or preferably tin in ethyl acetate solution, furnish principally the bis(aryl)stannyl dichlorides[677, 1266].

$$\mathrm{2\,ArN_2Cl\cdot SnCl_4 + 4\,Sn} \longrightarrow \mathrm{Ar_2SnCl_2 + 2\,N_2 + 4\,SnCl_2}$$

In acetone solutions, tin reacts directly to furnish the bis(aryl)dichloro stannane[1266].

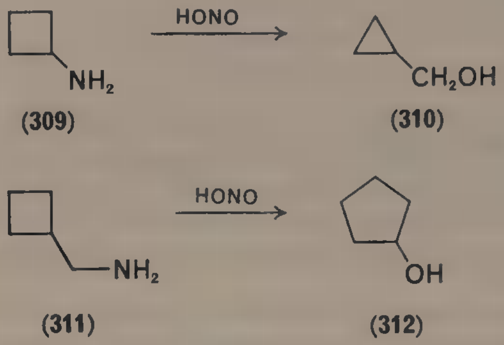
Decompositions of lead double salts in the presence of copper furnish poor yield of triaryl chloro plumbane and biaryl dichloro plumbanes[1266, 1268].

When aryl diazonium fluoroborates are decomposed with copper powder, small amounts of the aryl copper(I) derivatives are formed and these can be stabilized by chelation with pyridine[135, 1280].

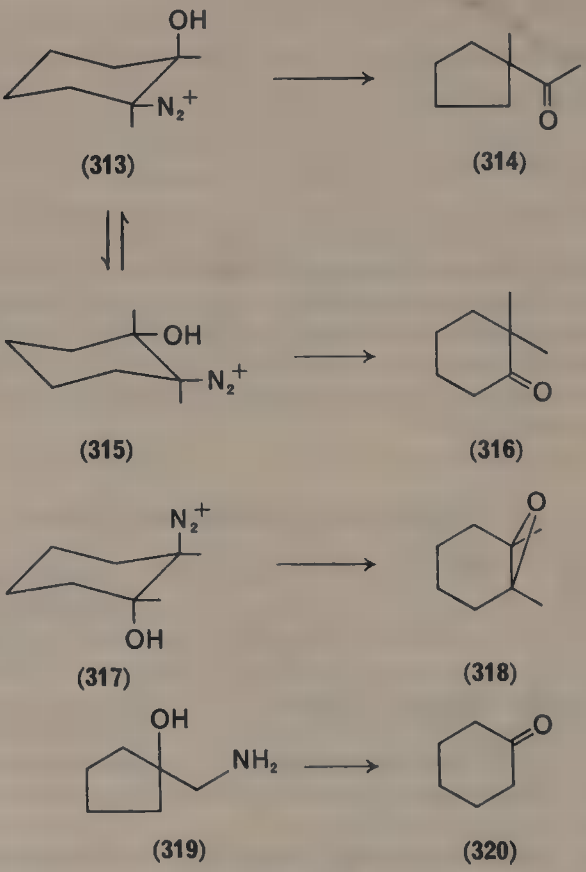
III. ALKYL DIAZONIUM IONS

The known reactions of alkyl diazonium ions unlike those of the arenediazonium ions are rather limited. It seems likely that many of the processes known for the arenes will ultimately become known when suitable reaction conditions are developed. Until fairly recently, alkyl diazonium ions have held the role of 'alleged intermediates' in deamination reactions. The basic features with numerous examples have been the subjects of several reviews[83, 115, 149, 183, 226, 258, 477, 478, 651, 714, 758, 825, 836, 996, 1040, 1056, 1077, 1105, 1142, 1157, 1278, 1282, 1326] and we shall only concern ourselves here with the synthetic uses of the nitrosation of alkyl amines and with species derived from acyl nitrosamines.

One of the more practical synthetic reactions of alkyl diazonium ions is the Tiffeneau–Demjanov reaction where an α-amino alcohol or an amine is treated with a nitrosating agent and rearrangement occurs with shortening or lengthening of the carbon chain (usually a ring is enlarged or contracted). The processes often proceed with excellent yields and in many instances provide routes which are competitive with the Wolff rearrangements and homologations with diazoalkanes, both of which are discussed in Chapter 18. An exhaustive review of both sets of processes has recently been presented by Gutsche and Redmore[478, 1040]. The Demjanov reaction[285] in a strict sense describes the rearrangement process of a nitrosated amine and can lead to a ring expansion or contraction.



SCHEME 63



SCHEME 64

The Tiffeneau reaction (sometimes referred to as a semi-pinacolic rearrangement) involves the nitrosation of an α-amino alcohol[701, 1205]. Since such compounds are readily attainable in good yield by a variety of routes from ketones, the process is of considerable synthetic utility. The reaction does not always lead to ring contraction[775] and the behaviour is a function of ring size[245, 267, 274, 322, 323, 582, 674, 743, 1194, 1209, 1210] and, as indicated in the hypothetical case illustrated, is a function of conformation.

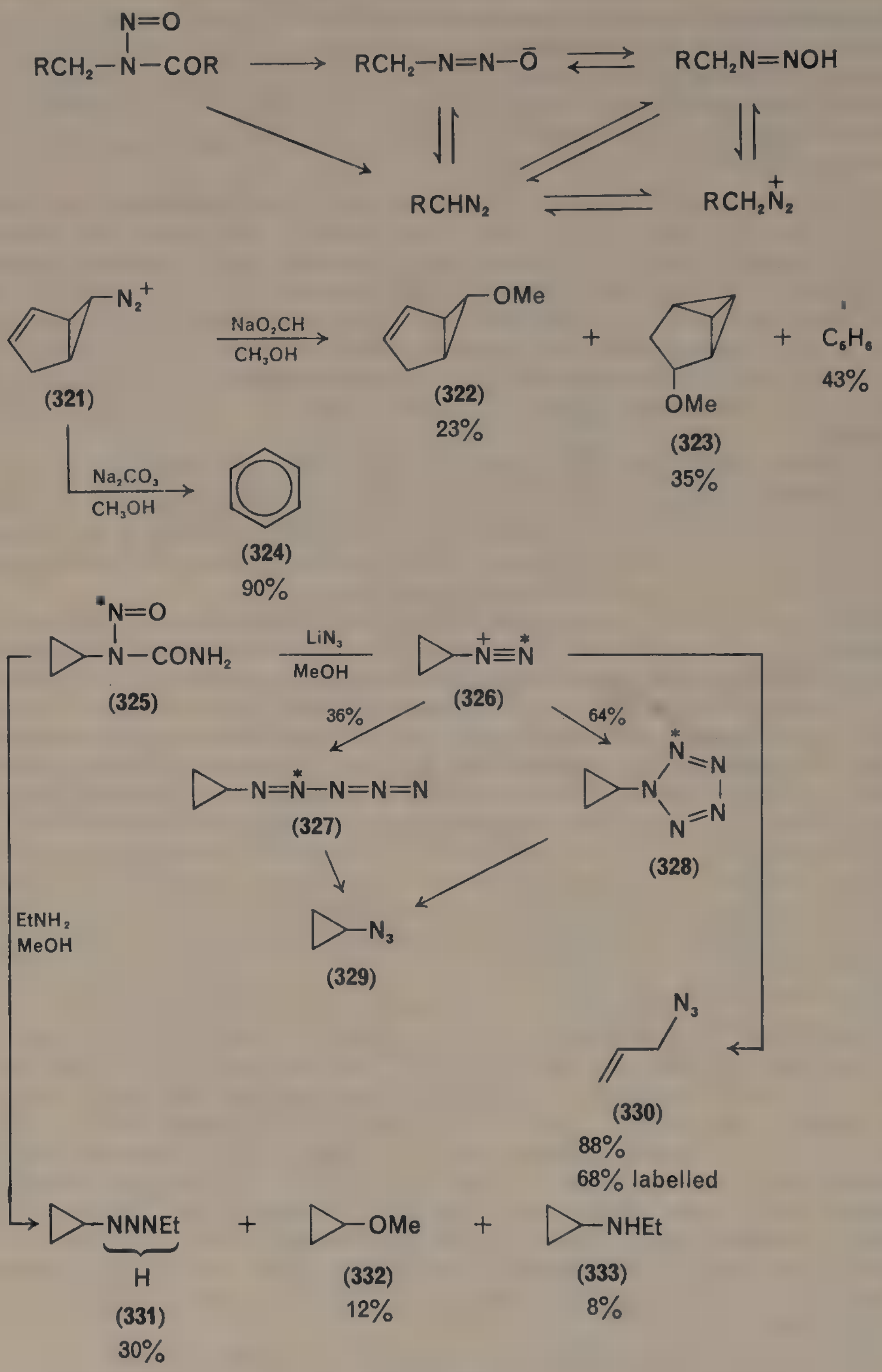
The overall question of conformational effects on deamination in rigid systems has been summarized by Kirk and Hartshorne[641]. The course of Tiffeneau–Demjanov reactions on a variety of aminocyclanols has been summarized according to ring size by Gutsche and Redmore[1040] and it is clear that conformational effects are of great importance. The difficulties encountered are often a direct consequence of the lack of conformational regularity encountered in seven or more membered rings. In the case of hydrochrysenes (e.g. D-homosteroids) a careful analysis has been made[1278]. The migrating group is always *anti* to the leaving diazonium nitrogen[267, 674].

With simple amines one encounters a variety of processes which are normally of little synthetic utility. The diazotization process normally furnishes mixtures of alcohols and olefins which, on occasion, prove to be rather complex as a consequence of Wagner–Meerwein rearrangements. Several reviews dealing with various aspects of the deamination via nitrosation have appeared.

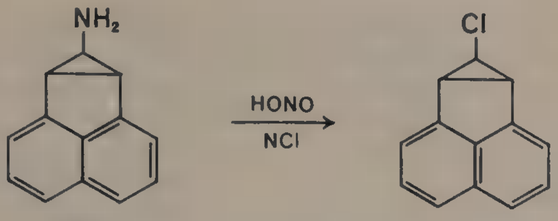
Fairly recently, work originating primarily in the laboratories of Moss[821–841], Newman[889–895] and of Kirmse[644–659] has led to the development of reasonable to excellent synthetic schemes dependent upon the transient existence of alkyl diazonium ions. Thus Steinheimer[1169–1171], upon discovering that diazo transfer to 7-aminonorcarane proceeded in only moderate yield, was able to convert the same amine via the 7-*N*-nitrosourea or urethane into the azide in excellent yield by employing Kirmse's reaction[646] with lithium azide. The reaction was followed by careful thermolysis to the 1-azetidine and represents a general route to the formal 2+2 cycloaddition of hydrogen cyanide to an olefin[1170, 1171]. The process had been postulated by him as proceeding through a diazonium ion and a pentazole[1171]. Simultaneous work in Kirmse's laboratory revealed this to be the case[662, 663] and that it did not involve the highly improbable cyclopropyl carbonium ion originally claimed[646].

Kirmse[644–654, 657–669] has subjected a variety of *N*-nitroso urethanes to basic conditions under which there appears to be a high probability that alkyl diazonium ions and alkyl diazotate ions are formed[644]. The reactions involve trapping these species prior to formation of a diazoalkane. It seems likely that similar behaviour is occurring in the synthetic studies of Newman[889–895], Hogan[57], Billett[121–123] and Moss[821–831, 833–841]. Kirmse has employed several bases of which formate, methoxide, carbonate and bicarbonate are dominant. Many of his reactions have been run in methanol but in some cases ethers have been employed. The solvent and base contribute markedly to the nature and distribution of the final products. Thus the 6-*exo*-bicyclo[3.1.0]hex-2-ene furnishes 90%+ benzene with sodium carbonate/methanol and 43% benzene, 23% **322** and 35% **323** when sodium formate/methanol is employed[653].

When the β-phenethyl system was treated with $NaBH_4$, the N_2 function was removed to furnish 61% ethyl benzene and a mixture of styrene and α- and β-phenethyl methyl ethers (7 : 9 : 84)[647]. The reaction to furnish cyclopropyl azide[646, 662, 663] has been studied using isotopic labelling and the reaction strongly resembles the related aromatic series with a mixed path resulting from pentazole and pentazene intermediates. This fact should not be particularly surprising since


N=O
RCH₂—N—COR
RCH₂—N=N—Ō
RCH₂N=NOH
RCHN₂
RCH₂N₂⁺
N₂⁺
NaO₂CH
CH₃OH
OMe
C₆H₆
(321)
(322)
23%
(323)
35%
43%
Na₂CO₃
CH₃OH
(324)
90%
*N=O
N—CONH₂
(325)
LiN₃
MeOH
N≡N*
(326)
36%
64%
N=N*—N=N=N
(327)
N*
N
N
N
N
(328)
N₃
(329)
EtNH₂
MeOH
N₃
(330)
88%
68% labelled
NNNEt
H
(331)
30%
OMe
(332)
12%
NHEt
(333)
8%

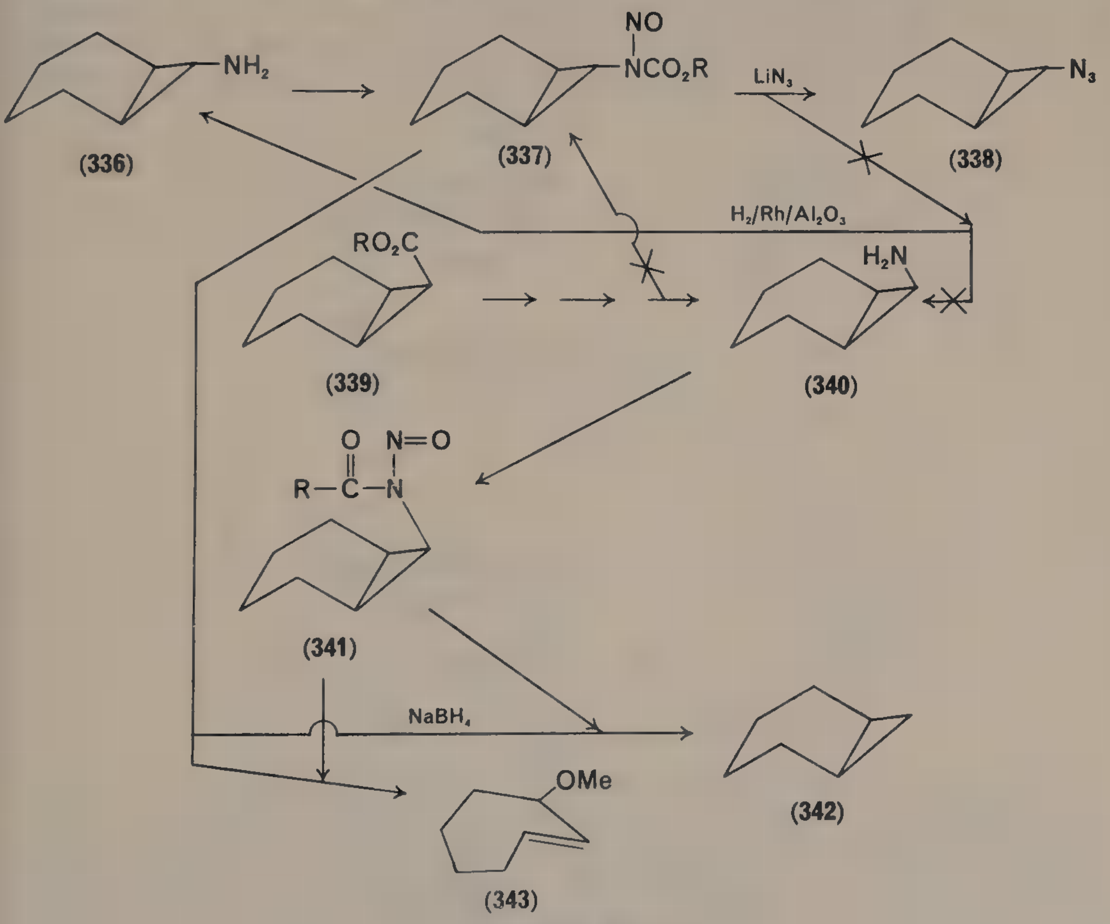
Scheme 65



(334) **(335)**

SCHEME 66

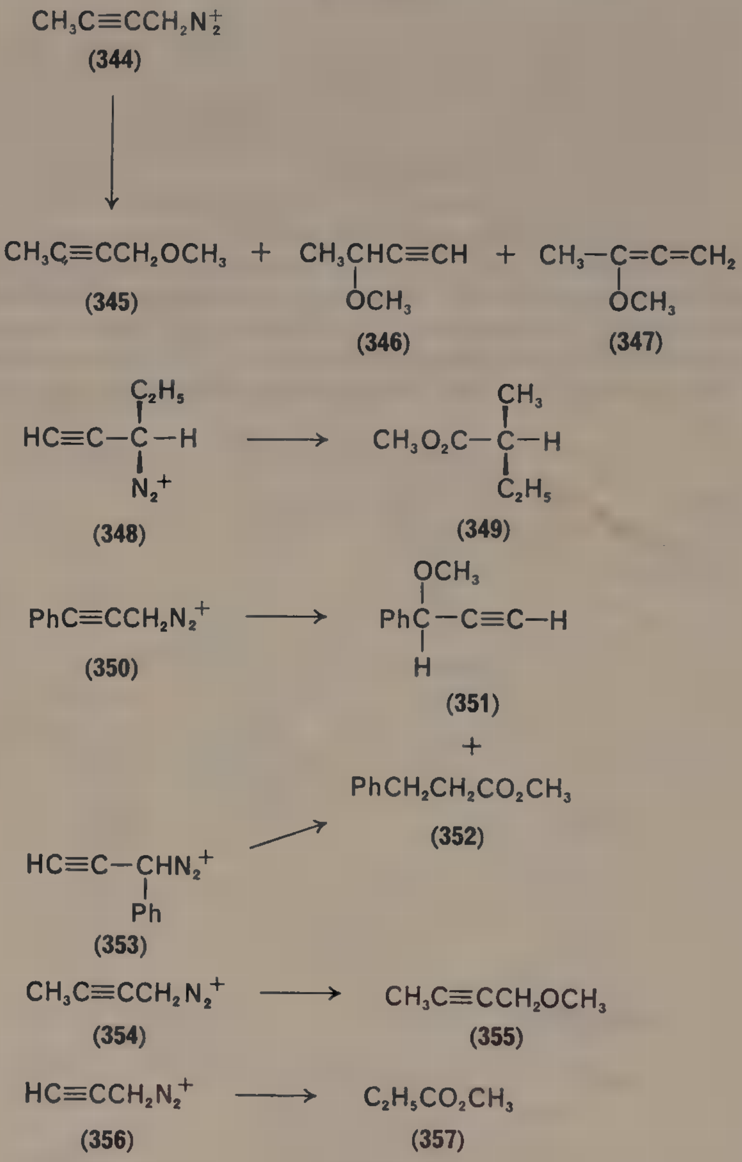
cyclopropyl carbonium ions are virtually non-existent with only one other substantiated example being known (**334** → **345**)[978]. Thus the claim of Jacquier of having observed the conversion of 7-*exo*- and 7-*endo*-norcaranylamines to the alcohols via nitrosation has been shown to be incorrect along with their subsequent conversion to a common cyclopropyl ketone[544, 607–609, 669]. What does occur is conversion to cyclohept-2-enyl alcohol[544, 669]. Steinheimer[1171] cycled the 7-*exo*-norcaranylamine (**336**) through the azide and back to the amine and found only the *exo*-azide (**338**) was formed (t.l.c. at both stages, with known *endo*-amine for comparison). Kirmse obtained allylic systems in the absence of azide ion[651, 657, 659]. When Kirmse examined the behaviour of the 7-*exo*- and 7-*endo*-norcaranylamines in the absence of azide ion, he obtained 97 and 91% of the *trans*-7-cycloheptenyl methyl ether ($MeOH/Na_2CO_3$) and 94 and 98% norcarane with sodium borohydride[651].



SCHEME 67

When 1,ω-diamines are subjected to the basic Kirmse sequence (amide, nitrosamide–base[650]), the nature of the final products was found to be a function of the chain length. With 1,3-diaminopropane, cyclopropyl methyl ether was obtained in 50% yield, but with larger chains the dimethoxy ethers and ω-methoxy-α-olefins occurred (with MeOH/MeONa, the diethers were the major products)[650].

When propargylic and allylic amines are subjected to the Kirmse series, rearrangements occur[654, 658, 665–667]. The propargylic systems offer routes to β-substituted propionic acids, alkoxy allenes and propargylic ethers (Scheme 68).

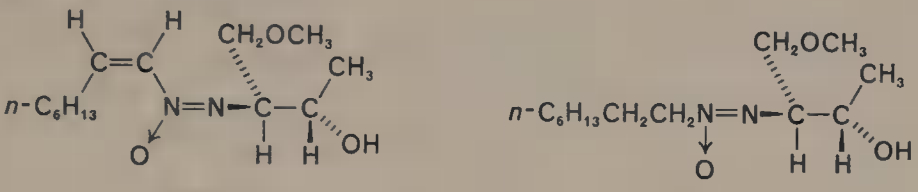


SCHEME 68

With allylic systems, allyl ethers (mixtures of isomers) are obtained[654, 658]. When cyclic substrates are employed (cyclopropyl and cyclopropyl carbinyl) rearrangements occur in good yield. In two of the examples, the diazonium species was generated by the addition of $H_2O/^{-}OH$ photochemically and the presence of rearranged products not available via a carbene process can be taken as evidence that reaction did involve a carbonium ion process[664].

Moss[821–831, 833–841] has examined the question of when does the action of base upon *N*-nitrosourethanes lead to alkyl diazotates and when do diazoalkanes result[821]. In the first paper of the Moss series and in a review, one finds a good summary of references to earlier work in the area by a number of workers[821, 836].

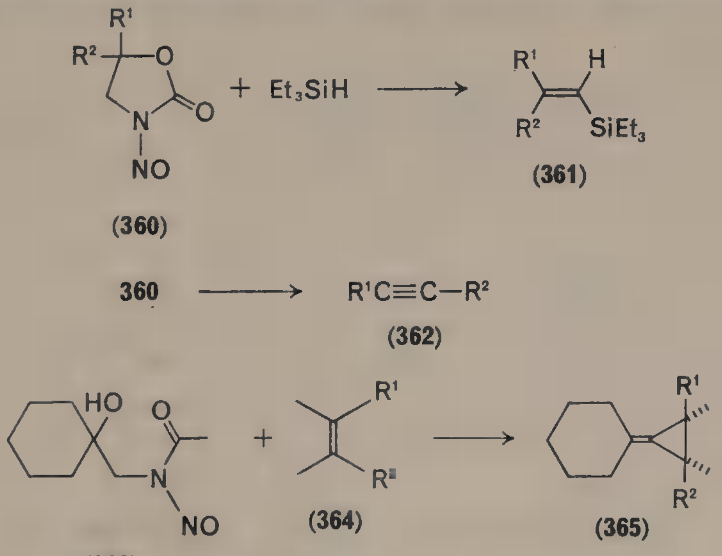
The reaction of α-phenethyl diazotates at −50 °C in CH_2Cl_2 with $Et_3\overset{+}{O}\overset{-}{B}F_4$ furnished the alkyldiazo ether which collapses to the α-phenethyl ether with 70% retention of configuration[826, 828]. Concurrent with *O*-alkylation, one obtains varying amounts of *N*-alkylation to furnish azoxyalkanes[830, 833, 834]. The yields are somewhat better in HMPA solutions than in CH_2Cl_2. The reaction has been employed to synthesize L-dihydroelaromycin (**359**). L-Elaromycin (**358**) has been reported to be an antibiotic and a carcinogen[834].



(358) **(359)**

SCHEME 69

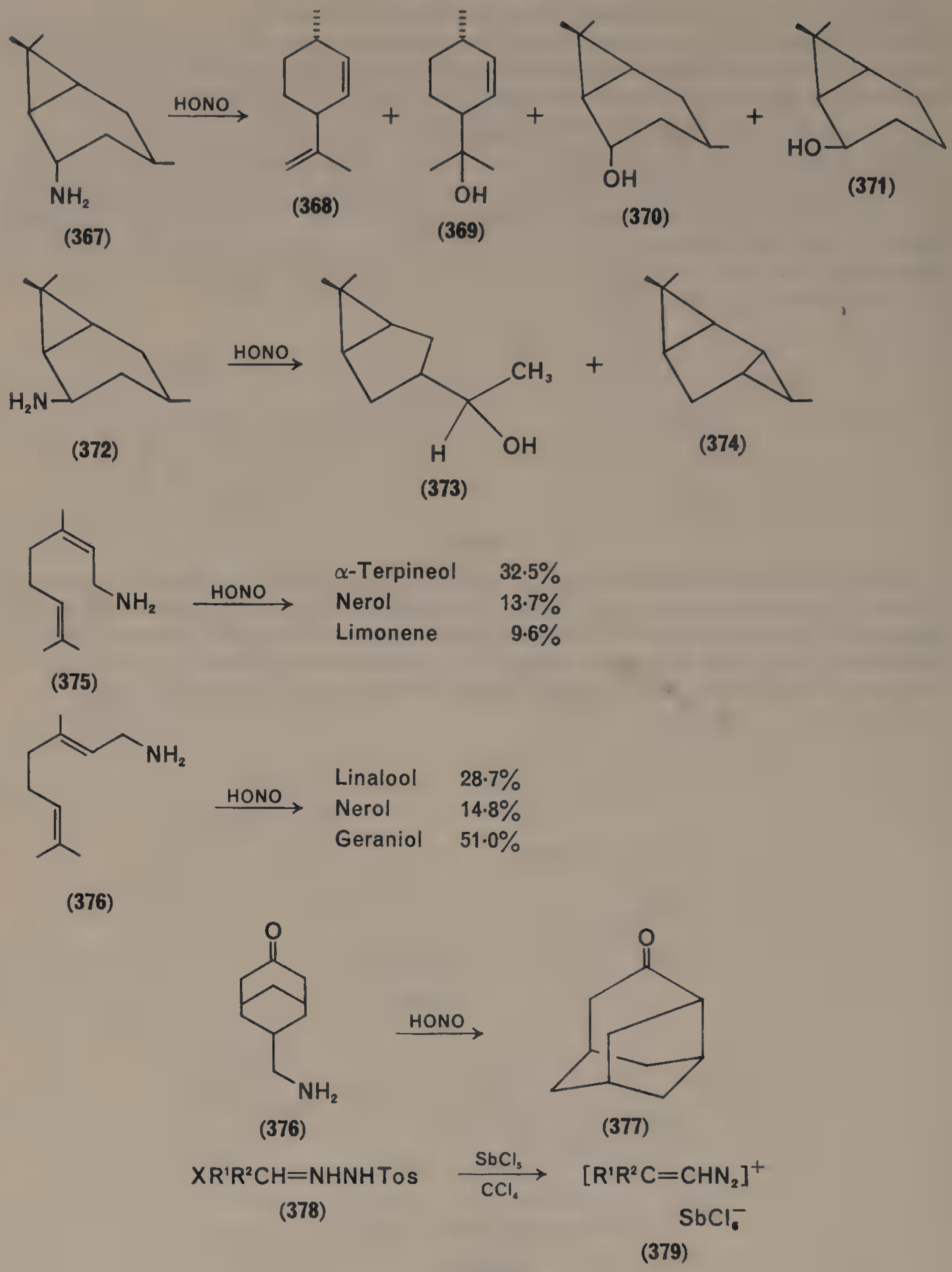
When α-phenethyl diazotates are treated with hydrazine[839], α-phenethyl hydrazine results with 54% net inversion. When ammonia is employed[835], inversion occurs along with some racemization. Similarly treatment with Grignard reagents leads to alkylation with some inversion. Maximum inversion was observed at the lowest temperature employed, with phenyl Grignard and *s*-butyl diazotate in ether.



(360) **(361)** **(362)** **(363)** **(364)** **(365)**

R¹	R²	Yield (% 362)
H	OBu	60
H	OPh	60
H	OEt	83
$-(CH_2)_4-$		78
$-(CH_2)_5-$		61
$-(CH_2)_6-$		60

SCHEME 70



Scheme 71

Ethyldiazotates react with acyl anhydrides and halides in ether solutions to furnish intermediate diazotate esters which collapse with loss of nitrogen leading to a stereoselective synthesis of esters, e.g. 17–21% inversion with acetic anhydride[831]. The reaction proceeds with little intermediacy of the carbonium ion for the cyclopropyl carbinyl system proceeds in ~80% yield to the cyclopropyl carbinyl ester.

Moss[841] has summarized a number of potential reactions of diazotate chemistry. These include the use of allenic diazotates to generate aryl diazomethanes[899, 900], photolysis of epoxy diazotates to furnish oxadiazotenes[961, 962] and the modification of D-nor-steroids via diazotate-generated carbonium ions[774, 776].

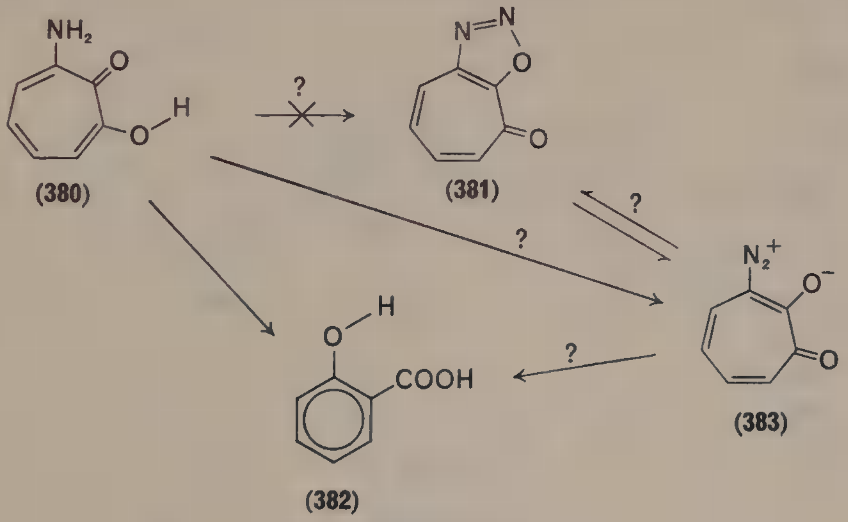
Recently, Newman's group[889–895] (Scheme 70) has expanded upon earlier work by Huisgen[585] and Müller[898] involving treatment of *N*-nitroso lactams (in one instance, oxazolidones) with bases to furnish several interesting systems (**360** → **362**) and (**363** → **365**). Related work by Hogan[573] (see also Reference 886) is summarized in Scheme 66 (**360** → **362**). Hassner has presented a detailed study of *N*-nitroso oxazalidone chemistry[511].

The use of acidic nitrosation to deaminate amines has received considerable attention in the past and a number of recent reviews have appeared. The reactions far too frequently lead to very complex mixtures (see, for example, References 184, 255, 773, 1236) but on occasion are relatively clean[736].

At 0 °C it has been possible to prepare β,β-disubstituted vinyl diazonium salts using β-halo-aldehyde-tosylhydrazones and $SbCl_5$ in CCl_4 [150].

The behaviour of 3 (or 7) amino tropolones towards diazotization is closer to that of alkyl amines than it is to the anilines but diazonium tropolones exhibit reasonable stabilities at other ring positions and have been used in the Pschorr synthesis with mixed success. It is therefore surprising that when the diazonium ion is in the 3-position, collapse to *o*-hydroxybenzoic acids occurs with great ease even though an intermediate oxadiazole should in principle exhibit considerable stability[9, 262, 521, 672, 843, 897, 914, 90, 927, 929, 932, 933, 938] by virtue of being a 10π electron system.

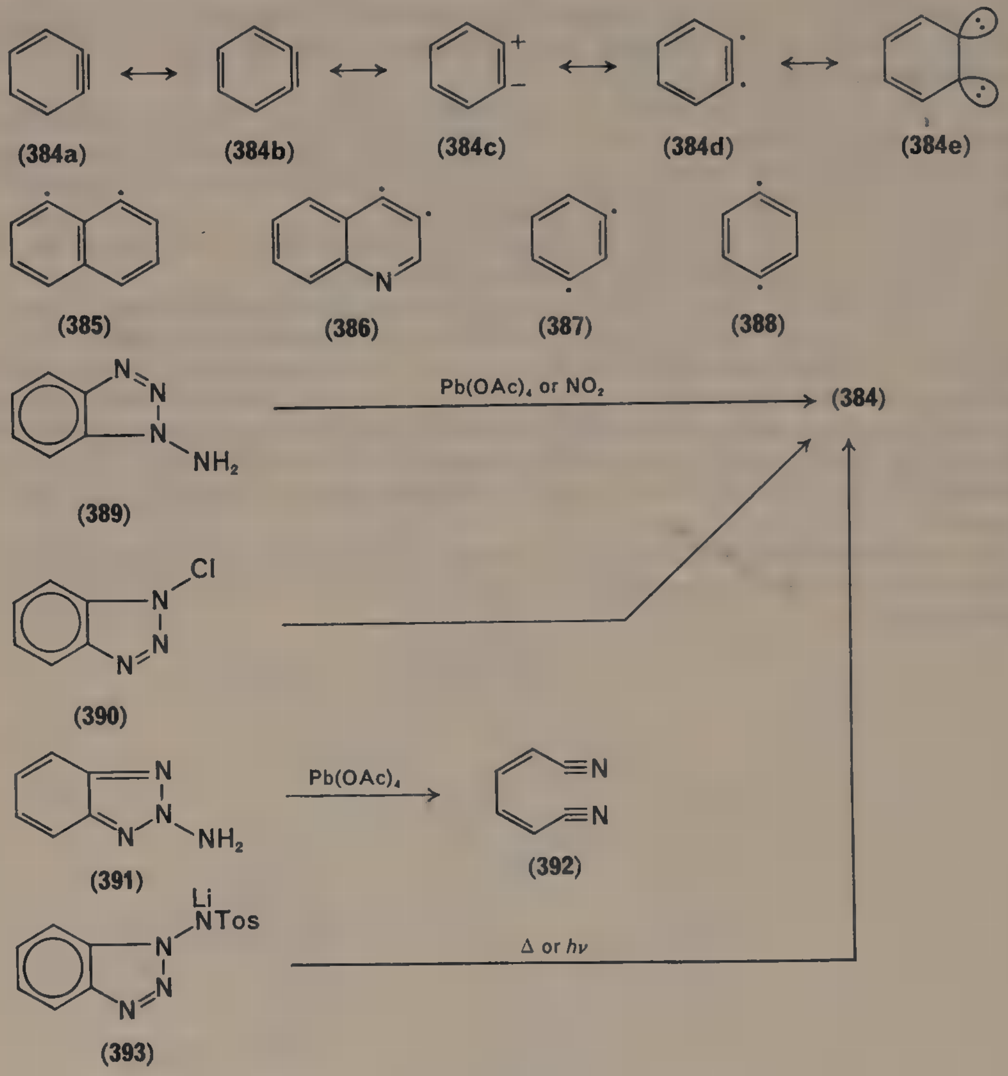
The oxadiazole ring system may of course be generated but under the acidic conditions reverts to the diazonium ion (**383**) which might collapse to the hydroxybenzoic acid.



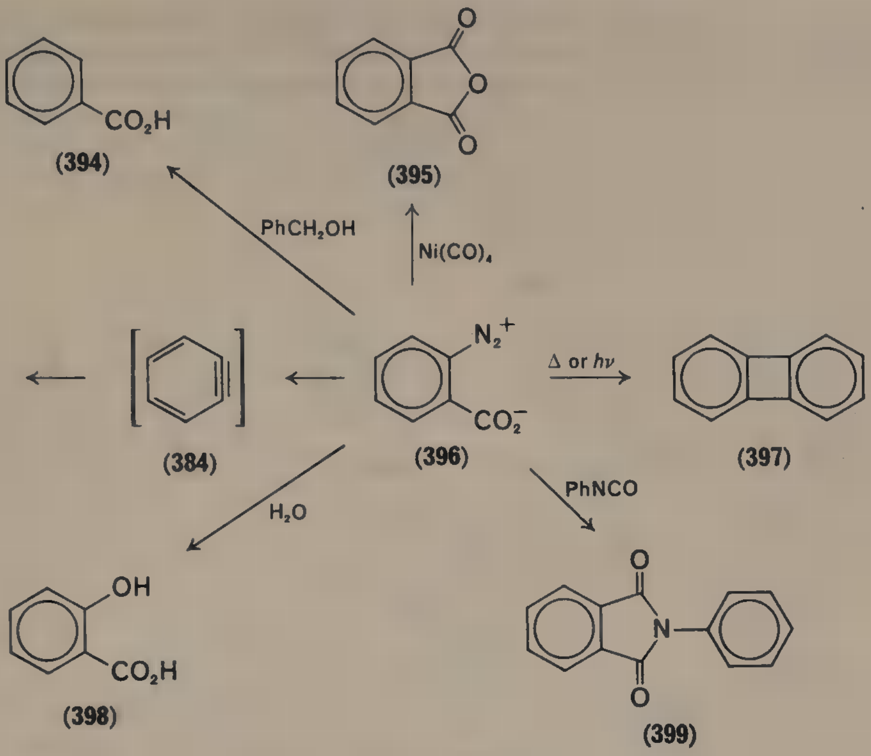
SCHEME 72

IV. BENZYNES, HETARYNES AND OTHER DIDEHYDROAROMATICS

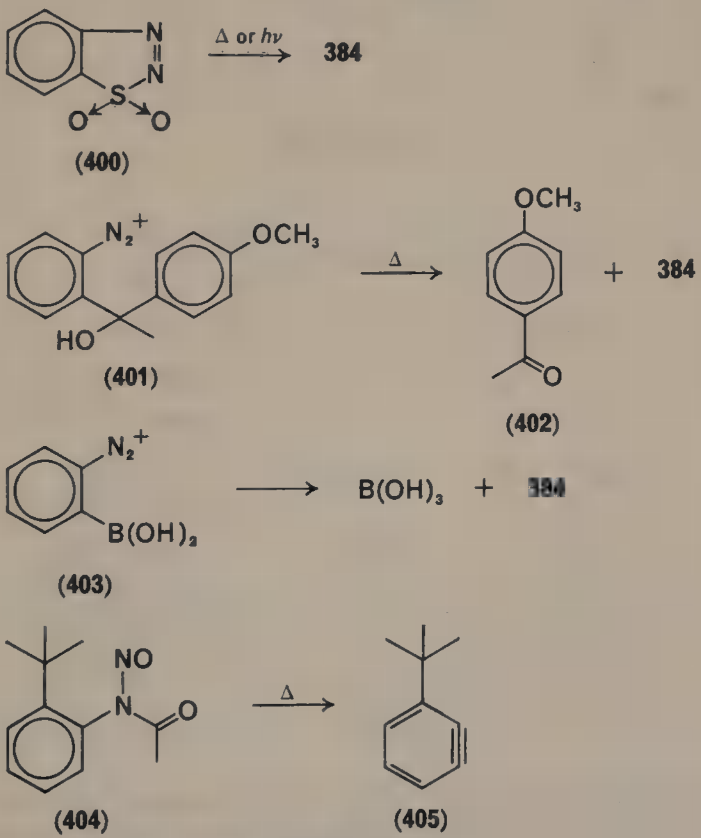
The generation and reactions of benzynes and hetarynes (Schemes 73–77) have been the subject of a monograph[570] and a chapter in *The Chemistry of Acetylene*[570a]. This type of species is often treated concurrently with carbenes and nitrenes in texts and *Annual Reports* of the Chemical Society, as a consequence of their high reactivity and chemistry and their exhibiting a valence state with carbon having fewer than four formal bonds (in one resonance form one has a bis-1,2-carbene). A number of syntheses involving benzynes start formally or actually with diazonium compounds. The recent innovations using the Pb^{IV} and 1-chlorobenzotriazole oxidation of *N*-aminobenzotriazoles (Schemes 73 and 77) both formally and practically involves the chemistry of N=N—X systems. Workers at the Robert Robinson Laboratories at the University of Liverpool have carried out a prodigious amount of work in this area. Earlier work involving the destruction of *o*-carboxydiazonium salts and benzothiadiazole *S*,*S*-dioxides has also furnished entry into this important synthetic area. The arynes can insert into X—Y bonds, act as hot dienophiles and dimerize to furnish biphenylenes. The ability of arynes to participate in cycloaddition reactions is very well documented (Schemes 76 and 77) and Hoffmann[570] has presented a 25-page tabulation of products.



SCHEME 73

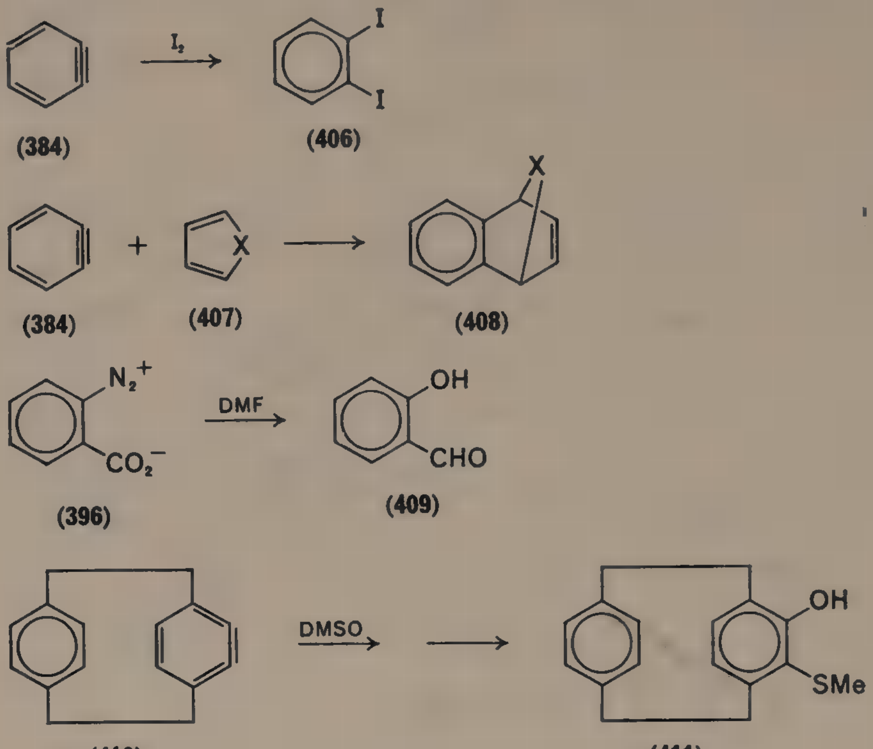


SCHEME 74



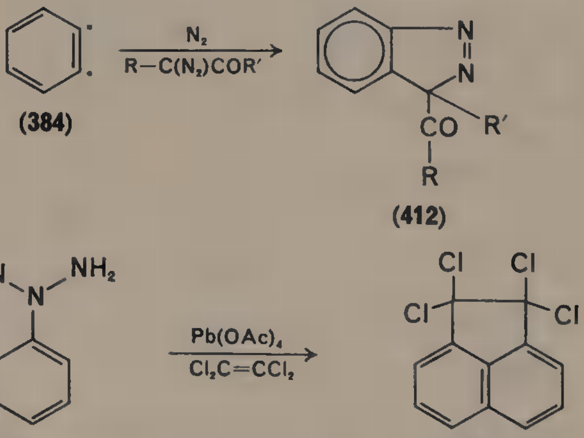
SCHEME 75

The arynes are not limited to 1,2-benzo-type systems. Photolysis of 3-carboxybenzenediazonium systems furnish the 1,3-arynes[113]. The oxidation of 1-aminonaphtho[1.8*a*.8.*de*]-1,2,3-triazine furnishes the 1,8-didehydroxnaphthalene[113, 624a, 776a].



(384) (406) (384) (407) (408) (396) (409) (410) (411)

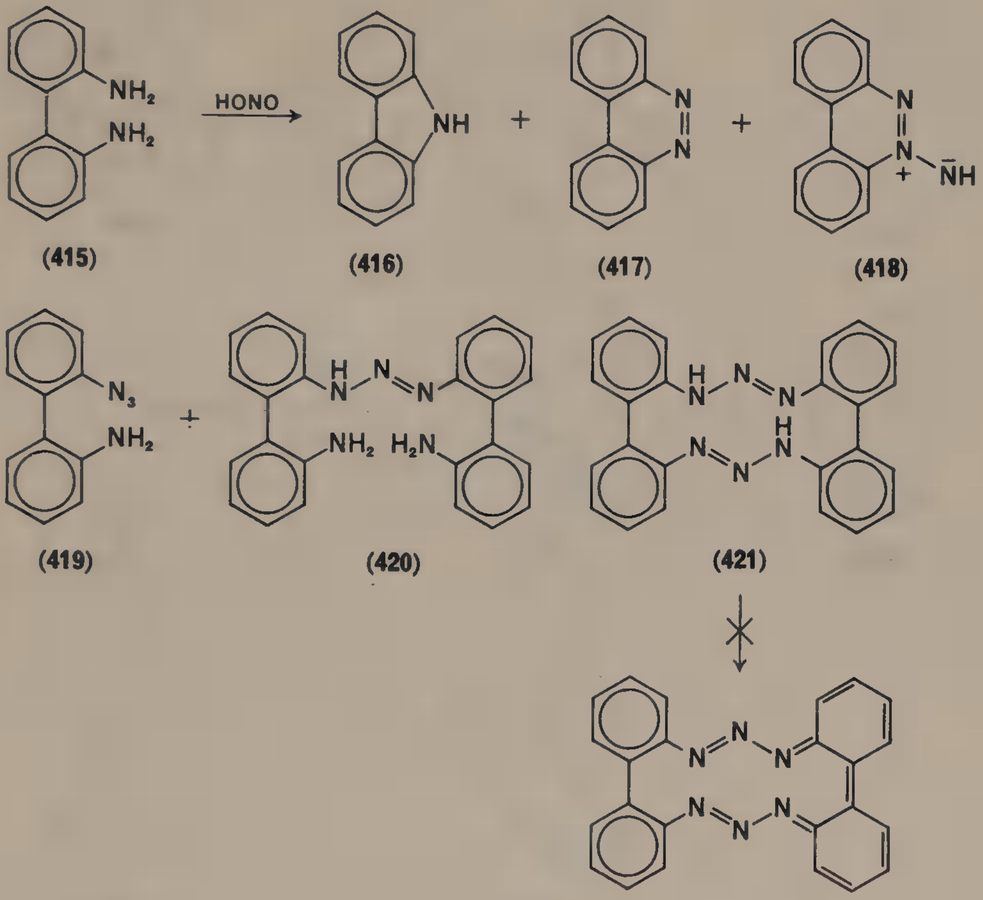
Scheme 76



(384) (412) (413) (414)

Scheme 77

The gas phase and flash photolysis of benzenediazonium 4-carboxylate furnishes the 1,4-didehydrobenzene[114]. Rees and his colleagues have performed extensive studies in this field as a consequence of syntheses directed towards preparing *x,y*-didehydroaromatic systems such as 1,8-didehydronaphthalene (**385**), 2,2′-didehydrobiphenyl and related compounds (e.g. 4,5-didehydrophenanthrene, 4,5-didehydrofluorenone[412]), as well as intermediates for preparing 1-azabenzocyclobutenes[6] and benzynes. Tetrazotization of 2,2′-diaminobiphenyl (**415**) in 2 N-HCl furnished six identifiable products (Scheme 78). Oxidation of **389** furnished **384** and related products but no **392**. Work with the related fluorenone systems was unsuccessful. When the 2,2′-diaminobiphenyl was tetrazotized and treated with ammonia, the triazepine (**428**) was obtained in high yield. Similar results were obtained employing 1,8-diaminonaphthalene which furnishes **429**. When **428** was treated with a variety of reagents it was evident that the system was a masked diazonium ion in much the same fashion as is observed with open chain triazenes.

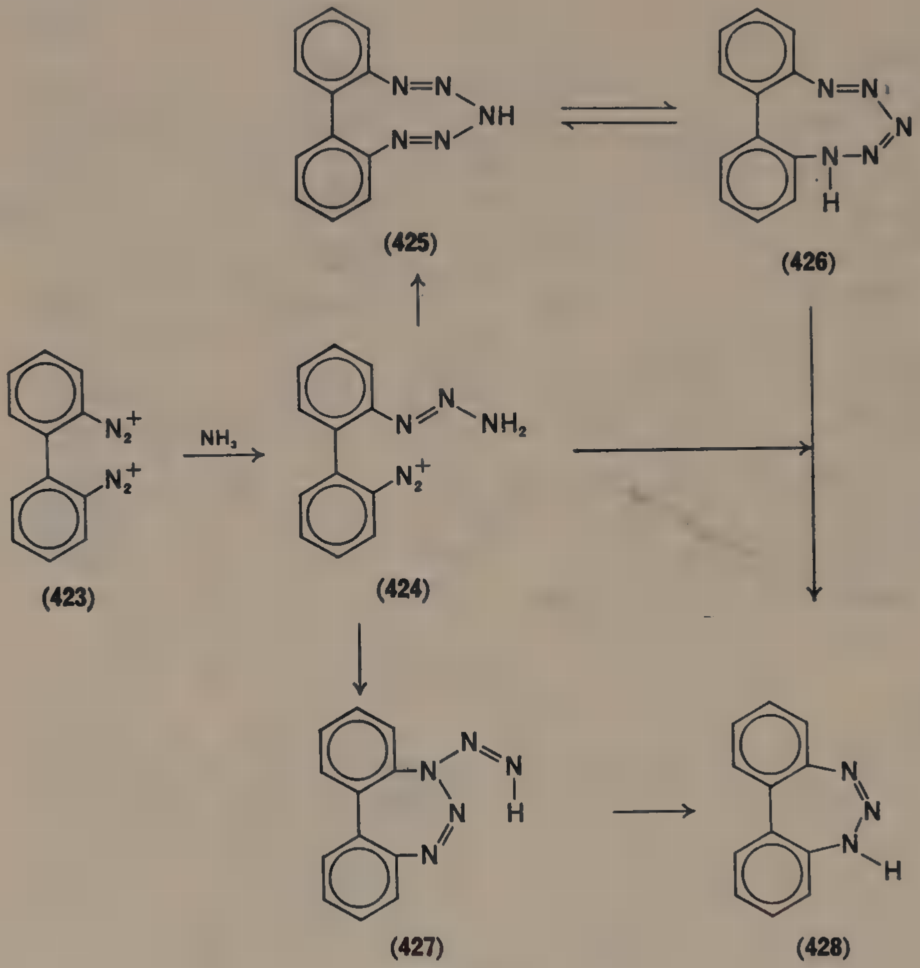


Scheme 78

When the tetrazotized biphenyl was allowed to react with methyl amine, **430** resulted.

The azimine (**418**) is a potential 1,3-dipole and is generated thermally from the triazipene. The carboxethoxy derivative (**435**, R = CO_2Et) was found to be a good 1,3-dipolar reagent[235]. The *N*-ethyl derivative (**435**, R = C_2H_5) behaves anomalously with *N*-alkylimides and acetylenic esters[1038]. The triazine (**439**) available from tetrazotized 1,8-diaminonaphthalene is unusual in that it behaves as a 1,11-dipole towards dimethyl acetylenedicarboxylate[1044].

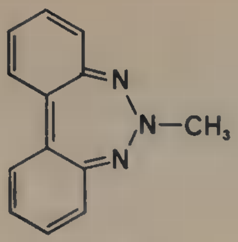
The iminoazimines (**441**) are readily prepared from **418** by reaction with the appropriate imidochlorides in acetonitrile solution in the presence of potassium carbonate. They undergo thermal rearrangement with the alkyl case proceeding slowly even at room temperature[86].



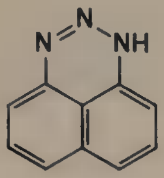
SCHEME 79

Although the formation of benzotriazene derivatives has been known for many years it was only in 1971 that Rees and Storrs reported the preparation of the parent compound. The syntheses grew out of their attempts (ultimately successful[5, 6]) to prepare benzazetes. Since these syntheses involve cyclizations of azido diazoalkanes, they will be treated in Chapter 18. An alternative route was through oxidation of *N*-aminoindazoles.

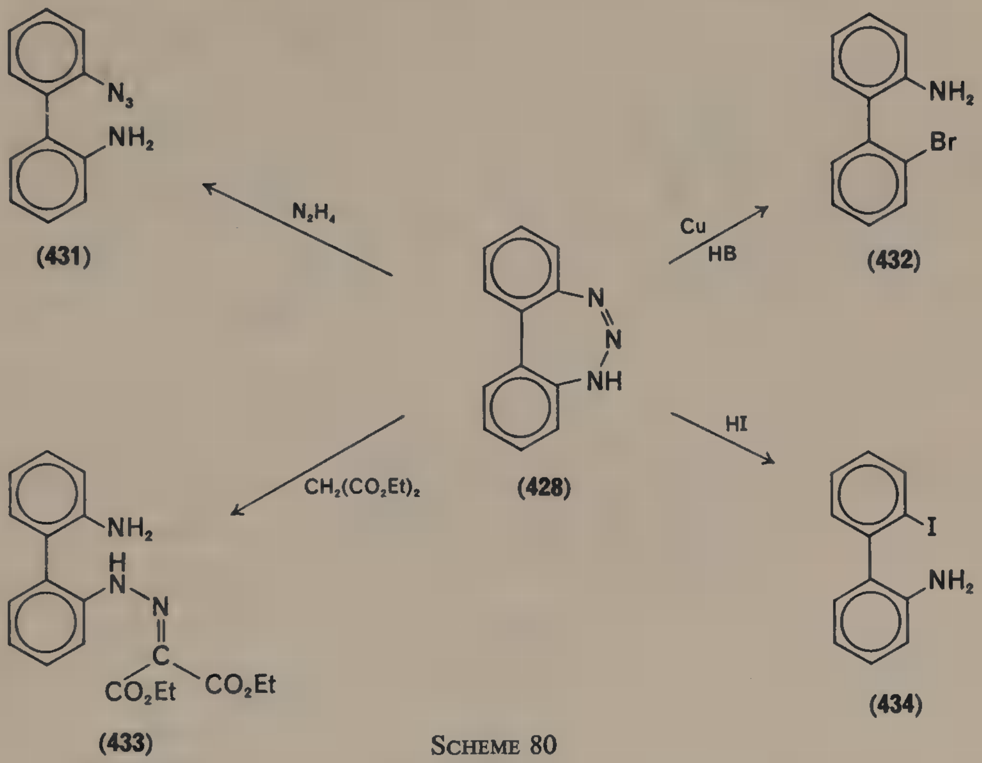
When 4-phenyl-1,2,3-benzotriazine was pyrolysed in the vapour phase at 420–450 °C/10^{-3} Torr, the benzazete (**445**) was formed along with several other products. The product was collected at −78 °C and on warming the dimer is formed. A number of possible dimeric structures are reasonable and the structure is currently unknown.



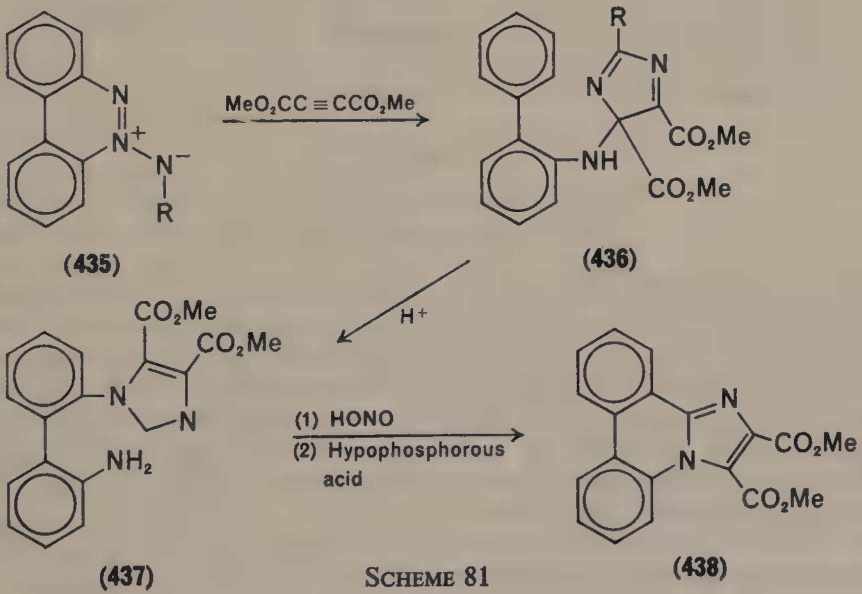
(430)



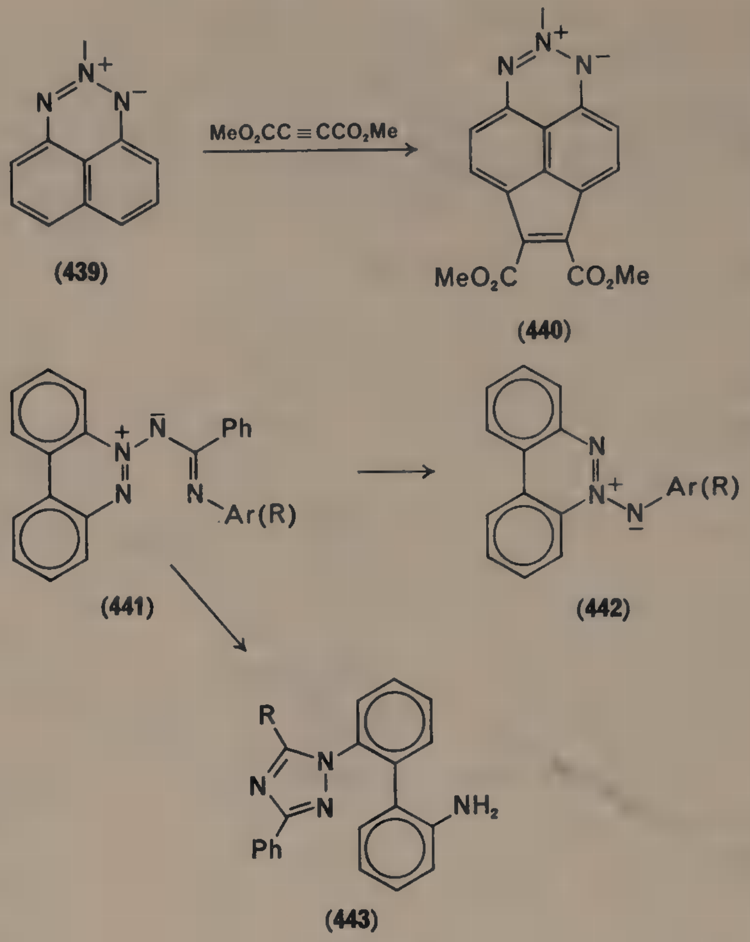
(429)



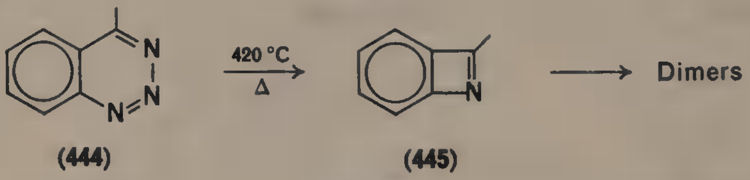
Scheme 80



Scheme 81



SCHEME 82



SCHEME 83

V. CYCLOALKYNES

The compound cyclononyne is known[129] and is quite reactive. Smaller ring systems would be expected to be even more reactive and to resemble the arynes. Hence one might expect to form on a transient basis such intermediates by elimination of HX from a 1-halocycloalkene by treatment with strong bases[1299]. The eliminations of the element of M—X from some metallated haloalkenes are extremely slow reactions as a consequence of the strain in a potential alkyne or the high energy of the didehydro species[1301]. The formation of strained cycloalkyne can however be reached via 1,2-diazocycloalkanes and their subsequent decomposition and related systems[130, 131, 166, 276, 278, 310, 481, 585, 1005, 1298]. This problem will be treated in Chapter 18 under dimerization processes in which two new C—C bonds are formed.

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1353. *Ger. Patent*, 222,929; *Chem. Abstr.*, **4**, 2882 (1910).

1354. *Ger. Patent*, 243,788; *Chem. Abstr.*, **6**, 2313 (1912).
1355. *Ger. Patent*, 247,592; *Chem. Abstr.*, **6**, 2543 (1912).
1356. *Ger. Patent*, 250,264; *Chem. Abstr.*, **6**, 3312 (1912).
1357. *Ger. Patent*, 254,092; *Chem. Abstr.*, **7**, 684 (1913).
1358. *Ger. Patent*, 264,924; *Chem. Abstr.*, **8**, 213 (1914).
1359. *Ger. Patent*, 266,944; *Chem. Abstr.*, **8**, 401 (1914).
1360. *Ger. Patent*, 268,172; *Chem. Abstr.*, **8**, 1644 (1914).
1361. *Ger. Patent*, 269,205; *Chem. Abstr.*, **8**, 2035 (1914).
1362. *Ger. Patent*, 444,325.
1363. *Ger. Patent*, 625,263.
1364. *Ger. Patent*, 633,867; *Chem. Abstr.*, **31**, 8179 (1937).
1365. *U.S. Patent*, 619,574.
1366. *U.S. Patent*, 1,061,587; *Chem. Abstr.*, **7**, 2286 (1913).
1367. *U.S. Patent*, 1,704,106; *Chem. Abstr.*, **23**, 1907 (1929).
1368. *U.S. Patent*, 1,706,489; *Chem. Abstr.*, **23**, 2188 (1929).
1369. *U.S. Patent*, 1,879,209; *Chem. Abstr.*, **27**, 997 (1933).
1370. *U.S. Patent*, 2,411,646; *Chem. Abstr.*, **41**, 1455a (1947).

Those patents lacking a *Chem. Abstr*. reference have not been abstracted therein and were encountered in other references (primarily 220 and 1103).

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[illegible] G. Zemplén, L. Mester, A. Messmer and [illegible]

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[illegible] Chem. Ber. [illegible]

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CHAPTER 9

Photochemistry of the diazonium and diazo groups

WATARU ANDO
Chemistry Department, The University of Tsukuba,
Niiharigun, Ibaraki 300-31, *Japan*

I. INTRODUCTION

Light can be transmitted, refracted, scattered or absorbed by a system. It is a fundamental tenet of photochemistry that only the light absorbed can be effective in producing chemical or physical changes in a molecule.

A. Photochemical Energy[1–5]

The energy of light in kcal/mol is given by the expression:

$$E = \frac{2{\cdot}86 \times 10^5}{\lambda\,(\text{Å})}\ \text{kcal/mol}$$

An energy of 1 kcal/mol corresponds to radiation of wavelength 286,000 Å or

$$1\ \text{kcal/mol} = \frac{10^8\ \text{Å/cm}}{286{,}000\ \text{Å}} = 353\ \text{cm}^{-1}$$

in the infrared portion of the spectrum. When electromagnetic radiation of these frequencies is absorbed, molecules are excited to higher vibrational states. Radiation of shorter wavelength (higher frequency) contains more energy. Visible light has a wavelength from 4200 Å (violet) to 7000 Å (red), i.e. it contains 68–41 kcal/mol. Ultraviolet light of 2000 Å corresponds to an energy of 143 kcal/mol.

B. Photochemical Excitation

Light in the ultraviolet-visible region has energy sufficient to excite molecules to higher electronic states. Consider now the potential energy curve for the ground state (E_0) and first excited state (E_1). According to the Franck–Condon principle transitions occur between vibrational levels for which the nuclear configurations are the same ($r' = r''$), i.e. we have vertical excitation as shown in Figure 1. The energy of the electronic transition is measured from ν_0 of the ground state to ν_0 of the excited state, $E_1(\nu_0) - E_0(\nu_0) = \Delta E = h\nu$.

The major events that occur following light absorption may be summarized in terms of a Jablonski diagram. The absorption of light raises the molecule from S_0 to S_2, as shown in Figure 2. In solution the excess vibrational energy of S_2 will be rapidly dissipated by radiationless processes. After conversion to S_1 the molecule may lose its energy by four important processes: (i) fluorescence, (ii) chemical reaction, (iii) return to a highly vibrationally excited ground state (S_1–S_0) and (iv) intersystem crossing. Intersystem crossing (S_1 to T_1) occurs between two excited states of similar energy and is very important in photochemistry, because the triplet state T_1 produced is even longer lived than S_1. The lifetimes of T_1 are limited by: (i) phosphorescence, (ii) chemical reaction and (iii) radiationless decay to S_0. Furthermore, an excited molecule may transfer its energy to another molecule; if this occurs the excited or donor molecule returns to its ground state and the acceptor molecule becomes excited. If the donor molecule (D) was in the triplet state at the time of its energy transfer, the acceptor molecule (A) gets promoted to its triplet state, and similarly we expect singlet–singlet energy transfer.

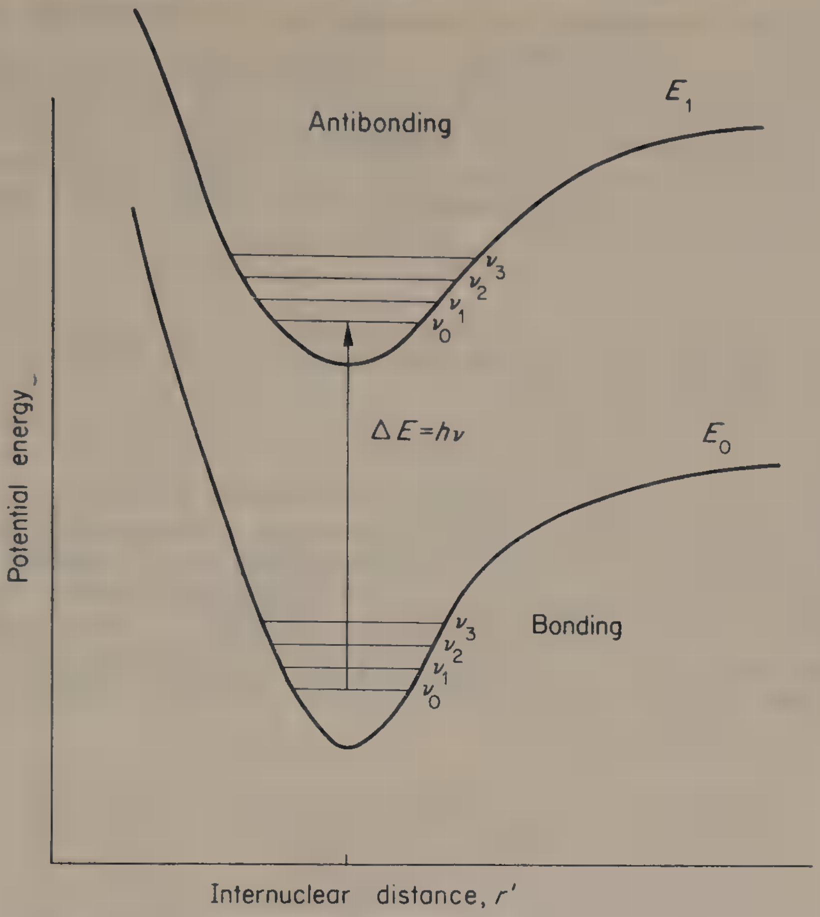


FIGURE 1. Potential energy curve for an electronically excited and ground-state diatomic molecule.

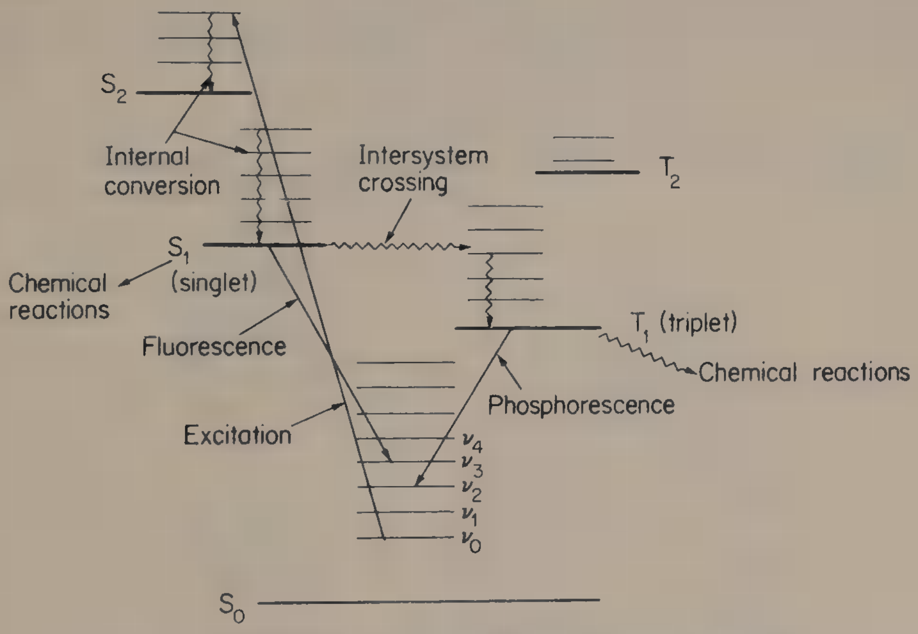
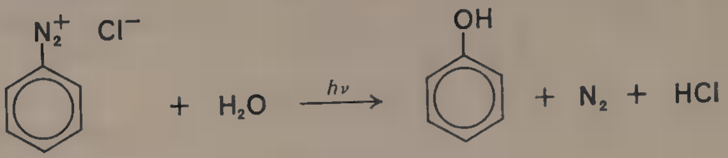


FIGURE 2. Jablonski diagram. Typical energy diagram.

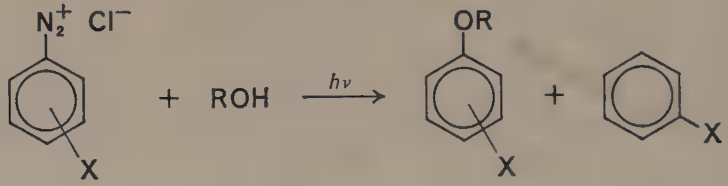
II. PHOTOCHEMISTRY OF AROMATIC DIAZONIUM SALTS

At the end of the last century, Andressen[6] established that aqueous solutions of diazo compounds decompose under the influence of light. The mechanism of the photochemical decomposition is not completely understood; it appears that it is largely determined by the environment and by the chemical species present. The effect of substituents on the light sensitivity of diazo compounds has been studied by many investigators[7, 8].



A. Deamination through Diazonium Salts

According to Andressen[6], diazonium salts irradiated in aqueous solution are decomposed into a phenol and nitrogen. Orton and coworkers[9] investigated the photolysis of diazonium salts in aqueous solutions and found a noticeable increase in the rate of decomposition as compared to that of the dark reaction. When *para*-substituted benzenediazonium derivatives are irradiated by ultraviolet light in methanol as the solvent, the formation of the phenol ether is rather a minor process, while the main reaction is the substitution of hydrogen for the diazo group[10].



When 2,4,6-tribromobenzenediazonium sulphate was irradiated in aqueous solution, Orton and coworkers obtained 2,4,6-tribromophenol in quantitative yield[9]. When this reaction was carried out in acetic acid, 2,4,6-tribromophenyl acetate was formed, whereas in formic acid only 1,3,5-tribromobenzene was obtained.

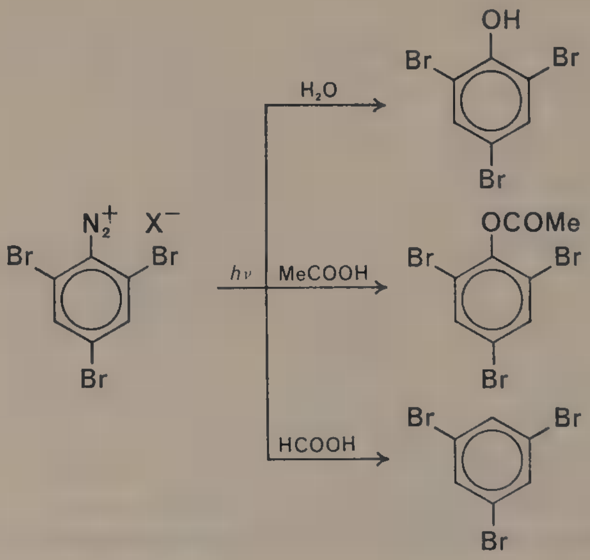
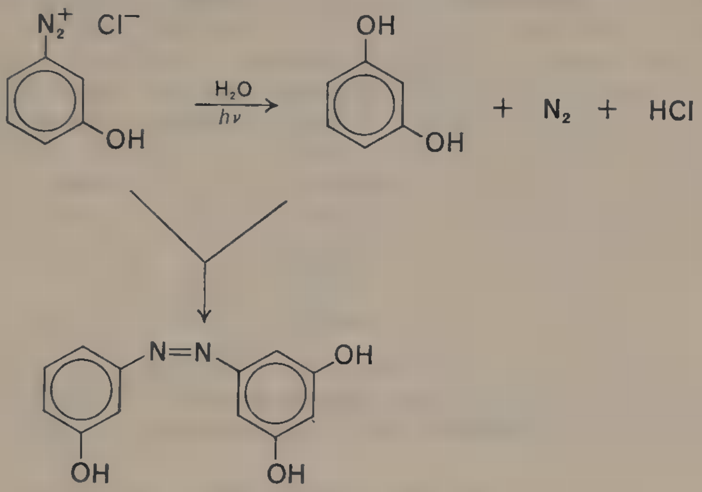


TABLE 1. Photolysis of compounds $[RC_6H_4N_2]^+ Cl^-$ in methanol solution

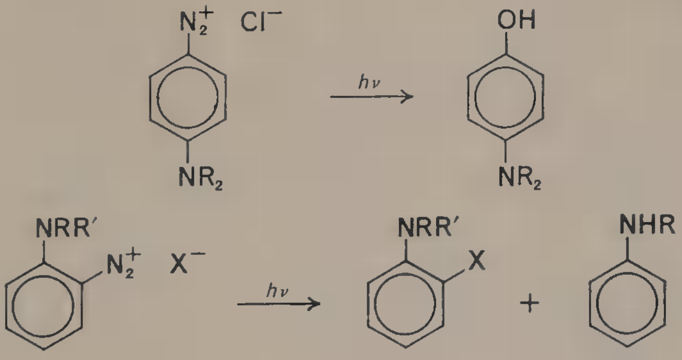
R	Reduction (%)	Ether (%)
p-NO_2	60	0
p-Cl	60	0
p-Me	40–50	20–30
p-OMe	40–50	20–25

If the photolysis product is reactive enough, it can react under favourable conditions with the non-decomposed diazonium compound and a dye is formed in the exposed areas but not in the areas protected from light. The reactions taking place can be expressed as follows:



This process was first proposed by West[11] and further explored by Feer[12], Andressen[13] and others.

When irradiating diazo compounds in concentrated hydrochloric acid, Süs obtained the corresponding *p*-halogenodiphenylamines. He also showed that the action of light on *p*- and *o*-dialkylaminobenzenediazonium compounds results, in the case of *para* substitution, in the corresponding *p*-dialkylaminophenols, whereas the *ortho* isomers produce a considerable quantity of secondary amine, along with the corresponding phenols[14, 15].



(1)

(2) X = OH
(3) X = Cl

(4)

TABLE 2. Photolysis of diazonium salts 1[16]

	R	R′	Solvent	2 (%)	3 (%)	4 (%)
1a	$-(CH_2)_4-$		H_2O (20 °C, *hν*)	51	0	0
1b	Me	Me	H_2O (20 °C, *hν*)	15	0	56
			1 M-HCl (20 °C, *hν*)	8	10	48
			1 M-HCl (100 °C, 90 min)	5	16	44
			H_2O (100 °C, 90 min)	20	0	57
1c	Et	Et	1 M-HCl (20 °C, *hν*)	—	—	92
			H_2O (20 °C, *hν*)	—	—	70

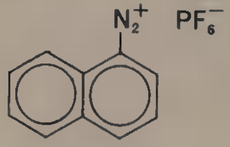
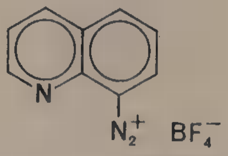
B. Substitution of the Diazonium Group by Fluorine

In the photolysis of crystalline diazonium fluoroborate and hexafluorophosphates, the corresponding fluoroarenes were usually the only volatile product, as in pyrolysis[17]. In some cases, the yield of fluoroarenes was higher than that obtained by pyrolysis of these salts (the Balz–Schiemann reaction), which remains the most generally used means of introducing a fluorine substituent into an aromatic ring[18]. Pure 4-substituted diphenylamine was isolated in 37% yield on the first attempt when the corresponding diazonium fluoroborate was irradiated as a solid film at 30 °C with 3500 Å light. Hexafluorophosphates sometimes gave better yields than tetrafluoroborates in the Balz–Schiemann reaction[19]:

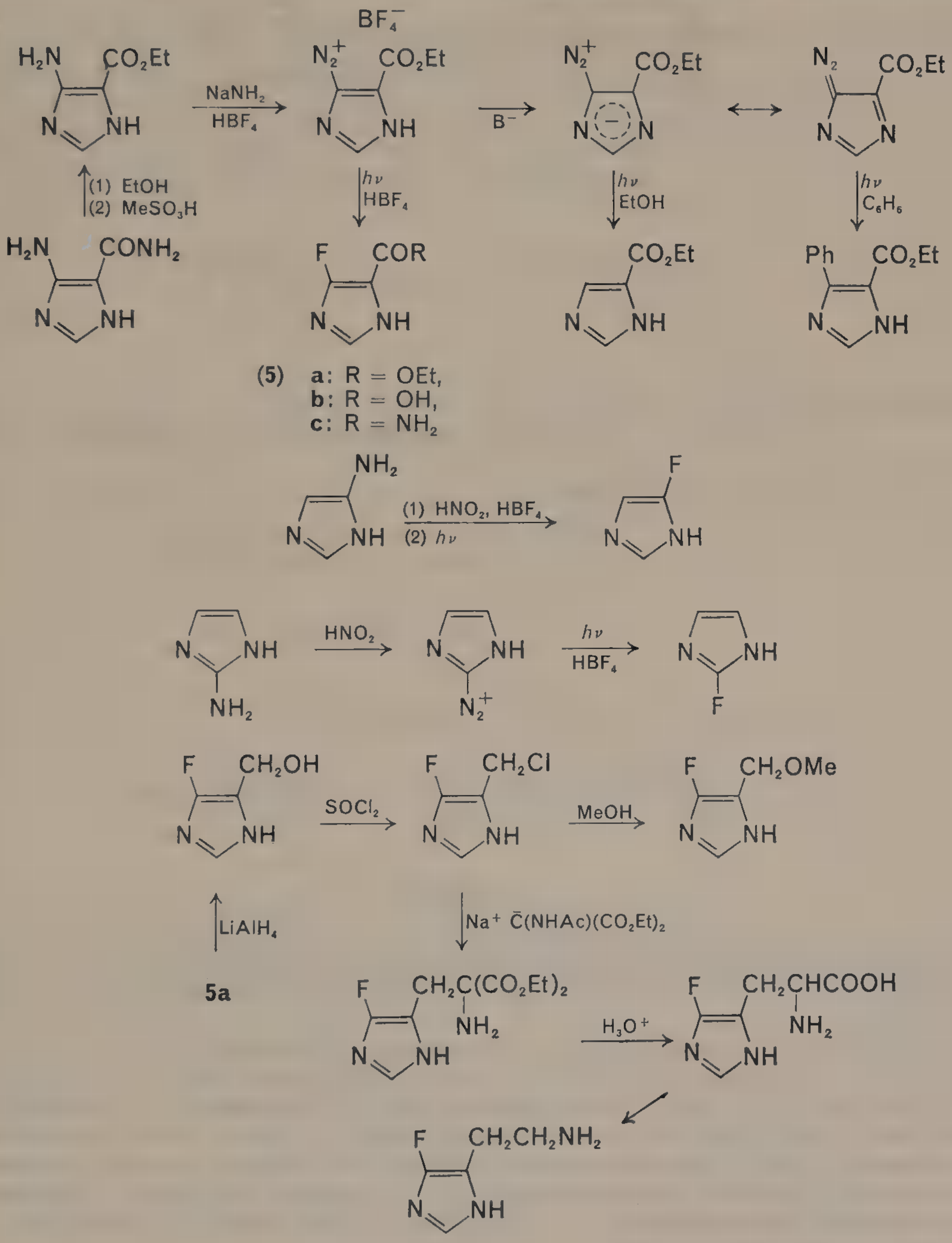
$$ArN_2^+\ BF_4^-\ (\text{or } PF_6^-) \xrightarrow[3500\ \text{Å}]{h\nu} ArF+N_2+BF_3\ (PF_5)$$

Photolysis of aryldiazonium salts substituted with electron-withdrawing groups gave much lower yields of fluoroarenes, perhaps because with a light source available the products absorbed light about as well as the starting material and the competing

TABLE 3. Photolysis of solid arenediazonium fluoroborates and fluorophosphates, $RC_6H_4N_2^+\ X^-$

R	X	Irradiation time (h)	Yield of RC_6H_4F (%)
4-Et_2N	BF_4	4·5–49	53–55
4-Et_2N	PF_6	4	72
4-Et_2N	PF_6	94	74
4-Me_2N	BF_4	17	55
4-MeO	BF_4	19	69
4-PhNH	BF_4	24	37
H	BF_4	2	34
4-Cl	BF_4	8	10
3-Ph	BF_4	2	29
		12	40
		54	19

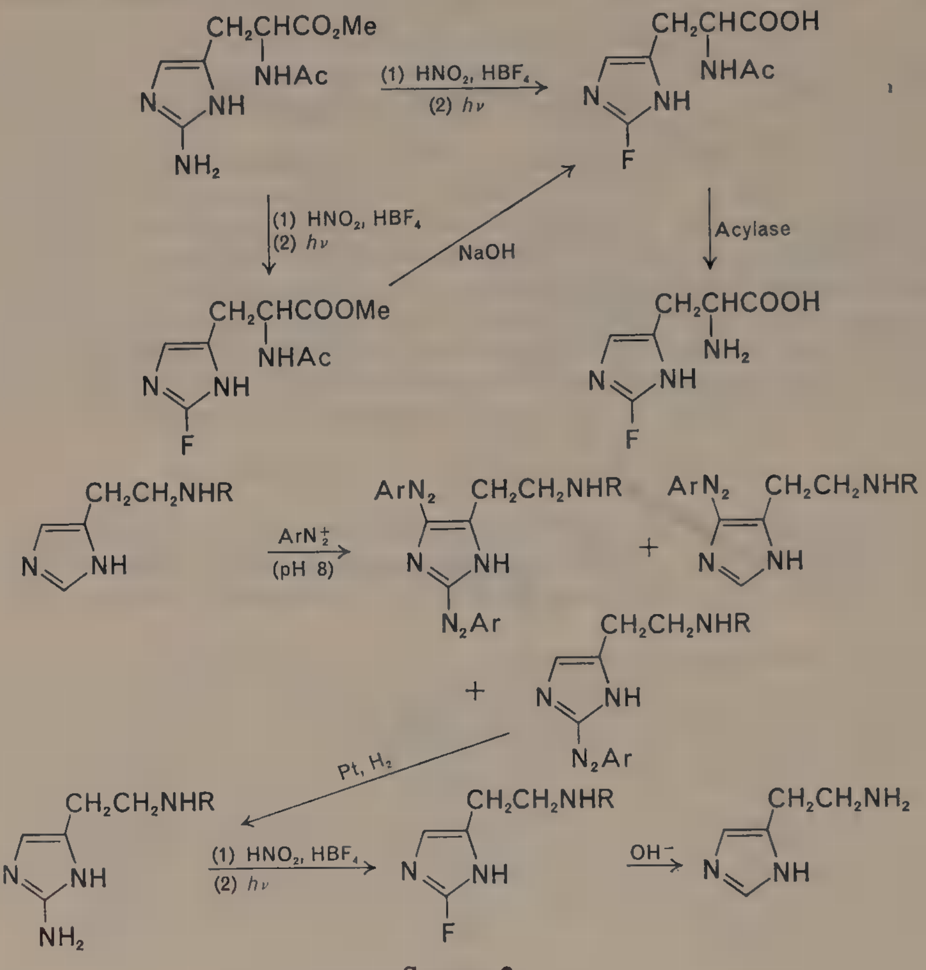
reaction destroyed them. An ionic intermediate or transition state of some sort appears to be implicated in the photolysis of solid arenediazonium fluoroborates and fluorophosphates. If aryl radicals were intermediates, they would be expected to abstract hydrogen atoms from other molecules of the starting material, especially when side-chains with alkyl groups are present. However, no reductive product was produced in the photolysis of even the dimethyl- and diethyl-amino compounds. In contrast, when crystalline *para-N,N*-dimethylaminobenzenediazonium chloride was irradiated, reduction to *N,N*-dimethylaniline (25%) competed strongly with conversion to chloro-*N,N*-dimethylaniline (33%). These observations are in accord



SCHEME 1

with the results of studies of isomer distribution in the phenylation products formed when solid benzenediazonium haloborates are pyrolysed or photolysed in the presence of a substituted benzene[20].

The lack of parallelism between fluoroarene yields for photolysis versus pyrolysis makes it unlikely that these reactions proceed exclusively through a common intermediate. Lewis and coworkers[21] compared photochemical with thermal reactions of diazonium salts in aqueous solution and concluded definitely that there was no single intermediate common to both.



SCHEME 2

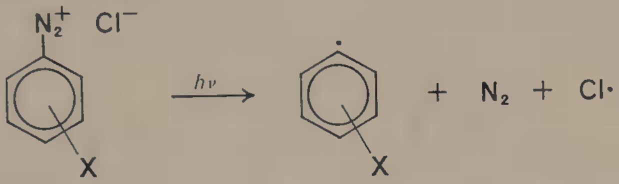
A wide variety of fluorinated analogues of biologically significant compounds have been synthesized and studied as potential enzyme inhibitors and as therapeutic agents[22].

Kirk and Cohen studied synthetic approaches to fluoroimidazoles[23]. Imidazolediazonium ions, prepared by diazotization of aminoimidazoles in tetrafluoroboric acid solution and irradiated *in situ*, decompose with formation of fluoroimidazoles in 30–40% yield. This procedure has been applied to 2-fluoroimidazoles, 4-fluoroimidazole and ethyl 4-fluoroimidazole-5-carboxylate. The ester, in turn, has served as the starting point for various transformations, including the synthesis of 4-fluorohistamine and 4-fluorohistidine. To date, fluorinated imidazoles have been obtained only by photochemical methods[24].

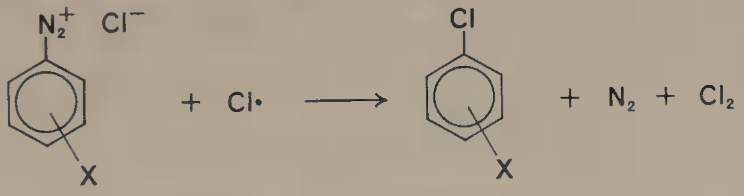
Irradiation of diazotized *N*-acetyl-L-histidine methyl ester in tetrafluoroboric acid solution provides the 2-fluoroimidazole derivative in 32% yield; 2-fluorohistidine is obtained after ester hydrolysis and enzymic deacylation of the latter derivative. An analogous approach to 2-fluorohistamine failed because of decomposition during acid or alkaline hydrolysis of the *N*-acetyl group. The histamine analogue was obtained, however, by use of the more labile trifluoroacetyl group for protection of the side-chain amine. In contrast to the very high degree of stability of 4-fluoroimidazoles, the 2-fluoro isomers are subject to fluorine displacement[25].

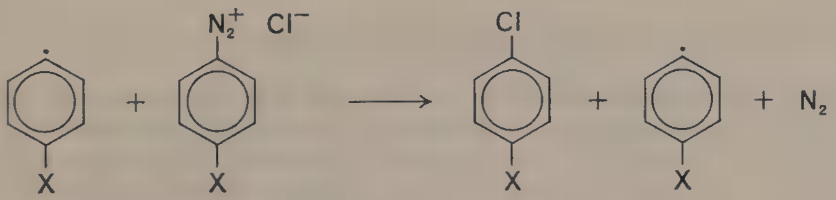
C. Substitution of the Diazonium Group by Chlorine or by Hydroxy Groups

Solid anhydrous chlorides completely free of polar influences were observed to be photolysed with a quantum efficiency of well over unity. These results can be explained by considering the covalent diazo tautomer of the diazonium chloride, which decomposes symmetrically in the first step[26]:



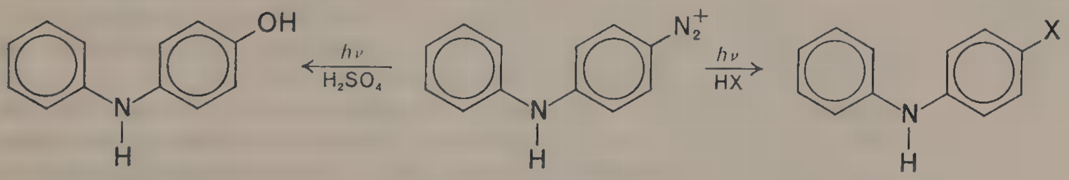
Free chlorine atoms and phenyl radicals so produced are capable of continuing the original function of the utilized photon. For example,





The observed quantum yields were of the order of two.

Aromatic diazonium salts react with hydrochloric or with hydrobromic acid under the influence of sunlight yielding halogenated aromatic compounds[27]. In this way, for example, **6** is converted to **7** or **8**, respectively.



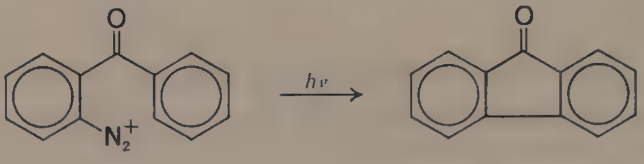
(9)

(6)

(7) X = Cl
(8) X = Br

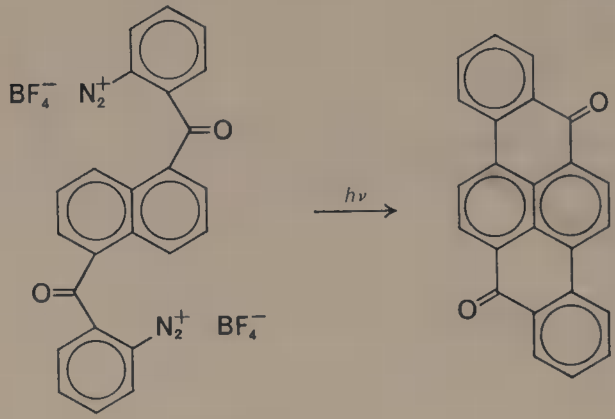
The photoreaction of diazonium salts in very dilute sulphuric acid, like the thermal decomposition of diazonium compounds in aqueous acid solutions, yields hydroxy compounds.

The photoreaction proceeds very smoothly in many cases, while the corresponding thermal decomposition often leads to resin formation. 4-Anilinobenzenediazonium sulphate (**6**) afforded **8**, and 4-dimethylaminobenzenediazonium chloride gave 4-dimethylaminophenol. Huisgen and Zahler have described the preparation of fluoren-9-one (**11**) by irradiation of **10** in aqueous sulphuric acid[28]:



(10) **(11)**

The photolysis of tetrazo compounds of 1,5-di(*o*-aminobenzoylnaphthalene) takes place by means of a double Pschorr reaction to give 1,2,6,7-dibenzopyrene-3,8-quinone[29].



D. Spectra and Excited States of Diazonium Salts

The spectra of diazonium salts are of interest here because they identify the excited states which arise in the act of light absorption and are potentially involved in the photolytic conditions. The simplest diazonium compounds absorb ultraviolet radiation in the range 2200–3300 Å, which is virtually non-existent in the spectrum emitted by conventional light sources. When dialkylamino, arylamino, arylthio or hydroxy groups are introduced into the molecule in the *ortho* or *para* positions with respect to the exceptionally strong electron attracting diazonium group, then the absorption is sharply moved to longer wavelengths. Since most substituted diazonium compounds are yellow and absorb in the region 3600–4500 Å, they are sensitive to near ultraviolet and blue light, and are virtually insensitive to red and green[10]. Figure 3 shows the absorption spectra change of p-$C_6H_5NHC_6H_4N_2^+\ HSO_4^-$ in water (pH 4·6) during u.v. irradiation[30].

In aqueous solution, diazonium salts stabilized by zinc chloride exhibited a major absorption band in the region 350–390 nm and a minor band in the region 245–260 nm. The introduction of progressively larger alkyl or phenyl groups into the *para* amino group causes a slight bathochromic shift in the major band. With every compound a minor band was observed in the region 245–260 nm [31].

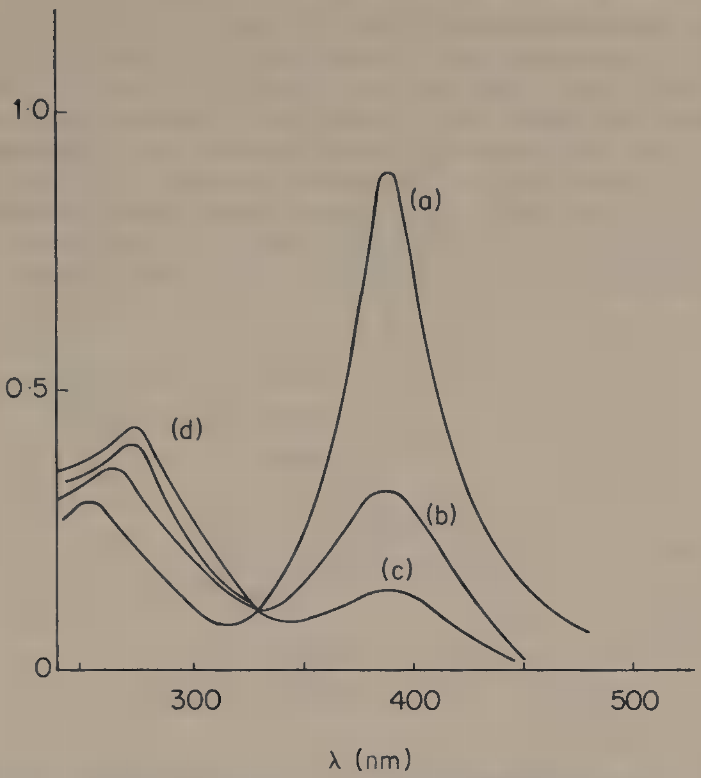
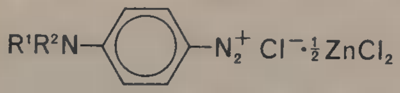


FIGURE 3. Absorption spectral change of 4-$C_6H_5NHC_6H_4N_2^+$ HSO_4^- in water (pH 4·6) during irradiation. Irradiation with a 500-watt, high pressure Hg arc at about 30 cm. Irradiation time (sec); (a) 0; (b) 15; (c) 20; (d) 30. [Reproduced, with permission, from Inoue, Kokado and Shimada, *Nippon Kagaku Kaishi*, **12**, 2272 (1974).]

TABLE 4. Ultraviolet absorption maxima of



R^1	R^2	λ_{max}	Molar extinction coefficient, ε
H	H	353	37,400
Me	Me	375	38,900
Et	Et	380	40,300
Me	H	366	38,600
Et	H	368	41,100
Ph	H	377	30,200
Ph	Ph	388	24,100

Although the *n*–π* transition is observable in the absorption spectra of azo compounds, it has not yet been observed with diazonium salts. The main absorption band with these salts is not greatly affected by solvents of different polarity and is probably due to π–π* electron excitation. Bathochromic shifts observed with *p*-NH_2-substituted derivatives also confirm this conclusion. In aqueous solution no difference in spectra between *p*-aminobenzenediazonium chloride and its zinc chloride double salt was found, indicating that interaction between the cation and zinc chloride was negligible.

The electronic states of the benzenediazonium cation were calculated by a method similar to that of Pariser and Parr[32]. On the basis of the calculations, the 259 and 295 nm absorption bands were attributed to $^1A_1$–$^1A_1$ and $^1A_1$–$^1B_1$ transitions, respectively. When the sample was irradiated in an alcoholic solution by a 295 nm light, no e.s.r. signal was detected, but fluorescence and phosphorescence were observed; the fluorescence and the absorption spectrum of the $^1A_1$–$^1B_1$ transition are mirror images of each other. On the other hand, upon irradiation by 259 nm light, this sample showed an e.s.r. spectrum which was attributed to the phenyl σ-radical, but no fluorescence or phosphorescence was observed. These results show that the electronically excited benzenediazonium salt releases its excess energy by the following processes: (i) There is radiative transition from the $^1B_1$ state to the ground state and intersystem crossing to the phosphorescent state, although it is as yet uncertain whether $^3B_1$ or other triplet states are involved. The photodecomposition does not proceed from the excited $^1B_1$ state. (ii) From the excited $^1A_1$ state, neither radiative transition to the ground state nor a non-radiative transition to any fluorescent or phosphorescent state occurs. The molecule decomposes rapidly to give a phenyl σ-radical after excitation to this electronic state.

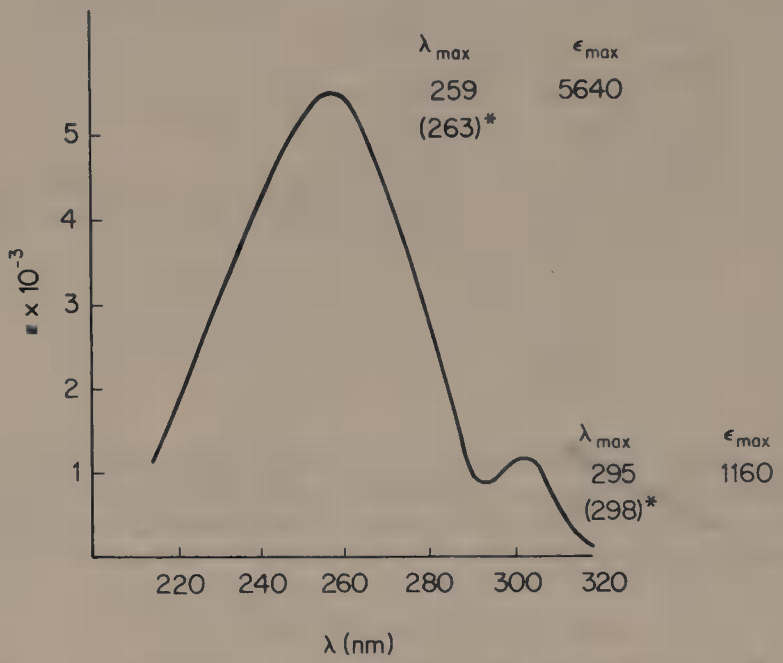


FIGURE 4. The near ultraviolet absorption spectrum of benzenediazonium fluoroborate in ethanol (* in water). [Reproduced, with permission, from Sukigahara and Kikuchi, *Bull. Chem. Soc. Japan*, **40**, 462 (1967).]

Electronic structures and absorption spectra of *p*-halogeno-, *p*-methoxy- and *p*-dimethylamino-benzenediazonium cations showed that when an electron-donating group is introduced at the *para* position, the $^1A_1$–$^1A_1$ transition shows a very large shift to longer wavelengths, while the $^1A_1$–$^1B_1$ transition is not so much affected[33].

Tsunoda and Yamaoka reported the relationship between the charge density and the photolytic rate[34]. It was observed that the benzenediazonium cations having electron-releasing groups such as —OMe and —NMe_2 in the *para* position have relatively large quantum yields, while electron-attracting groups, such as —NO_2 and —Br, substituted in the *para* or *ortho* position lower the quantum yields. As

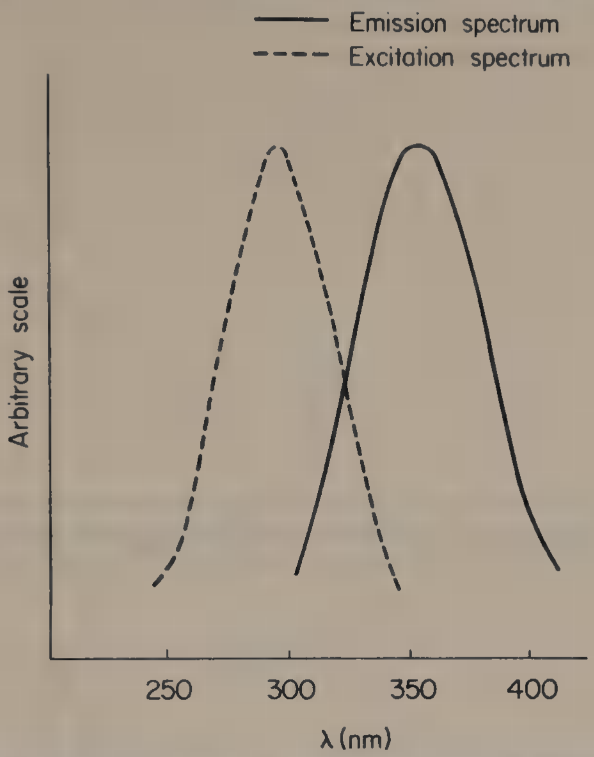


FIGURE 5. The fluorescence emission and excitation spectra of benzenediazonium fluoroborate. [Reproduced, with permission, from Sukigahara and Kikuchi, *Bull. Chem. Soc. Japan*, **40**, 462 (1967).]

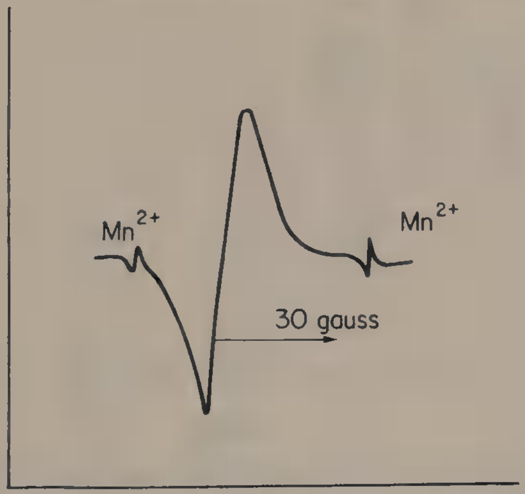


FIGURE 6. The e.s.r. spectrum of irradiated benzenediazonium fluoroborate (at 77 K in methanol). [Reproduced, with permission, from Sukigahara and Kikuchi, *Bull. Chem. Soc. Japan*, **40**, 462 (1967).]

the conjugated system extends, the peak of the absorption band is shifted to longer wavelengths, but the quantum yield tends to be lower. The tetrazonium cations also have low quantum yields, which might be the effect of the strong electrophilicity of two diazonium groups.

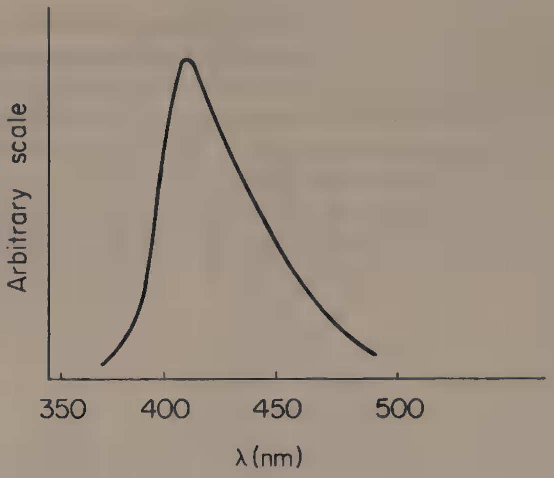


FIGURE 7. The phosphorescence spectrum of benzenediazonium fluoroborate at 77 K. [Reproduced, with permission, from Sukigahara and Kikuchi, *Bull. Chem. Soc. Japan*, **40**, 462 (1967).]

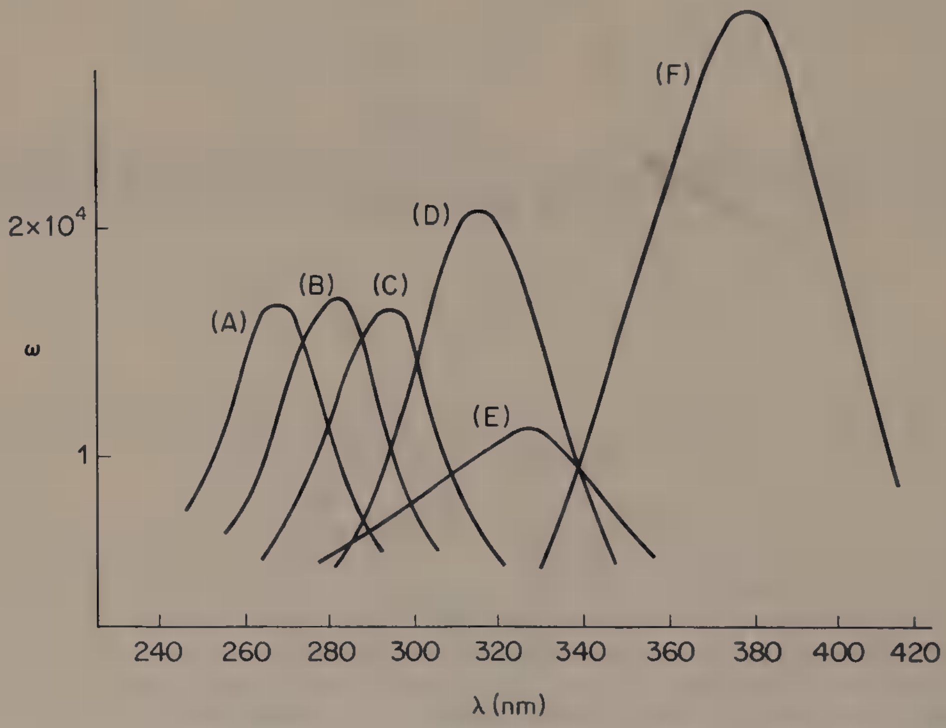


FIGURE 8. The visible and near ultraviolet absorption spectra of the *para*-substituted benzenediazonium fluoroborates. (A) *p*-F; (B) *p*-Cl; (C) *p*-Br; (D) *p*-MeO; (E) *p*-I; (F) *p*-NMe_2. [Reproduced, with permission, from Sukigahara and Kikuchi, *Bull. Chem. Soc. Japan*, **40**, 1078 (1967).]

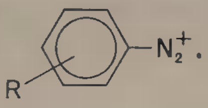
Table 6 shows the transition energy and the charge density of the π-electrons calculated by the Hückel theory. The charge density of, for example, the *p*-dimethylaminobenzenediazonium cation having a high quantum yield is much greater than that of, for example, the *p*-nitrobenzenediazonium cation with its low quantum

TABLE 5. Wavelength maxima and molar extinction coefficients for *para*-substituted benzenediazonium cations. [Reproduced, with permission, from Sukigahara and Kikuchi, *Bull. Chem. Soc. Japan*, **40**, 1078 (1967).]

Substituent	λ_{max} (nm)	log ε_{max}
F	267	4·229
Cl	281	4·195
Br	393	4·178
I	327·5	4·036
OMe	315	4·283
NMe_2	380	4·448

yield. A correlation between the quantum yield and the charge density of the diazonium group also exists, even in the excited state. Figure 9 shows that the diazonium cation with a high charge density at the diazonium group in the excited state has a tendency to give high quantum yield. The *ortho* isomers do not follow this tendency, because of steric hindrance.

TABLE 6. Quantum yields and charge densities of diazonium cations,



[Reproduced, with permission, from Tsunoda and Yamaoka, *J. Photographic Sci. Japan*, **29**, 197 (1966).]

			Charge density[a]		Transition energy (eV)	
R	λ_{max}	Quantum yield	G	E	Calcd	Found
H	264	0·38	2·0428	2·5590	4·81	4·70
p-Cl	283	0·29	2·0485	2·5073	4·42	4·40
m-Cl	266	0·41	2·0424	2·5527	4·38	4·66
o-Cl	269	0·18	2·0500	2·5395	4·40	4·60
p-Br	293	0·35	2·0522	2·5307	4·22	4·23
p-F	269	0·50	2·0606	2·5632	4·19	4·60
p-Me	279	0·23	2·0446	2·4795	4·67	4·44
m-Me	279	0·35	2·0348	2·5288	4·69	4·44
o-Me	269	0·30	2·0416	2·5269	4·68	4·60
p-OMe	315	0·52	2·0534	2·5521	4·12	3·93
m-OMe	275	0·24	2·0417	2·1611	2·33	4·40
o-OMe	355	0·18	2·0550	2·5469	4·07	3·49
p-OH	350	0·54	2·0544	2·5854	3·32	3·54
p-NMe_2	385	0·58	2·0662	2·5957	2·97	3·22
m-NO_2	232	0·17	2·0426	1·9742	3·79	5·30
o-NO_2	280	0·10	2·0434	2·0489	3·66	4·43

[a] G = ground state, E = excited state.

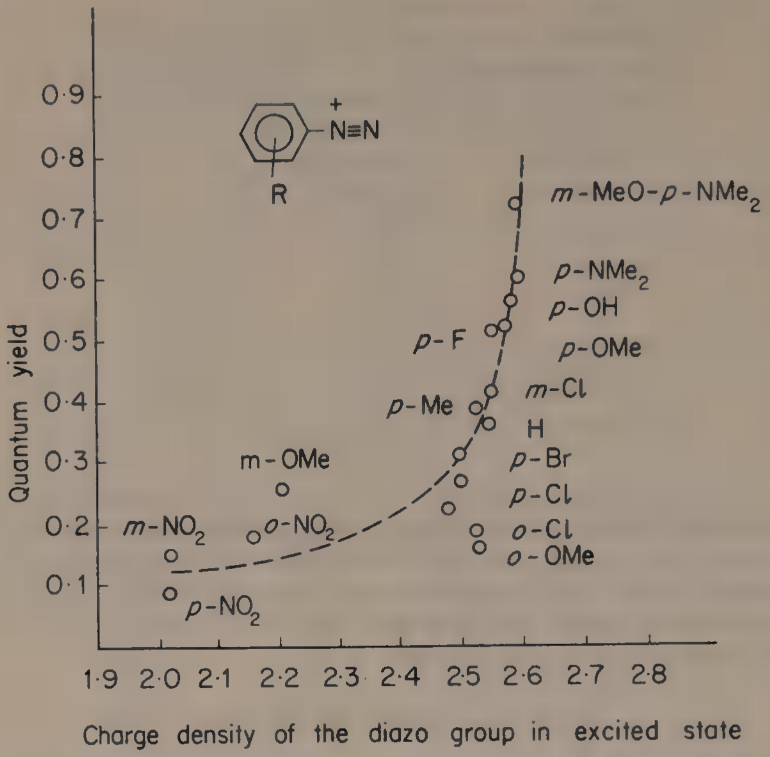


FIGURE 9. The relationship between the quantum yield and the charge density of the diazonium group. [Reproduced, with permission, from Tsunoda and Yamaoka, *J. Photographic Sci. Japan*, **29**, 197 (1966).]

E. Reaction Intermediates

I. Radical species and carbonium ions

The products of the photodecomposition of *p*- and *m*-nitrobenzenediazonium salts have been studied in various solvents. It was found that the dominant primary process in alcohol solution leads to nitrophenyl radicals, and the products are those generally expected of a reaction involving a homolytic scission of the C—N bond.

TABLE 7. Photolysis of p-$NO_2C_6H_4N_2^+Cl^- \cdot \frac{1}{2}SnCl_4$ in ethanolic solution

Product	EtOH at 0 °C (%)	EtOH at −10 °C (%)	EtOH+I_2 at 0 °C (%)
$PhNO_2$	76·6	83·5	17·7
p-$NO_2C_6H_4OC_2H_5$	5·4	5·2	4·5
p-$NO_2C_6H_4CH(OH)CH_3$	3·6	5·3	*a*
p-$NO_2C_6H_4CH_2CH_2CH_2OH$	2·3	2·8	*a*
CH_3CHO	74·1	*a*	*a*
$(CH_3CH(OH))_2$	1·54	*a*	*a*
$(p$-$NO_2C_6H_4—)_2$	0·0	0·0	0·0
p-$NO_2C_6H_4I$	—	—	65·5
$(\sum p$-$NO_2C_6H_4\cdot)$	82·5	—	83·2

[a] Analysis not carried out but compound presumed present.

Nitrobenzene, α- and β-arylethanol and butanediol are formed but no dinitrobiphenyl[35]. Addition of 2,2-diphenylpicrylhydrazyl, halogen or nitric oxide confirmed the importance of nitrophenyl radical formation in the photodecomposition. However, all of the products cannot be explained on the basis of the one primary process. The results are consistent with the occurrence of two primary processes, (1) and (2):

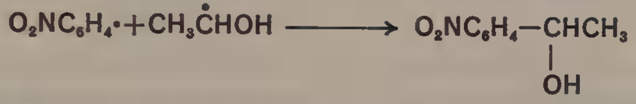
$$O_2NC_6H_4N_2^+\,X^- + h\nu \longrightarrow O_2NC_6H_4\cdot + N_2 + X\cdot \qquad (1)$$

$$O_2NC_6H_4N_2^+\,X^- + h\nu \longrightarrow O_2NC_6H_4^+ + N_2 + X^- \qquad (2)$$

where X^- is Cl^-, $SnCl_5^-$ or ion solvent dipole complexes, etc. Presumably (1) is followed by the secondary radical reactions which lead to the final products; in ethanol solution the suggested secondary reactions are:

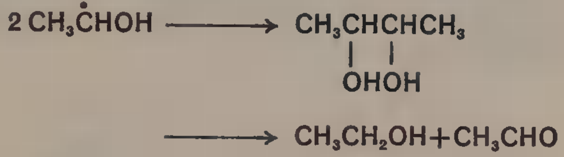
$$O_2NC_6H_4\cdot + CH_3CH_2OH \longrightarrow C_6H_5NO_2 + CH_3\dot{C}HOH \qquad (3)$$

$$O_2NC_6H_4\cdot + CH_3CH_2OH \longrightarrow C_6H_5NO_2 + \cdot CH_2CH_2OH \qquad (4)$$



$$O_2NC_6H_4\cdot + CH_3\dot{C}HOH \longrightarrow O_2NC_6H_4-\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$$

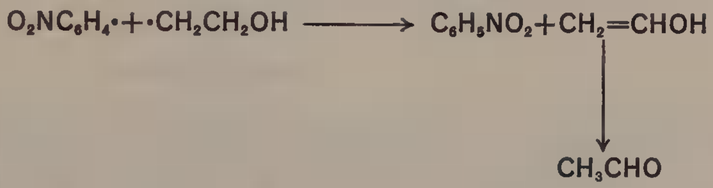
$$O_2NC_6H_4\cdot + \cdot CH_2CH_2OH \longrightarrow O_2NC_6H_4CH_2CH_2OH$$



$$2\,CH_3\dot{C}HOH \longrightarrow CH_3\underset{\displaystyle OH}{\underset{|}{C}}H\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$$

$$\longrightarrow CH_3CH_2OH + CH_3CHO$$

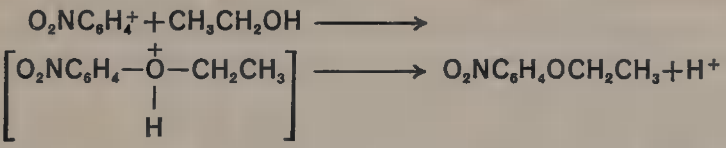
$$O_2NC_6H_4\cdot + CH_3\dot{C}HOH \longrightarrow C_6H_5NO_2 + CH_3CHO$$



$$O_2NC_6H_4\cdot + \cdot CH_2CH_2OH \longrightarrow C_6H_5NO_2 + \underset{\displaystyle CH_3CHO}{\underset{\downarrow}{CH_2{=}CHOH}}$$

The absence of dinitrobiphenyls in the reaction products suggests that the nitrophenyl radicals are converted primarily to nitrobenzene and other products via reactions (3) and (4).

The second primary process (2) of lower probability was suggested to explain the ether formation in the ethanol solutions:



(5)

$$O_2NC_6H_4^+ + CH_3CH_2OH \longrightarrow \left[O_2NC_6H_4-\underset{\displaystyle H}{\underset{|}{\overset{+}{O}}}-CH_2CH_3\right] \longrightarrow O_2NC_6H_4OCH_2CH_3 + H^+ \qquad (5)$$

To test the mechanisms (2) and (5), the diazonium salt was photolysed in the presence of iodine. The amount of *p*-nitrophenetole was not essentially decreased although the yield of nitrobenzene, which reflects the activity of the *p*-nitrophenyl radical, was greatly decreased due to the very fast reaction (6):

$$O_2NC_6H_4\cdot + I_2 \longrightarrow O_2NC_6H_4I \qquad (6)$$

There is a striking contrast between the products of the photodecomposition of the diazonium salt in alcohol and in aqueous solution. Nitrobenzene, the major product in alcohol, is not detected in aqueous solution. Nitrophenol and nitrochlorobenzene dominate in water solutions. These results, coupled with product studies with nitric oxide and hydroquinone, suggest that free radical formation is unimportant in the photodecomposition of nitrobenzenediazonium salts in aqueous solution. The results are consistent with the occurrence of a single primary photodecomposition mode, process (2), under these conditions. The product distribution in solutions of varied chloride content results from the competition between Cl^- and H_2O for the carbonium ion.

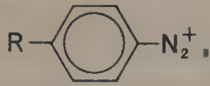
TABLE 8. Variation of product yield in the photolysis of $p\text{-}NO_2C_6H_4N_2^+\ Cl^- \cdot \frac{1}{2}\ SnCl_4$ in various solutions

	Solvent (%)					
Product	EtOH	MeOH	H_2O	5·3 M-NaCl(aq)	9 M-HCl(aq)	4·3 M-H_2SO_4(aq)
$PhNO_2$	76·6	71·9	0·0	0·0	0·0	0·0
$p\text{-}NO_2C_6H_4OR$	5·3	3·5	0·0	0·0	0·0	0·0
$p\text{-}NO_2C_6H_4Cl$	0·0	0·0	7·4	30·2	61·6	0·0
$p\text{-}NO_2C_6H_4OH$	0·0	0·0	73·5	50·8	23·2	84·3
Coupled product	0·0	0·0	4·1	5·2	0·0	0·0

$$\begin{tikzcd} O_2NC_6H_4^+ + Cl^- \arrow[r] & O_2NC_6H_4Cl \\ O_2NC_6H_4^+ + H_2O \arrow[r] & ON_2C_6H_4OH_2^+ \arrow[d] \\ & ON_2C_6H_4OH + H^+ \end{tikzcd}$$

Boudreaux and Boulet[36] have made magnetic measurements on the irradiated aqueous solutions of *p*-dimethylaminobenzenediazonium chloride. They have suggested that the observed magnetism is due to the Cl• radical and to the $Me_2NC_6H_4\cdot$ radical, and they have estimated that the steady-state concentration of radicals is about 1×10^{-3} M. This conclusion seems untenable in view of the work of Zandstra and Evleth[37]. Photolytic decomposition of *p*-dimethylaminobenzenediazonium chloride in aqueous solution at pH above 5 leads to the formation of a paramagnetic species. The e.s.r. spectrum is the same as that obtained in air oxidation of *p*-dimethylaminophenol in the same pH range. Hence the structure of the photolytic radical could be established as the *p*-dimethylaminophenoxy radical. Similarly, *p*-diethylaminobenzenediazonium chloride was photolytically decomposed to yield the corresponding phenoxy radical.

In the presence of chloride ion, aryl chlorides as well as phenols result from the photolysis of arenediazonium salts in aqueous solution, as in the thermal reaction[21]. Benzenediazonium ion in aqueous sodium chloride yields just as much chlorobenzene by photolysis as it does thermally at the same temperature, but the *p*-methyl- and *p*-chloro-benzenediazonium salts give a significantly higher yield of the chloride photochemically than thermally[38]. A similarity, but not identity, of product-determining steps is indicated. When $p\text{-}MeC_6H_4{}^{15}N^+{\equiv}N$ and $p\text{-}MeOC_6H_4{}^{15}N{\equiv}N$

TABLE 9. Yield of aryl chloride from photolysis of diazonium salt, , in aqueous sodium chloride

R	NaCl	ArCl (%)
H	0·2	2·5 (2·5)[a]
	1·0	8·5
	3·0	19·3
Me	0·2	3·2 (2·1)[b]
	1·0	11·0 (6·8)
	3·0	24·1 (16·6)
Cl	0·2	3·8 (2·5)[c]
	1·0	11·9 (7·7)
	3·0	24·2 (18·7)

[a] Thermolysis at 3 °C.
[b] Thermolysis at 49 °C.
[c] Thermolysis at 80 °C.

are exposed to light insufficient to complete the photolysis, the residual diazonium salt is in part rearranged to $ArN^+{\equiv}^{15}N$, significantly more than in the corresponding dark reaction. This allows us to reject the aryl cation as the only intermediate. A simple mechanism adequate to describe all results is given below:

$$Ar{-}^{15}N^+{\equiv}N \xrightarrow{h\nu} D^* \tag{7}$$

$$D^* \longrightarrow Ar{-}^{15}N^+{\equiv}N \tag{8}$$

$$D^* \longrightarrow ArN^+{\equiv}^{15}N \tag{9}$$

$$D^*+H_2O \longrightarrow ArOH+N_2+H^+ \tag{10}$$

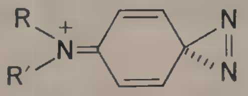
$$D^*+Cl^- \longrightarrow ArCl+N_2 \tag{11}$$

Reaction (7) conceals the complex process following the absorption of light and leading to a state D* (unestablished multiplicity) stable enough to undergo the bimolecular reactions (10) and (11). Reaction (8) is included simply because it seems unreasonable that reaction (9) would occur without reaction (8). It is attractive to identify D* with the intermediate in the photolysis of the *p*-nitrobenzenediazonium ion, which may participate in water reactions (10) and (11) as well as in ethanol, reactions (12) and (13), to account for all the observed products:

$$D^*+EtOH \longrightarrow ArOEt+N_2+H^+ \tag{12}$$

$$D^*+EtOH \longrightarrow Ar\cdot+N_2+CH_3\dot{C}HOH+H^+ \tag{13}$$

One may speculate that D* corresponds to the species observed by Lee, Calvert and Malmberg[35] in the low temperature irradiation of *p*-dimethylaminobenzenediazonium hexachlorostannate, for which the symmetric structure (12) was tentatively suggested by Calvert and Pitts[39].

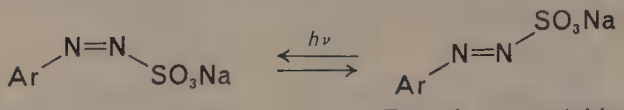


(12)

2. *Cis–trans* isomerization

The light-induced rearrangements of diazo compounds also give some information for the reaction intermediate of diazonium salts, but only the diazosulphonates $ArN{=}NSO_3Na$ and the diazocyanides $ArN{=}NCN$ have been studied in detail[7].

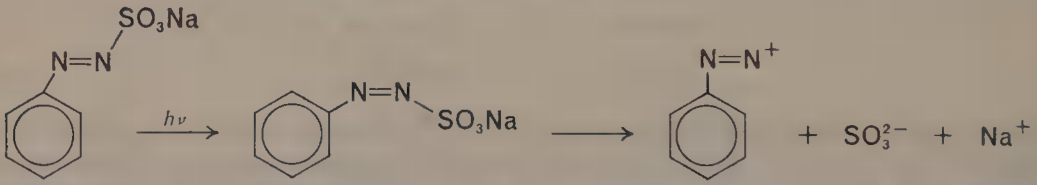
It is assumed that these exist in two forms: the unstable *cis* form, able to take part in the reaction of azo coupling, and the stable, inactive, *trans* form which either takes part in such a reaction only with great difficulty or not at all.



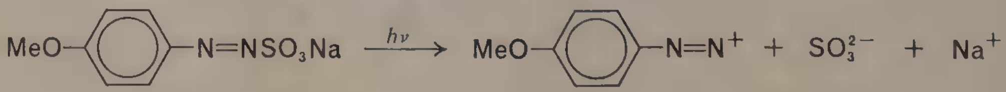
Cis isomer, unstable active form

Trans isomer, stable inactive form

Hartley[40] found that, when irradiated in a non-ionizing solvent (benzene), the stable diazocyanide is converted to the unstable isomer which is in a state of equilibrium with the stable form, and can be detected by its absorption spectrum. While irradiating the stable diazocyanide in ethanol in the presence of silver nitrate, Stephenson and Waters[41] showed that when the irradiation lasts a sufficiently long time, silver cyanide precipitates quantitatively from the solution, and the diazocyanide is converted to the diazonium nitrate. When comparing these results with the results of Hartley, they arrived at the conclusion that diazonium cyanide could be obtained only as a result of the action of light on the labile form of diazocyanide, since they were able to show that the stable form of diazocyanide was unable to undergo this reaction in the dark and, consequently, no direct conversion of the stable diazocyanide to diazonium cyanide took place on irradiation. In non-polar solvents the process of photostereoisomerization is confined, as a rule, to the formation of the unstable stereoisomer, whereas irradiation in polar solvents, e.g. ethanol or acetone, results in the complete decomposition of the diazo group:



Contrary to the above work, de Jonge and Dijkstra[42] noticed that immediately after irradiation of the stable diazosulphonate in solution, the anion of sulphurous acid and the diazonium cation are detected, which slowly reacted with one another in darkness, to give the initial stable diazosulphonate. The elimination of one of the ions, for instance the precipitation of the SO_3^{2-} anions with lead salts and/or the conversion of the diazo cation to an azo dye, cuts short the dark reaction, and the system does not revert to the initial state. A short duration, high intensity irradiation of neutral solutions of *p*-methoxy- or *o*-chloro-*p*-methyl-benzenediazosulphonate results in an intermittent increase in the pH of the solution. After the light source has been turned off, the solution reverts gradually to the original state, and the pH decreases to the initial value. This phenomenon becomes understandable if we assume that, as a result of the action of light, there occurs at least partial dissociation of diazosulphonate according to the equation:



Now, the solution of the initial diazosulphonate is neutral, but the product is a salt of the weak sulphurous acid, and the pH of the solution therefore increases. During more prolonged exposure the process becomes irreversible because of the decomposition of the diazonium cation.

$$ArN_2^+ + H_2O \xrightarrow{h\nu} ArOH + N_2 + H^+$$

3. Sensitized photolysis of diazonium salts

The photolysis of diazonium salts in solution has been spectrally sensitized with dyes in the presence of activators, such as amine associates, thiourea and its derivatives, and benzenesulphinate ion[43]. *p*-Anilinobenzenediazonium sulphate (**13**) was photolysed in the presence of methylene blue and of 1,4-diazobicyclo[2.2.2]-octane (DABCO) or sodium *p*-toluenesulphinate (STS). Figure 10 shows the absorption spectra of the solution before and after irradiation. The quantum yields were also pH sensitive. Figure 11 shows the variation in the quantum yields as a function of pH under aerobic conditions. It is seen that the pH for greatest dye sensitization differs markedly between the two activators. In the DABCO system, the dye sensitization was restricted to an alkaline range starting at about pH 7. Lower pHs may accentuate the formation of the protonated form of DABCO which results in a loss of photo-initiating activity.

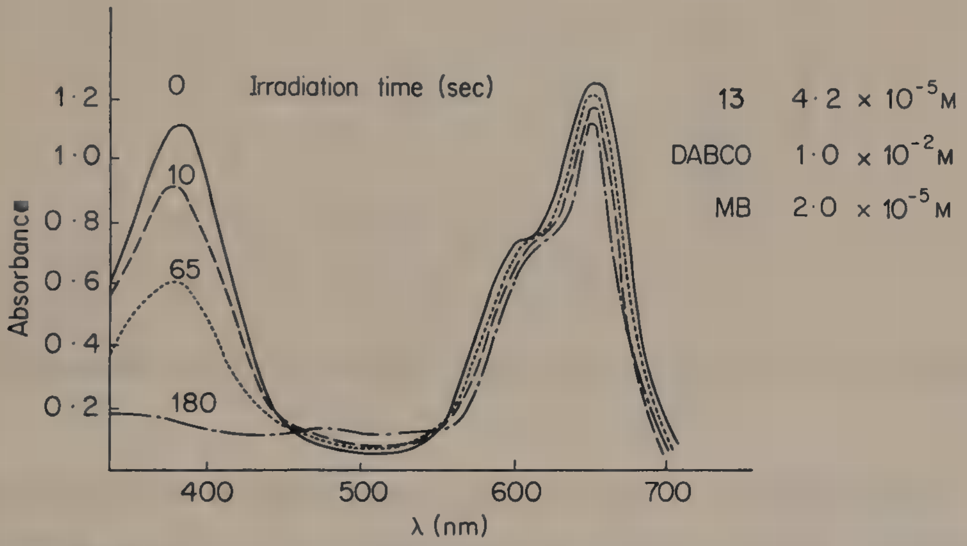


FIGURE 10. Absorption spectra of solutions of **13** containing methylene blue and activator under anaerobic conditions.

The data given show clearly a greater range of activity in the STS system. The quantum yield increased with an increase in solution in the pH range below 7, and decreased with greater alkalinity.

It may be inferred that the dye-sensitized photolysis of (**13**) does not take place via the sulphonyl radical, which is formed from the dye triplet reaction with a sulphinate ion, and which is an efficient initiator for polymerization.

The reaction related to the sensitization may be written as follows:

$$\text{Sens (G)} + h\nu \longrightarrow {}^3\text{Sens}^*$$

$$ {}^3\text{Sens}^* + \text{DABCO} \longrightarrow (\text{Sens}\text{---}\text{DABCO}) \longrightarrow \text{Sens}\cdot + \text{DABCO}$$

$$\text{Sens}\cdot + (\mathbf{13}) \longrightarrow \text{Sens (G)} + N_2 + \text{Ar}\cdot$$

The key step of the sensitizing system may be the escape of Sens•, semi-methylene blue, from the dye–activator complex, Sens---DABCO, which is formed by interaction of the excited triplet dye with unprotonated DABCO. The complex undergoes collisional deactivation and dissociation to the semi-methylene blue and a half-oxidized activator.

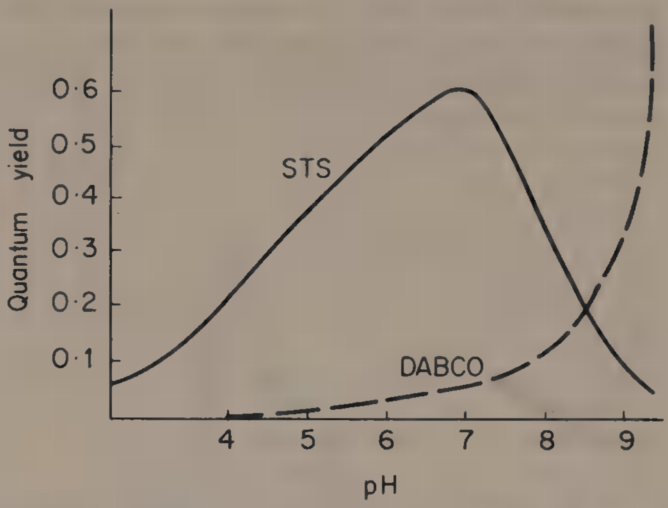
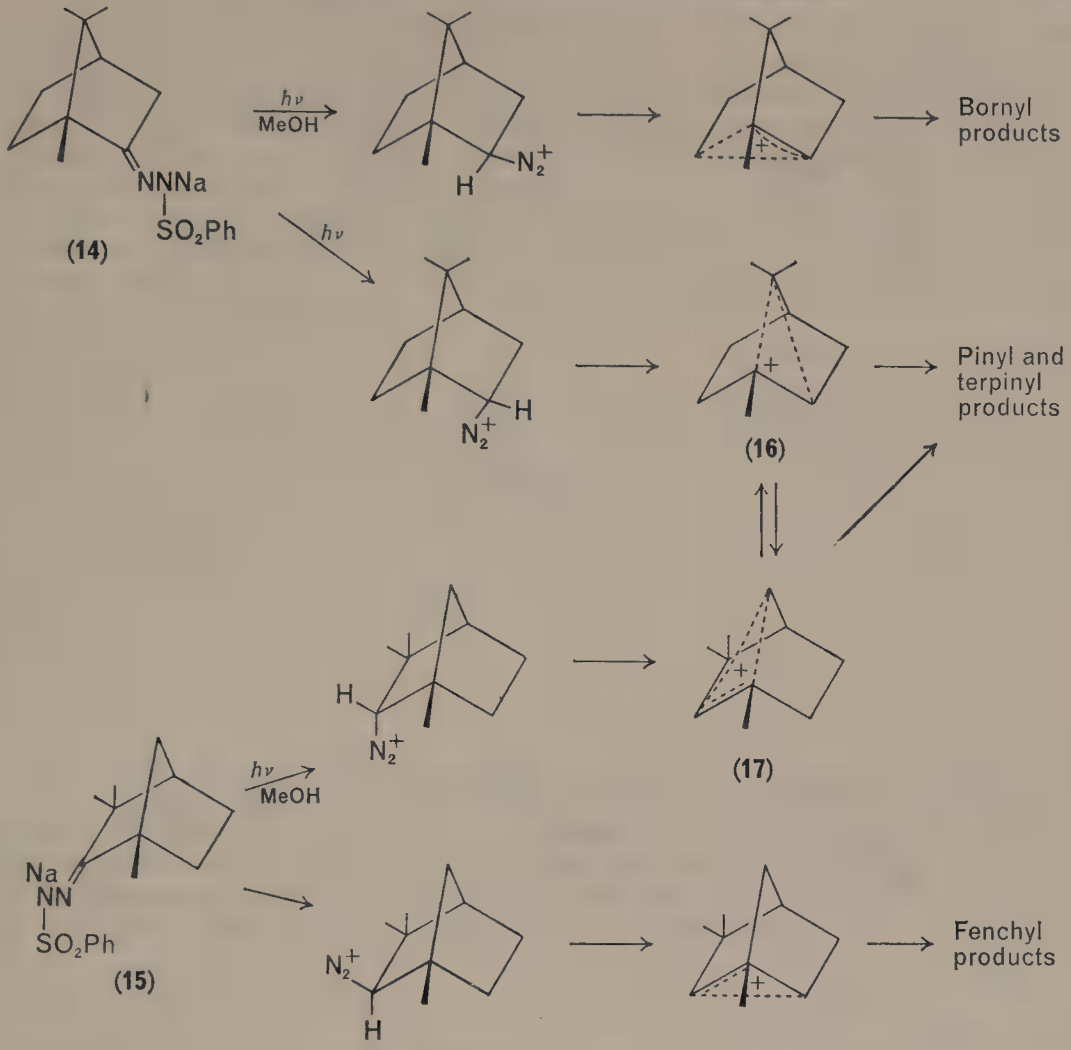
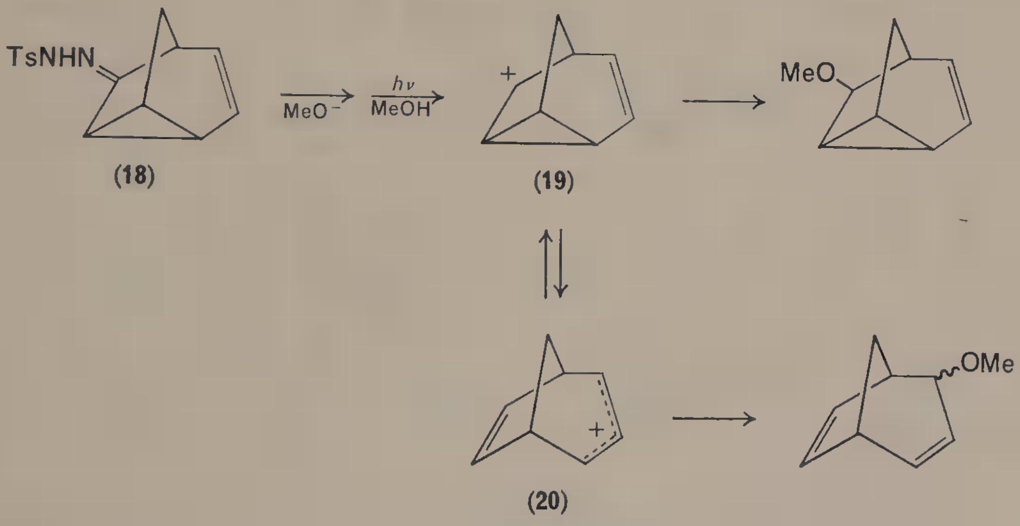


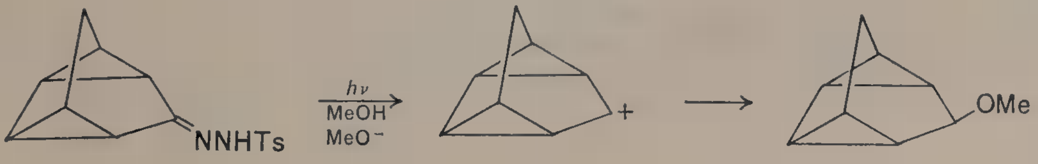
FIGURE 11. Dependence of quantum yields on solution pH under aerobic conditions.

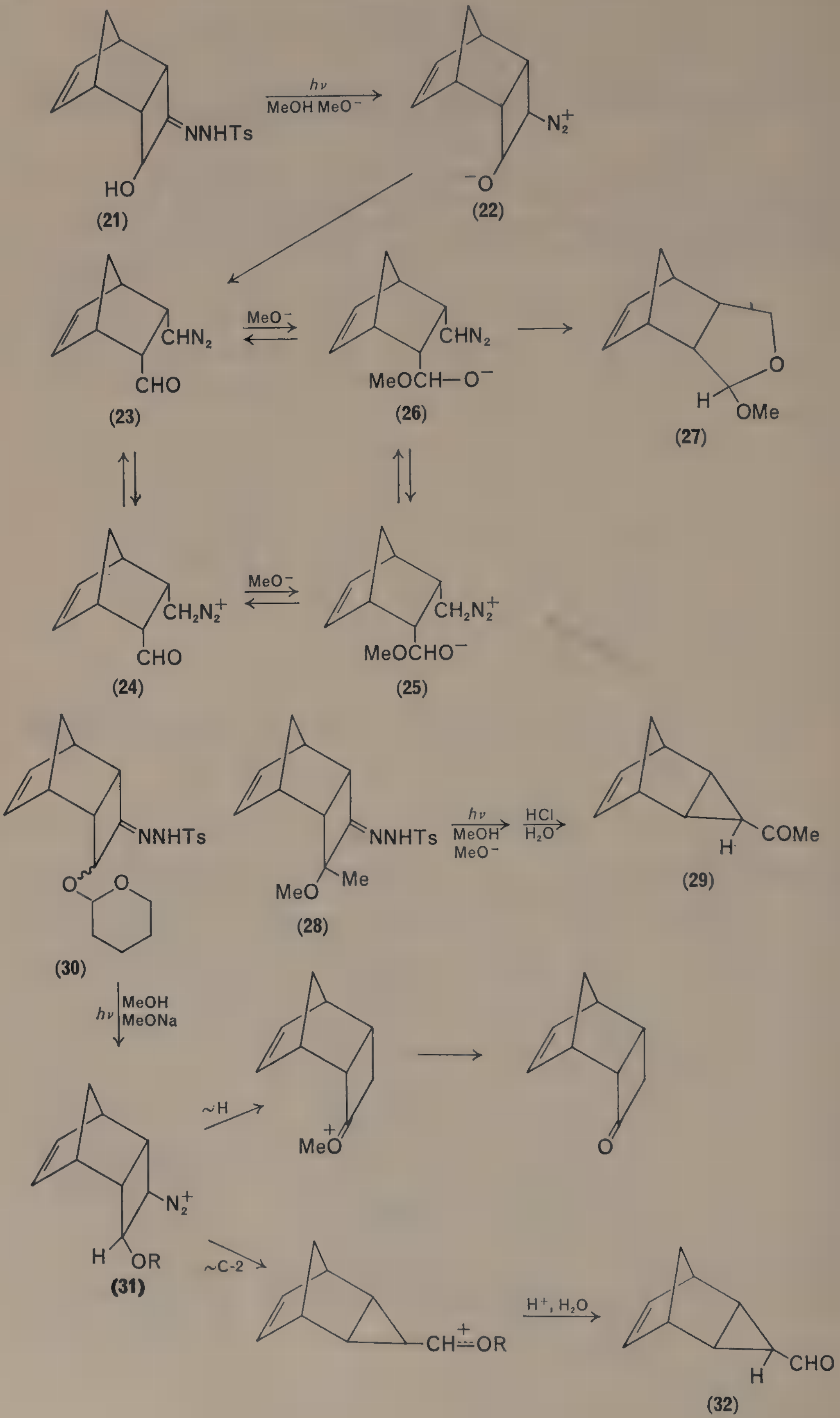
III. PHOTOLYSIS OF ALIPHATIC DIAZONIUM COMPOUNDS

Photolysis of the sodium salts **14** and **15** of camphor and fenchone arenesulphonyl hydrazone, respectively, gives both *exo*- and *endo*-diazonium ions. In each case a mixture of pinyl and terpinyl products is formed together with bornyl products from **14** and fenchyl from **15**, without any cross-over of these series. The ratio of pinyl to terpinyl products requires that two isomeric, interconverting cations of pinyl type **16** and **17** are formed. Similar results are reported for the apocamphor series[44]. On the other hand, the *p*-toluenesulphonylhydrazone of norbornanone protonates exclusively from the *endo* face, affording *exo*-2-norbornanediazonium ion which gives nortricyclene and *exo*-2-norbornyl ether[45]. Photolysis of the tosylhydrazone (**18**) gives the tricyclo[3.2.1.$0^{2,7}$]oct-3-en-6-yl cation (**19**), which rearranges reversibly to **20** at a rate competing with solvent attack[46]. The tosylhydrazones, **21**, **28** and **30**, were prepared from 4-hydroxy-*endo*-tricyclo[4.2.1.$0^{2,5}$]non-7-en-3-one and utilized in the deaminative pinacol rearrangement to *endo*-tricyclo[3.2.1.$0^{2,4}$]-oct-6-ene derivatives[47]. The hydroxy compound **21** underwent retroaldol cleavage exclusively on irradiation in methanol/NaOMe; **28** and **30** afforded the desired *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene derivative, **29** and **32**, respectively. Competing processes such as double-bond participation in the case of **28**, and hydride shift in the case of **30**, render these pinacol rearrangements less efficient than the related

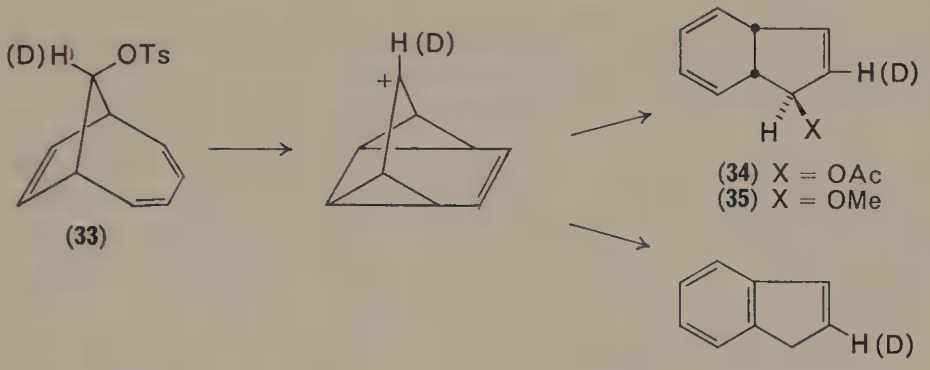

hν
MeOH
NNNa
SO₂Ph
(14)
hν
N₂⁺
H
Bornyl products
H
N₂⁺
(16)
Pinyl and terpinyl products
H
N₂⁺
(17)
hν
MeOH
Na
NN
SO₂Ph
(15)
N₂⁺
H
Fenchyl products


TsNHN
(18)
MeO⁻
hν
MeOH
(19)
MeO
(20)
OMe


NNHTs
hν
MeOH
MeO⁻
OMe


NNHTs
HO
(21)
hν
MeOH MeO⁻
N$_2^+$
⁻O
(22)
CHN$_2$
CHO
(23)
MeO⁻
CHN$_2$
MeOCH—O⁻
(26)
O
H
OMe
(27)
CH$_2$N$_2^+$
CHO
(24)
MeO⁻
CH$_2$N$_2^+$
MeOCHO⁻
(25)
NNHTs
O
O
(30)
NNHTs
MeO
Me
(28)
hν
MeOH
MeO⁻
HCl
H$_2$O
H
COMe
(29)
hν
MeOH
MeONa
~H
MeO
+
O
N$_2^+$
H
OR
(31)
~C-2
CH$\overset{+}{=}$OR
H⁺, H$_2$O
H
CHO
(32)

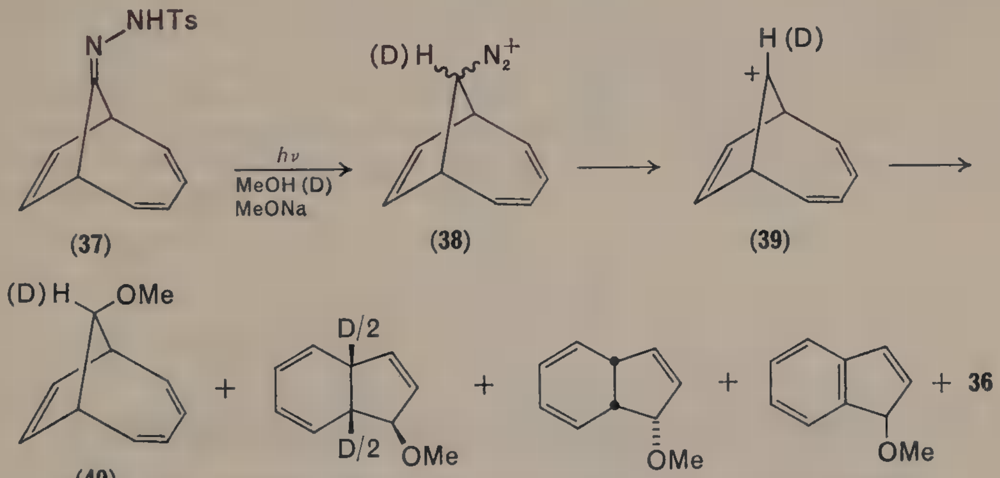
Favorskii reaction. The bicyclo[4.2.1]nona-2,4,7-trien-9-yl cation has invoked interest because of its potential homoaromaticity[48] and bicycloaromaticity[49]. The solvolysis of *syn*-bicyclo[4.2.1]nona-2,4,7-trien-9-yl *p*-toluenesulphonate **(33)** afforded *exo*-dihydroindenyl acetate **(34)**[50] and/or indene[51, 52], depending on the reaction conditions. Deamination, on the other hand, starting from the highly energetic diazonium ion, passes its transition state 'early' and without significant distortion of nuclear positions (vertical ionization)[53]. Consequently, deamination may produce cations of undistorted geometry which are by-passed in solvolysis (leading directly to more stable bridged species). Photolysis of bicyclo[4.2.1]nona-2,4,7-trien-9-one tosylhydrazone **(37)** in MeOH–MeONa afforded *syn*-9-methoxybicyclo[4.2.1]-nona-2,4,7-triene **(40)** and **(35)** as the major products. Minor products were *endo*-dihydroindenyl methyl ether **(41)**, indenyl methyl ether **(42)** and indene. Photolysis of tosylhydrazone sodium salts generates diazo compounds which are protonated by protic solvents to give diazonium ions and products derived therefrom. Various



(33)

(34) X = OAc
(35) X = OMe

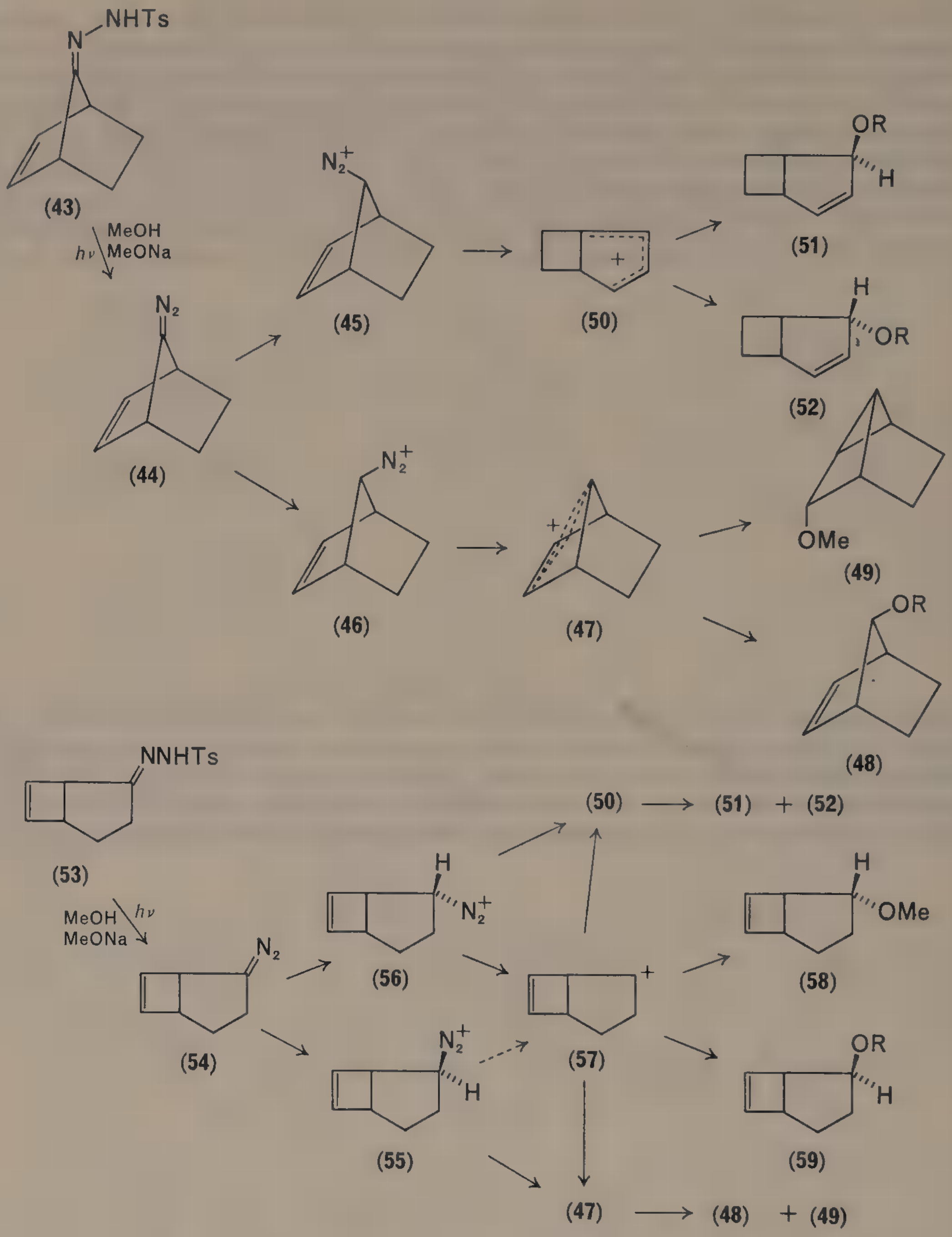
(36)



(37) **(38)** **(39)**

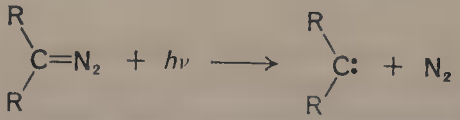
(40) **(35)** **(41)** **(42)**

bicyclo[2.2.1]heptenyl **(47)** and bicyclo[3.2.0]heptenyl **(50)** cations have been generated by decomposition of suitable diazonium precursors **(43** and **53)**. The cations **47** and **50** do not equilibrate, and their substitution pattern is largely independent of the specific precursor[54].



IV. PHOTOLYSIS OF DIAZO COMPOUNDS

The photolysis of diazo compounds is an important route to the formation of carbenes:



$$R_2C{=}N_2 + h\nu \longrightarrow R_2C\colon + N_2$$

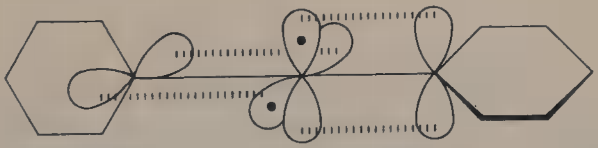
Many reviews and descriptions of carbenes are available[55–85].

A. The Structure of Carbenes

Two electronic configurations may occur: a singlet configuration (A) or a triplet configuration (B).

The electronic spectrum of methylene produced in the gas phase by flash photolysis of CH_2N_2, $CHDN_2$ and CD_2N_2 was recorded by Herzberg and Shoosmith[86]. E.s.r. spectra of methylene trapped in a xenon matrix at 4·2 K have been one of the most recent achievements in this field[87, 88].

The e.s.r. signal survived warming to 20 K but disappeared upon warming to 77 K. Analysis of the results demonstrated the production of a linear or near-linear species with a C—H bond length of 1·03 Å, which absorbed u.v. radiation at about 1414 Å, and a bent species, bond angle 102–103°, C—H bond length 1·12 Å, which absorbed radiation in the 5500–9500 Å region. Moreover, in the presence of a large excess of nitrogen, the absorption of the short wavelength, linear CH_2 increased at the expense of that of the long wavelength, bent CH_2. This experiment pointed to triplet CH_2 as ground state. The short-lived bent or singlet CH_2 was being degraded through collisions with the moderator, nitrogen, and dropping to the more stable species. Wasserman and coworkers[88] observed two species with $D = 0{\cdot}6636\ \text{cm}^{-1}$, $E = 0{\cdot}002\ \text{cm}^{-1}$ and $D = 0{\cdot}6844\ \text{cm}^{-1}$, $E = 0{\cdot}00347\ \text{cm}^{-1}$, respectively. The value of D is related to the average $1/r^3$ where r is the distance between the two spins, so that a high value of D implies a large spin–spin interaction and a close proximity of the two spins. The value of E indicates qualitatively the magnitude of the deviation of the spin–spin interaction from cylindrical symmetry. The site with the lower D and E values in methylene is believed to allow greater motional freedom; a bent molecule which rotates freely about the long axis will have $E = 0$. Wasserman and coworkers arrived at a $H—\ddot{C}—H$ angle of 136° in good agreement with most theoretical calculations. Angles of 150–155° have been estimated for phenyl- and diphenyl-carbenes. It was found that for diphenylcarbene the magnitude of $D = 0{\cdot}4055\ \text{cm}^{-1}$ and $E = 0{\cdot}0194\ \text{cm}^{-1}$ shows a small dependence on the nature of the host matrix:



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The higher D value of diphenylcarbene shows that two unpaired electrons are largely localized on the divalent carbon atom[89].

An orbital representation comparing a triplet ground-state molecule with a phosphorescent triplet state is given by Figure 12. Several carbenes have been assigned a triplet ground state by e.p.r. experiments[90–95]. Non-radical products of photolysis of diazo compounds can not be determined by the e.p.r. technique, so that it became necessary to study the optical spectroscopy of the carbene species. Ultraviolet spectroscopy, fluorescence excitation and absorption spectroscopy have been used to study the carbene problem.

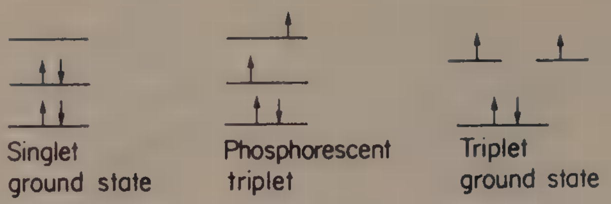


FIGURE 12. Orbital representation of spin state. [Reprinted, with permission, from Trozzolo, *Accounts Chem. Res.*, **1**, 329 (1968). Copyright by the American Chemical Society.]

Closs and coworkers reported the long-wavelength absorption band of diphenylcarbene oriented in single crystals of 1,1-diphenylethylene[96]. Moritani and coworkers found two new absorption bands in photolysed solutions of diphenyldiazomethane, by correlating e.s.r. studies, fluorescence, fluorescence excitation and absorption spectroscopy[97]. Gibbons and Trozzolo reported the luminescence, excitation and absorption spectra of diphenylcarbene[98]. The same spectrum was obtained for all excitation wavelengths in the range 230–470 nm. The emission was identified as the fluorescence of triplet ground-state diphenylcarbene[99, 100].

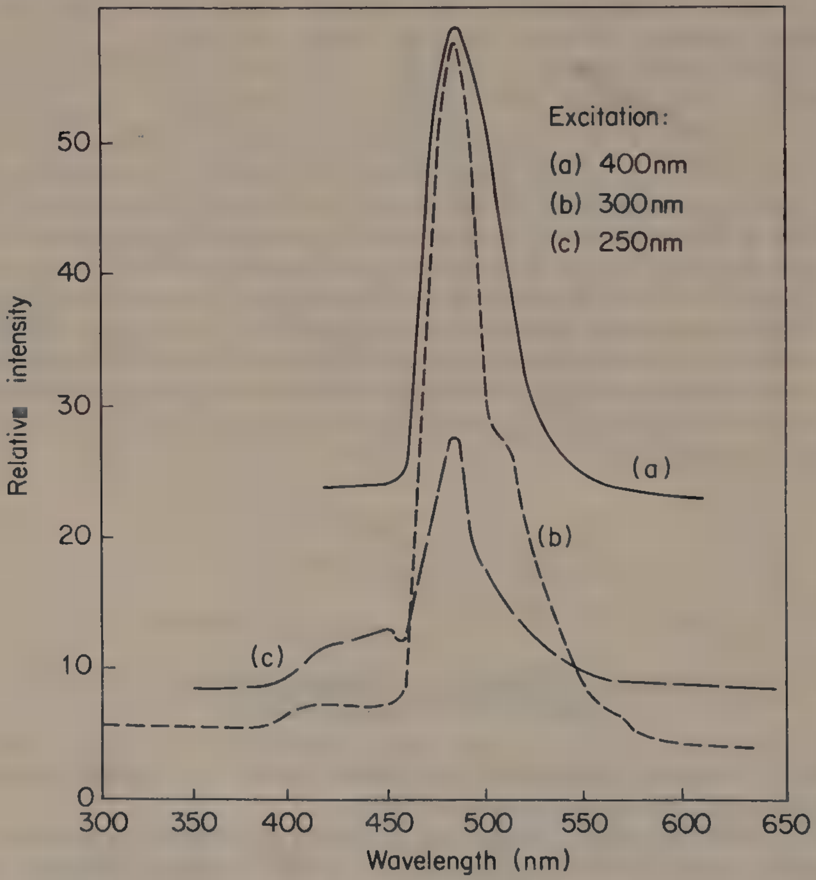
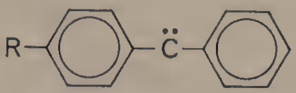


FIGURE 13. Luminescence of diphenylcarbene. [Reprinted, with permission, from Trozzolo, *Accounts Chem. Res.*, **1**, 329 (1968). Copyright by the American Chemical Society.]

The photolysis of other diaryldiazomethanes gave almost exclusively the corresponding substituted diphenylmethylene which e.s.r. studies have shown to be ground-state triplet molecules in each case.

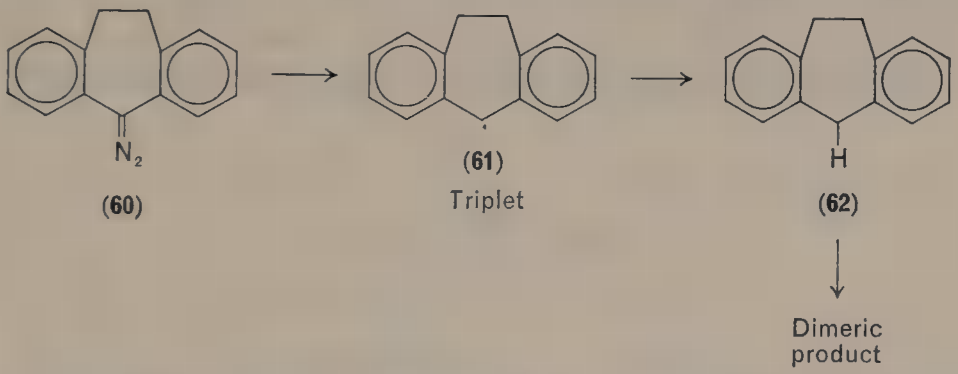
The maxima of both the absorption and emission bands were shifted to longer wavelengths from those of diphenylcarbene; the short wavelength bands were more intense than the visible range bands. The absorptions are considered to involve π–π^* transitions (Table 10). Moritani and coworkers[97, 101] have obtained the electronic spectrum of **61** (λ_{max} 510 nm) by photolysis of the corresponding diazo compound (**60**) in a variety of rigid matrices at 77 K and also in liquid paraffin at room temperature. The final product is the free radical dimer, and the decay of **61** was assigned to the doublet free-radical **62**. The e.s.r. spectra obtained by photolysis of 3-bis(diazomethyl)benzene and 1,3-bis(α-diazobenzyl)benzene were much more complex than those observed with triplet states[102, 103]. The data have been analysed in terms of the corresponding quintet ground states of the dicarbenes **63** and **64**.

TABLE 10. Spectra of diphenylmethylenes,

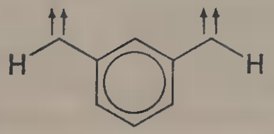


in 2-methyltetrahydrofuran. [Reprinted, with permission, from Trozzolo, *Accounts Chem. Res.*, 1, 329 (1968). Copyright by the American Chemical Society.]

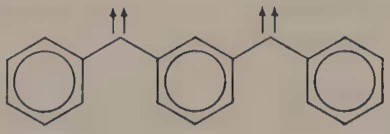
R	Absorption max. (nm)	Emission max. (nm)
H	300, 465	480
Cl	311, 475	487
Me	301, 472	487
OMe	335, 345	495
NO_2	265, 370, 555	No emission
Ph	355	555



(**60**) (**61**) (**62**)



(**63**)



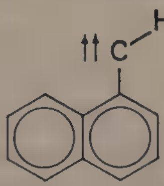
(**64**)

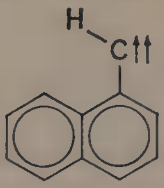
In a *para* arrangement, resonance interaction permits the ground state to be a quinonoid triplet, rather than a quintet[104].

Quinonoid triplet

Quintet

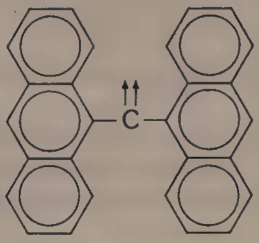
E.s.r. experiments also show that at 4 K or 77 K, such triplets as α-naphthylcarbene can exist in two non-interconverting isomeric forms, which are possible since the





triplet is not linear. Delocalization of one of the triplet's electrons over the π-system presumably provides enough double-bond character between the carbenic centre and the ring to provide a barrier to rotational interconversion at 77 K [105].

The spectrum of 9,9′-dianthrylcarbene **(65)** reveals that it is linear, however, with two aromatic systems lying orthogonally. This structure permits extensive delocalization through allenic resonance forms such as **65a** [106]. The septet ground



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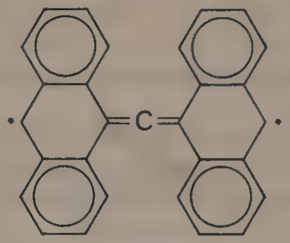
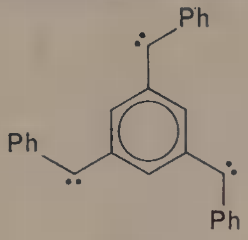


(65a)

state is suggested for the tris-carbene **(66)** on the basis of its e.s.r. spectrum[107].



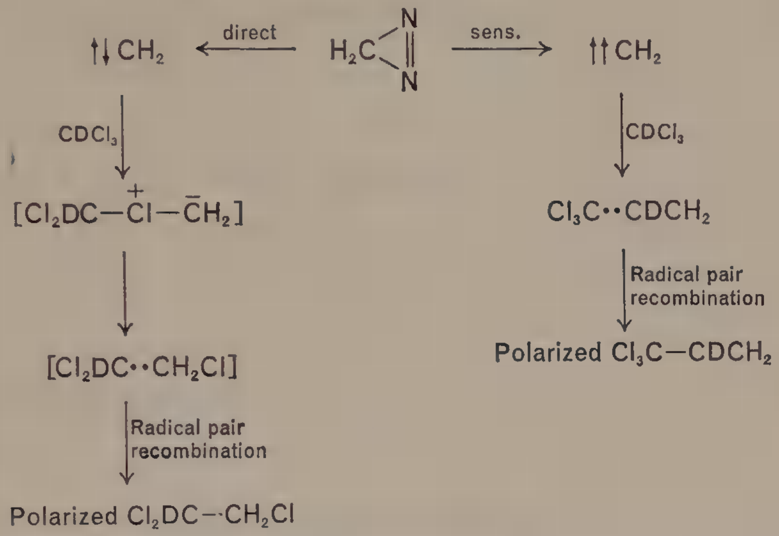
(66)

B. *Chemical Induced Dynamic Nuclear Polarization (CIDNP) Studies*

In the CIDNP method, the existence of a radical intermediate in a reaction is implied through n.m.r. investigation of the product of that reaction as it is being formed. Polarization of the product by radical precursors may be observed experimentally as enhanced absorption or as emission in the n.m.r. spectrum of the product[108]. The observed signal directions are determined by the initial electron spin multiplicity of the radical pair and of its precursor[109–113]. A set of simple selection rules based on the radical pair model has been developed to permit qualitative prediction of the effects[114].

Methylene has been the subject of extensive CIDNP investigation in its reactions with alkyl halides and polyhalomethanes[115–118].

Singlet methylene produced via direct photolysis of diazirine reacts with a chlorine atom of $CDCl_3$ to give polarized $Cl_2DC—CH_2Cl$ [119], probably through the formation of a chloronium ylide which gives the polarized product via a radical-pair intermediate. Similar reaction of diazirine forms a triplet radical pair by deuterium atom abstraction from $CDCl_3$; recombination of the resulting radical pair then affords polarized $Cl_3C—CDCH_2$ [119, 120].



The fundamental difference in the mechanism of reaction of singlet and triplet methylene with toluene has been shown by an investigation of the direct and sensitized photolysis of diazomethane[118]. Ethyl benzene is formed in both cases, but direct photolysis gives methylene which inserts concertedly (no CIDNP signal being observed) whereas the sensitized photolysis gives a signal consistent with a mechanism involving energy transfer and triplet methylene (equations 14–17). The

$$\text{Sens}\,(S_0) \xrightarrow{h\nu} \text{Sens}\,(S_1) \longrightarrow \text{Sens}\,(T_1)$$

$$\text{Sens}\,(T_1) + RR'C{=}N_2(S_0) \longrightarrow \text{Sens}\,(S_0) + RR'C{=}N_2(T_1) \qquad (14)$$

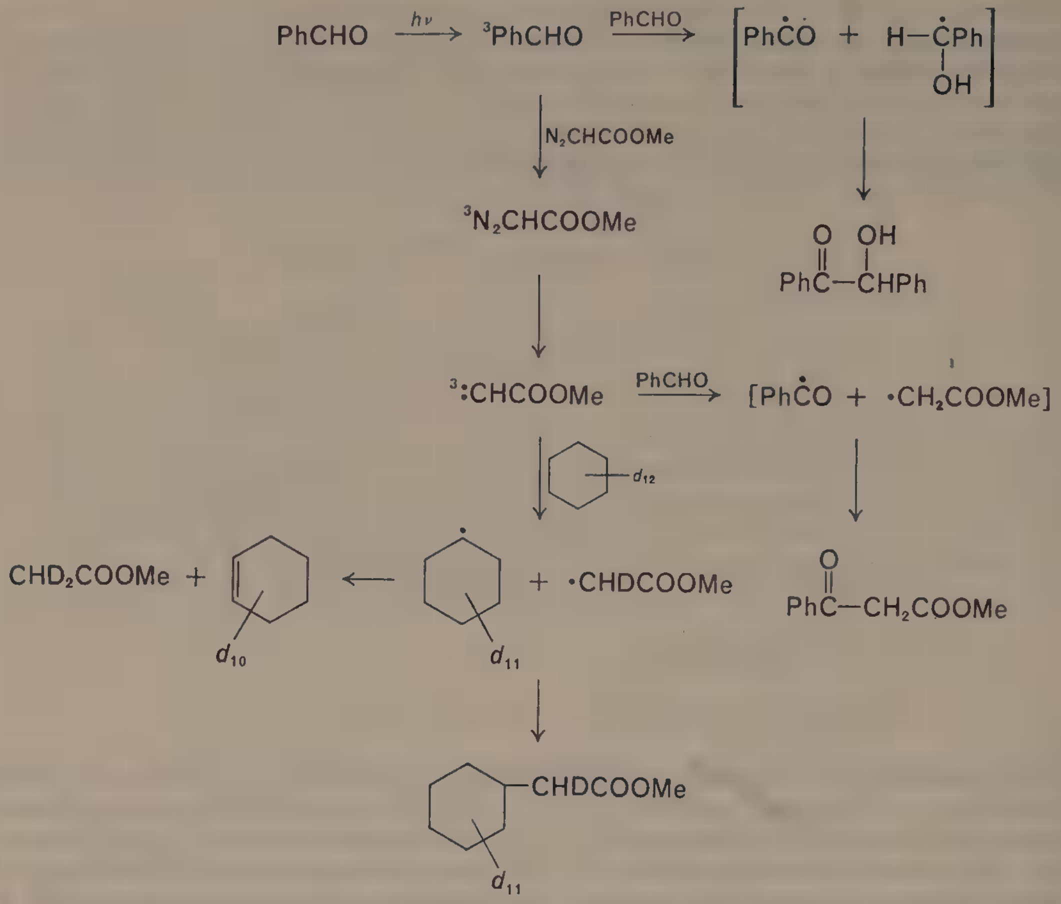
$$RR'C{=}N_2(T_1) \longrightarrow RR'C{:}(T_1) + N_2 \qquad (15)$$

$$RR'C{:}(T_1) + SH \longrightarrow RR'\dot{C}H + S\cdot \qquad (16)$$

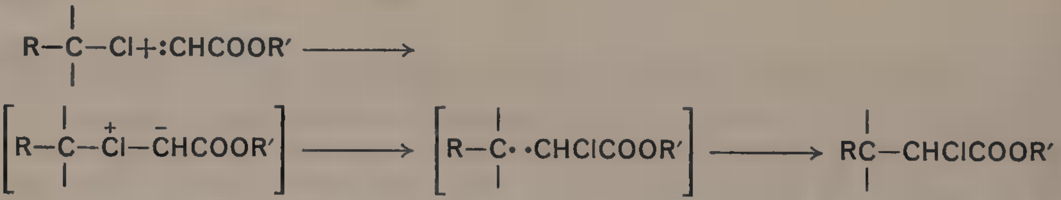
$$RR'\dot{C}H + S\cdot \longrightarrow RR'CHS \qquad (17)$$

photosensitized decomposition of methyl diazoacetate was studied by examining the effect of the diazoacetate on the CIDNP phenomena observed during the irradiation of benzaldehyde and benzoin in deuterated cyclohexane–benzene solutions. The CIDNP spectra generated by photolysis of benzoin were not changed significantly by the addition of the diazoacetate. In contrast, the spectra observed during the irradiation of benzaldehyde were suppressed by addition of diazoacetate and replaced by CIDNP signals of products formed by reaction of diazoacetate with benzaldehyde or with cyclohexane-d_{12}. These results show the energy transfer from benzaldehyde to methyl diazoacetate leading to triplet carbomethoxycarbene[121].

Photolytic decomposition of methyl diazoacetate in the presence of carbon tetrachloride and deuterochloroform affords methyl 2,3,3,3-tetrachloropropionate and methyl 3-deutero-2,3,3-trichloropropionate, respectively[122]. The slow decay of



the observed emission signals due to these polarized products suggested that the products of the reaction were being formed after irradiation ceased. Primarily on the basis of this observation, a free radical chain mechanism was forwarded for the reactions of carbomethoxycarbene with carbon tetrachloride and deuterochloroform. However, this conclusion has recently been reconsidered in the light of the radical-pair theory of CIDNP which does not allow spin polarization in a radical-induced recombination step[123]. The preferred mechanism to account for the formation of the methyl propionates involved carbene attack at halogen with consequent ylide formation[124]:

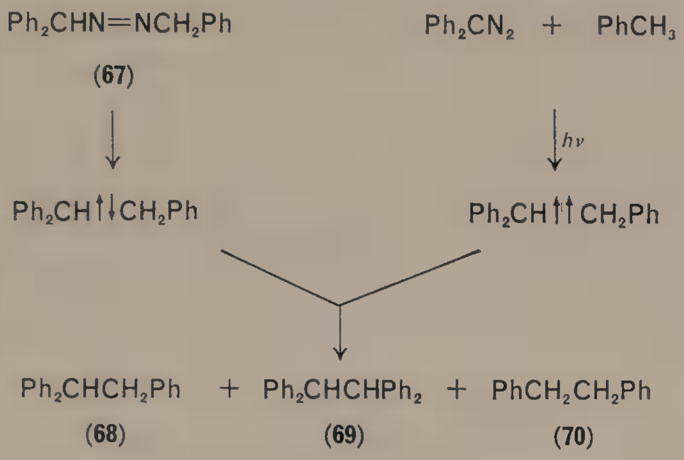


$$R-\overset{|}{\underset{|}{C}}-Cl+:CHCOOR' \longrightarrow$$

$$\left[R-\overset{|}{\underset{|}{C}}-\overset{+}{Cl}-\overset{-}{C}HCOOR'\right] \longrightarrow \left[R-\overset{|}{\underset{|}{C}}\cdot\ \cdot CHClCOOR'\right] \longrightarrow R\overset{|}{\underset{|}{C}}-CHClCOOR'$$

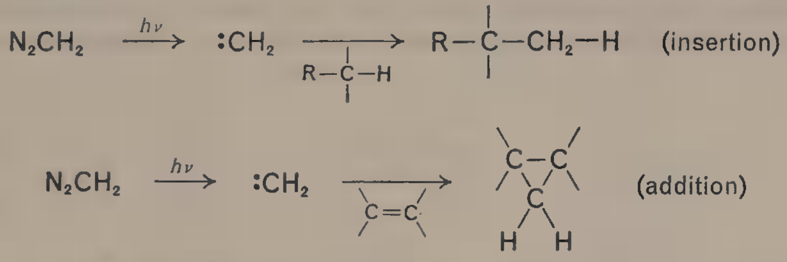
The recombination of geminate pairs formed presumably by homolysis of a chloronium ylide is the more likely mechanism. The ^{13}C CIDNP patterns are in accord with the cage recombination of radical pairs, but inconsistent with a radical chain mechanism[123].

Closs compared the photolysis of diphenyldiazomethane in toluene solution[111] and the thermal or photolytic decomposition of the azo compound **67**. Both reactions afforded the same products **68–70**, but the ratio of unsymmetrical to symmetrical products **68**/(**69**+**70**) was higher in the reaction of **67** (ratio 1·5 : 1) than in the diphenylcarbene reaction (ratio 1 : 1). The n.m.r. spectra obtained from the two reactions showed opposite polarization in confirmation of theoretical predictions for radical pairs of different multiplicity. Since there is little doubt that acyclic azo compounds decompose through the singlet state[125], this experiment assigns triplet multiplicity to the radical pairs intervening in the diphenylcarbene reaction.

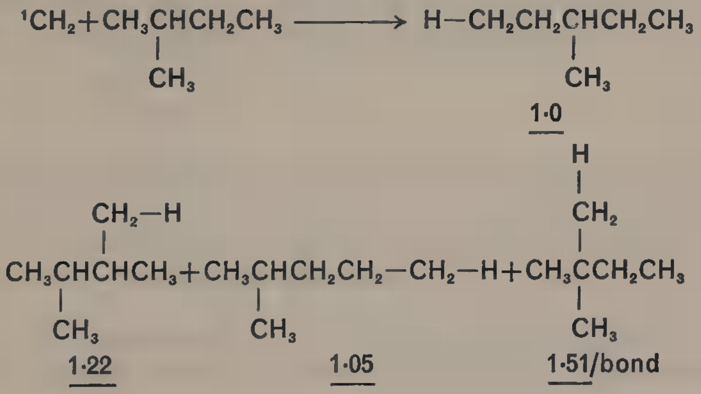


C. *Spin Multiplicity and Reactivity of Methylene*

A principal aim in the photochemistry of diazo compounds is to correlate the observed chemistry with the multiplicity, singlet or triplet, of the carbenes formed. Two typical reactions are observed: insertion into a C—H bond and addition to an unsaturated bond:

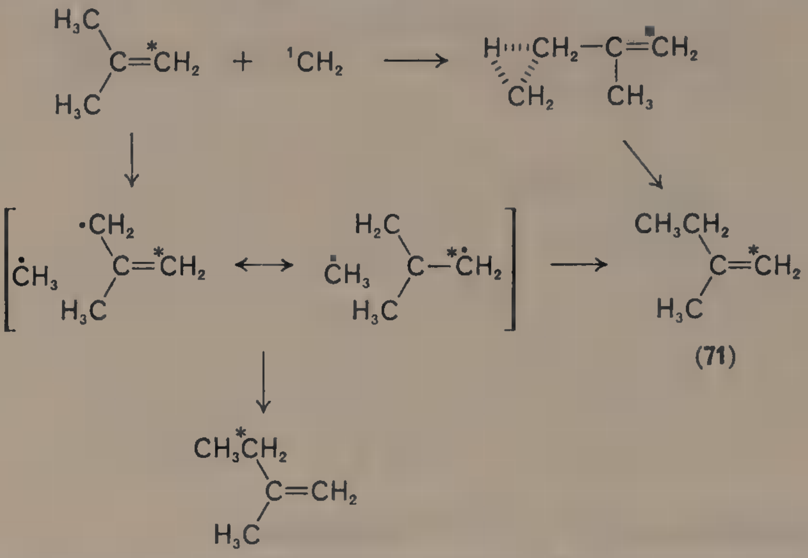


Singlet methylene $^1CH_2$ generated by the photolysis of diazomethane inserts into the C—H bonds of alkanes with nearly random statistical preferences. An example is provided by the liquid phase photolysis of diazomethane in 2-methylbutane[126]:



Only slight preferences for the tertiary hydrogen (1·51) and the secondary hydrogen (1·22) appear.

One may ask whether the CH_2 insertion is direct or whether some intermediate, such as a radical pair, is involved. Doering and Prinzbach[127] photolysed diazomethane in the presence of 2-methyl[1-^{14}C]propene and studied the distribution of the radioactive label within 2-methyl-1-butene, the product of allylic C—H insertion.

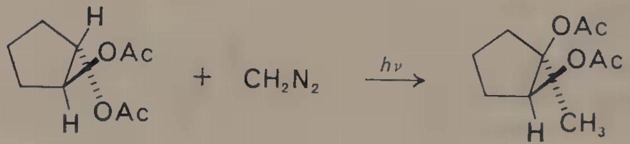


(71)

(72)

In the liquid phase less than 2% scrambling occurred, whereas 8% of **72** was obtained in the vapour phase.

Studying the configurational relationship between substrate and insertion product, Franzen reported that methylene reacted with the tertiary carbon–hydrogen bonds in the *trans* diacetate (73) with inversion[128, 129]. However, generally the insertion of carbene has been shown to proceed with retention[130]. Optical activity is maintained in the reaction with the methoxycarbonylcarbene[131] and methyl-(−)(*S*)-2-methoxypropionate and silicon–hydrogen bond[131, 132].



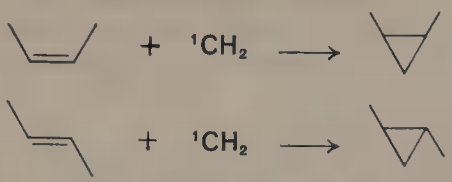
(73)

Ho and Noyes had shown that the reaction of triplet methylene with propane involved abstraction[133], since dimeric products, hexane and 2,3-dimethylbutane, were isolated:

Average values for the relative rates of abstraction by triplet carbene are: primary/secondary/tertiary = 1/2/7.

Incisive information concerning the chemical characteristics of singlet and triplet carbenes comes from study of addition reactions involving carbon–carbon double bonds[134–137].

As in C—H insertion, singlet methylene adds stereospecifically in a concerted step: both bonds of the cyclopropane are formed simultaneously since such a step may occur with spin conservation. The additions of $^1CH_2$ (from photolysis of diazomethane in liquid phase) to *cis*-2-butene and *trans*-2-butene yield only *cis*-1,2-cyclopropane and *trans*-1,2-dimethylcyclopropane, respectively. These additions are stereospecific; the geometrical relationship of the olefinic substituents is preserved in the products:



This behaviour has been taken as evidence that the addition of $^1CH_2$ to an olefin is a direct reaction and no diradical intermediate intervenes. Triplet methylene generated in the gas phase by the mercury photosensitized decomposition of ketene adds to olefins with greater discrimination: e.g. its addition to butadiene is 6·6 times faster than to isobutene; the corresponding ratio with singlet methylene is 3·2. The increased preference of $^3CH_2$ for butadiene can be attributed to the radical character of this addition, which presumably involves a diradical intermediate somewhat stabilized by allylic resonance:

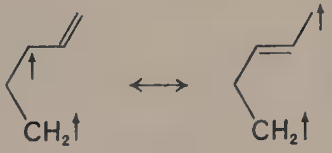
TABLE 11. Relative rates of methylene addition to olefins[138]

Olefin	$^1CH_2$ [a]	$^3CH_2$ [b]
	0·91	0·96
	1·07	0·64
	1·00[c]	1·00[c]
	0·58	0·33
	0·65	0·31
	3·20	6·64
	0·87	0·56
	0·72	0·35
	0·68	0·35

[a] From photolysis of ketene with 2600 Å.

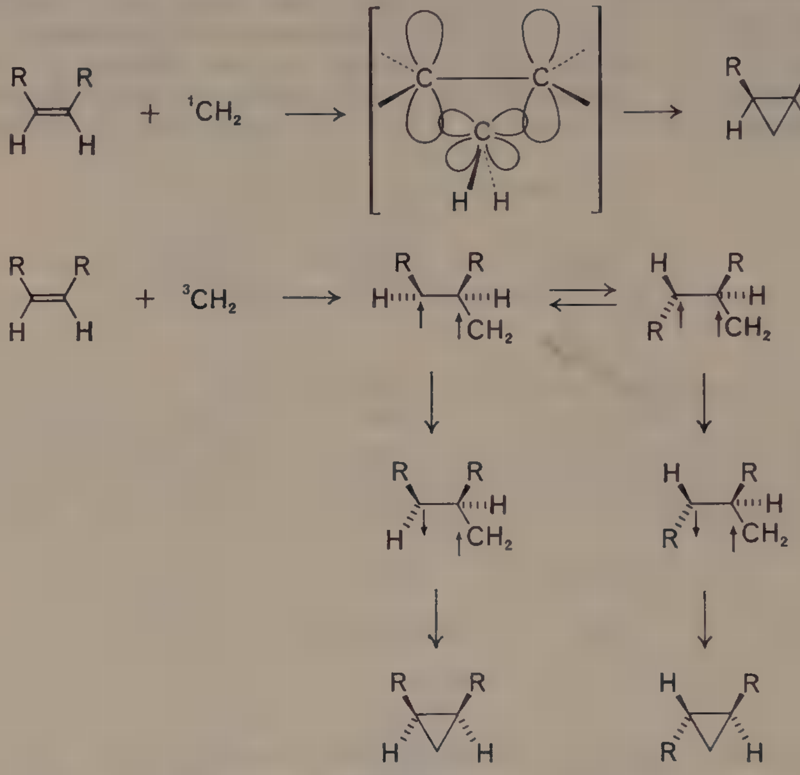
[b] From mercury photosensitized reaction of ketene with 2537 Å.

[c] Standard.



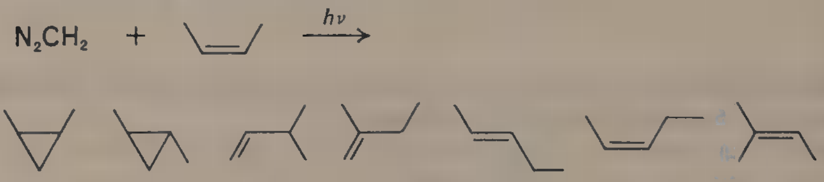
The addition of triplet methylene to *cis*- and *trans*-2-butenes is an indirect, two-step reaction and takes place non-stereospecifically. Both *cis*- and *trans*-1,2-dimethylcyclopropanes are formed from either starting olefin. This phenomenon, which is now believed to be diagnostic for triplet carbene additions, is most readily understood in terms of the Skell–Woodworth hypothesis.

Skell argued that the addition of a triplet carbene to an olefin would generate a triplet trimethylene intermediate, in which rotation about the single C—C bonds would be at least as rapid as the spin inversion needed before formation of the final cyclopropane C—C bond could occur. The addition of a triplet carbene to *cis*- or *trans*-2-butene should then yield both *cis*- and *trans*-1,2-dimethylcyclopropanes. On the other hand, addition of a singlet carbene could be stereospecific, since there would be no spin restriction on the simultaneous formation of both cyclopropane C—C bonds.



SCHEME 3

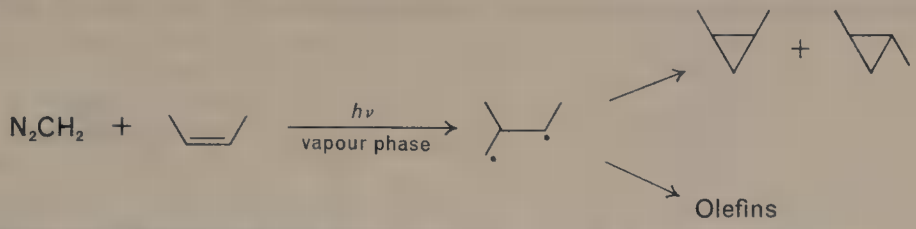
Dilution with a 200-fold excess of inert perfluoropropane induces some intersystem crossing in either the diazomethane, or more likely in the methylene itself, as the following product distributions reveal[139, 140]:



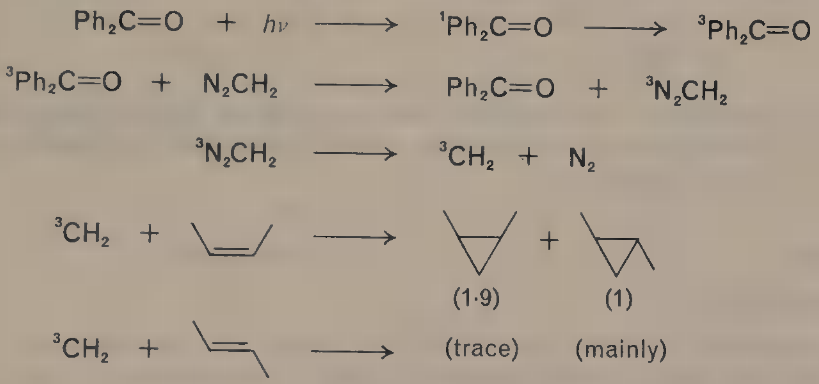
C_3F_8							
None (%)	47·5	0·4	0·2	0·3	0·0	39·1	12·5
Excess (%)	60·4	13·3	6·1	1·9	7·1	9·3	1·9

SCHEME 4

Methylene produced by irradiation of diazomethane in the vapour phase in the presence of high pressure inert gases gives non-stereospecific addition to 2-butene[140, 141]:



Benzophenone-photosensitized decomposition of diazomethane induces a limited non-stereospecificity in the addition reaction[142]. The sensitized reactions should produce triplet methylene, while direct irradiation is known to produce the singlet. In the presence of an inert gas or in inert solvents, singlet methylene may decay to the triplet before reacting with the unsaturated substrate.

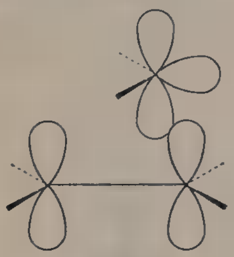


SCHEME 5

A number of factors can influence the stereospecificity of the addition, notably solvent cage effects or unusual rapid intersystem crossing. In spite of some difficulties, Skell's criterion appears to work well in practice in distinguishing between singlet and triplet carbene species.

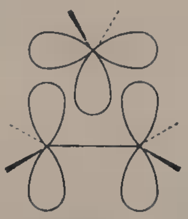
Theoretical justification has been forthcoming, through Extended Hückel Theory (EHT) calculations[143–146].

A theoretical analysis of the addition of $^1CH_2$ to ethylene suggests initiation of the reaction as in **74**, a 'π-approach' in which the vacant p orbital of the carbene begins to overlap with the π-system. As reactants move along the reaction coordinate towards product geometry, the π-approach goes over to a 'σ-approach'[143]. Transfer of electron density from the olefin's π-system to the carbene's p orbital occurs; this is an electrophilic addition[134, 147–149].



(74)

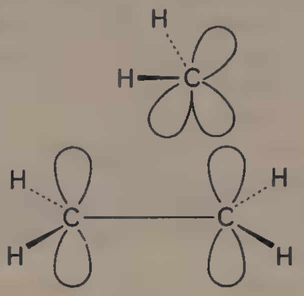
π-approach



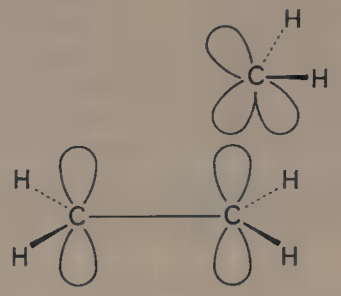
(75)

σ-approach

More recent calculations suggest that π-approach **74a** is energetically preferable to π-approach **74b** in the addition of singlet methylene. Addition of CF_2 is calculated to follow a similar course, with less charge transfer from olefin to carbene in the transition state[150]. Related calculations for additions of CH_2 and CF_2 to isobutene



(74a)



(74b)

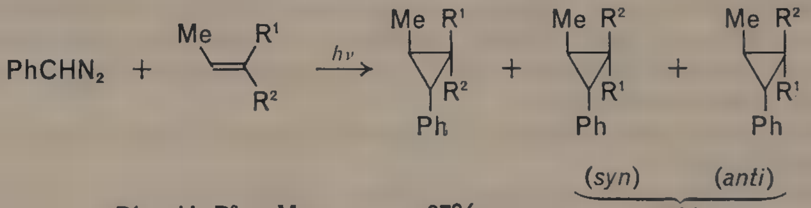
again suggest that **74a** is preferred to **74b**, but only by a small energy difference. The results of these calculations must be treated cautiously, as a guide to thought rather than as firm conclusions.

D. *Photolysis of Aromatic Diazo Compounds in Olefins*

1. Phenylcarbene

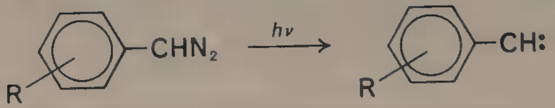
The ground state of phenylcarbene has been designated as triplet on the basis of matrix isolation[151], which has been extended to 4 K [152], and of its emission spectrum[153], and by extended Hückel calculation[154].

The chemical behaviour of phenylcarbene generated by photolysis of phenyldiazomethane appears to be substantially singlet rather than triplet. Gutsche reported only about 3% non-stereospecificity in the addition of phenylcarbene to



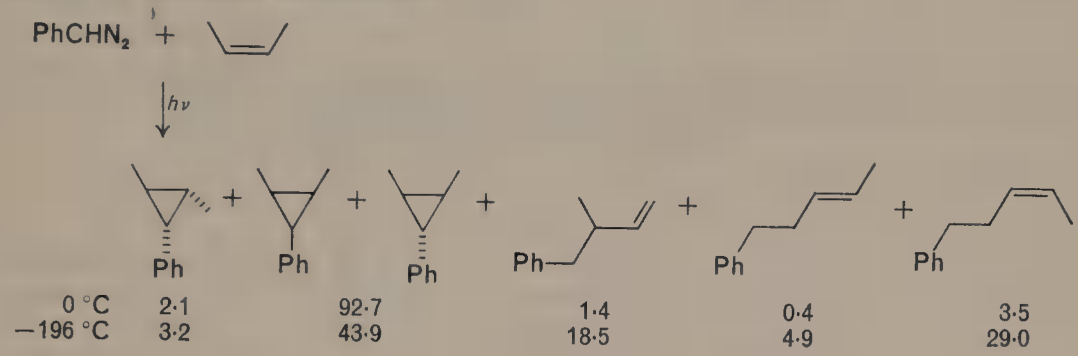
		(syn)	(anti)
R¹ = H, R² = Me	97%	3%	
R¹ = Me, R² = H	2·5%	51·1%	46·4%

TABLE 12. Relative rates of addition of arylcarbenes to olefins

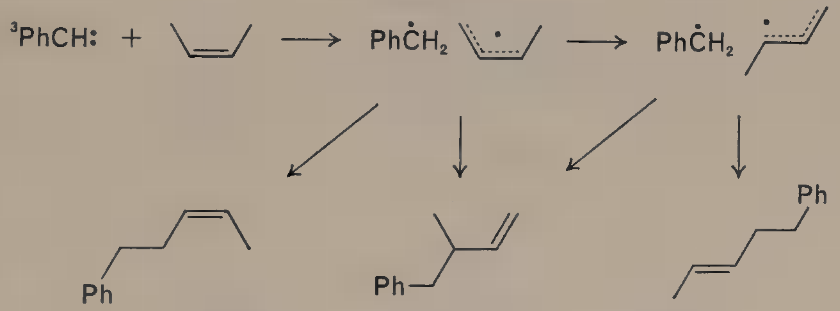


R					
H	1·02	1·80	1·00	0·91	3·3
m-Cl	1·27	1·79	1·00	1·2	—
p-Cl	1·14	1·9	1·00	1·1	—
p-Me	0·84	1·78	1·00	0·83	2·4
p-OMe	0·70	1·6	1·00	0·77	—

trans-2-butene and about 2·5% non-stereospecificity in its addition to *cis*-2-butene [155]. Closs reported corresponding values of 0·5–1% and 3–5% [156]. The high stereospecificity can be taken as support for a singlet state of the reactive intermediate[137]. The results could be consistent with triplet phenylcarbene addition if there was a very fast ring closure allowing only incomplete rotamer equilibration in the intermediate trimethylene diradical. Moss and Doelling have presented evidence that the properties of triplet phenylcarbene are quite different from those of the singlet[157]. These authors find that irradiation of a frozen solution of phenyldiazomethane in *cis*- or *trans*-2-butene yields not only cyclopropanes but products of abstraction–recombination reactions as well. They suggest that triplet phenylcarbene reacts largely by hydrogen abstraction.



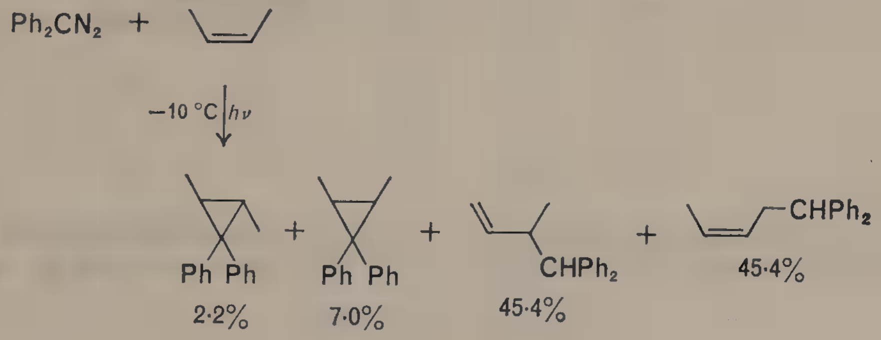
SCHEME 6



SCHEME 7

2. Diphenylcarbene

In the photolysis of diphenyldiazomethane in the presence of olefins the major reaction path with *cis*- and *trans*-2-butene is hydrogen abstraction from the allylic positions, followed by recombination of the radical fragments. More highly substituted olefins give even greater percentages of abstraction–recombination:



With less substituted olefins cyclopropanes predominate, and with isobutene and propene only cyclopropanes result. Clearly the mode of reaction of diphenylcarbene (Table 13) depends intimately upon the olefin[158]:

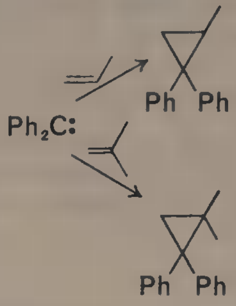
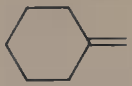
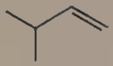
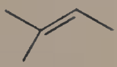
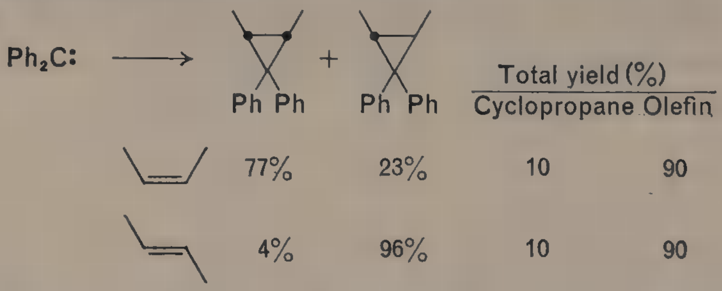


TABLE 13. Mode of reaction of diphenylcarbene with olefins

Olefin	Cyclopropane (%)	Abstraction–Recombination (%)
	100	0
	100	0
	87	13
	74	26
	52	48
	22	78
	8	92
	0	100

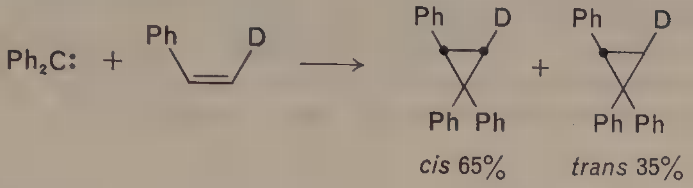
Closs reports that *cis*-2-butene gives a *cis* : *trans* ratio of either 87 : 13 [159] or 77 : 23 [160] and that *trans*-2-butene gives a *trans* : *cis* ratio 96 : 4 [159]. Thus they must be formed mainly from the singlet state:



There is a growing conviction that singlet and triplet diphenylcarbene are in equilibrium, thus leading to reactions of both spin states occurring at the same time:

$$ {}^1\mathrm{Ph_2C}: \rightleftarrows {}^3\mathrm{Ph_2C}: $$

From *cis*-β-deuterostyrene and diphenylcarbene roughly 65% *cis* and 35% *trans* adducts were formed[158]:



Obviously, in systems in which triplet abstraction is the primary reaction, the cyclopropanes will be formed largely from the singlet. This appears to be the case with the 2-butene.

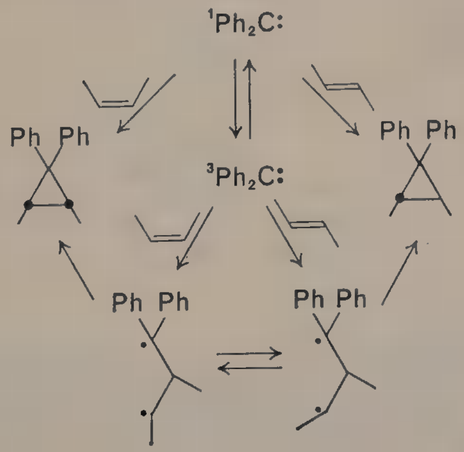
The stereospecificity increases at lower temperatures, for example, at −10 °C with *cis*-2-butene, *cis*- and *trans*-1,2-dimethyl-3,3-diphenylcyclopropanes are formed in a ratio of 3·2, while the corresponding ratio with *trans*-2-butene is only 0·04; at −66 °C the product ratio obtained from *cis*-2-butene is 9·0.

The *cis* : *trans* cyclopropane ratio can be affected by addition of hexafluorobenzene, a molecule inert to diphenylcarbene[158]. With 80–95% hexafluorobenzene, there can be no more than 12% singlet reacting. Presumably unreactive collisions allow diphenylcarbene to approach equilibrium more closely and the ground-state triplet is naturally favoured. The presence of oxygen does not change the isomer ratio although the total yield of cyclic and acyclic hydrocarbons is greatly diminished and approaches zero for high oxygen concentration.

TABLE 14. Addition of diphenylcarbene to styrene in the presence of added hexafluorobenzene

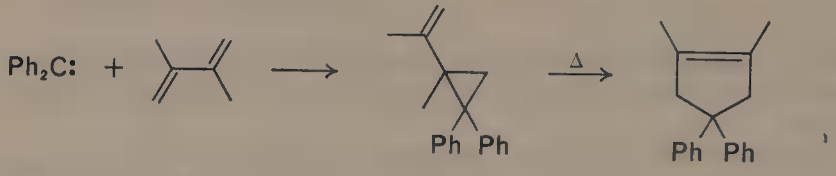
C_6F_6 (mol.-%)	*Cis* adduct (%)	*Trans* adduct (%)
0	65	35
36	60	40
50	59	41
80	56	44
90	55	45
95	56	44

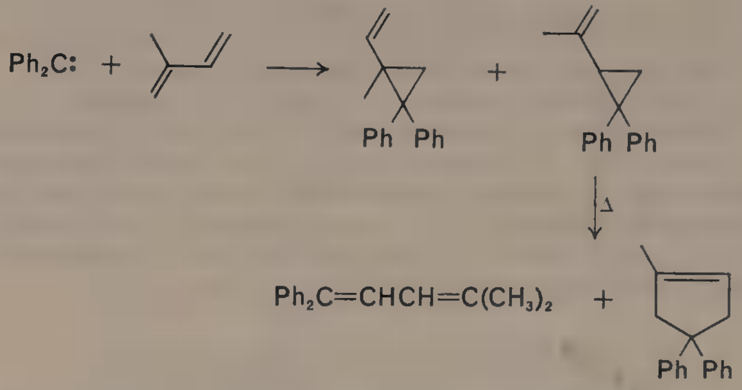
All these observations are most consistent with a mechanistic scheme as outlined in below:



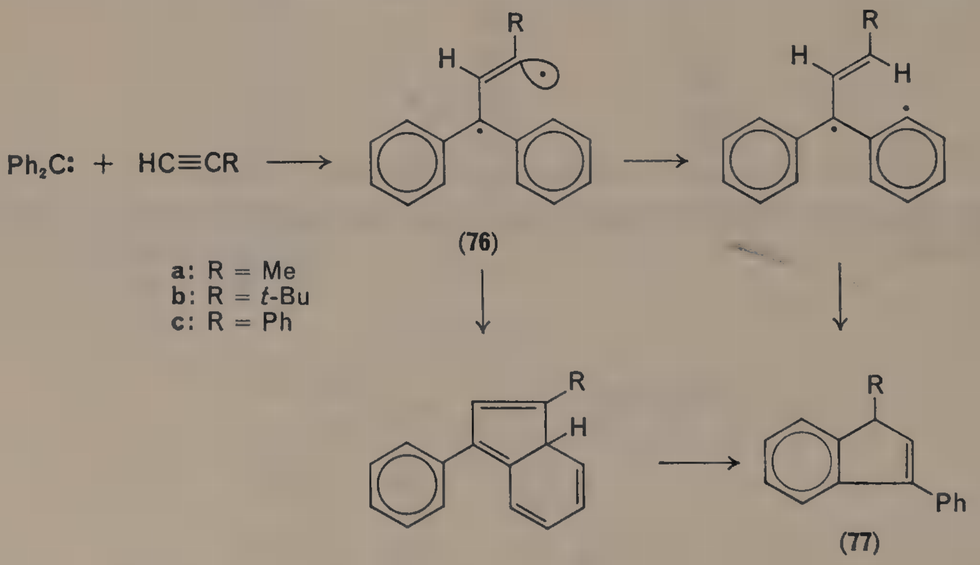
It is postulated that intersystem crossing is much faster than any other reaction. Furthermore, it is assumed that the reverse crossing is also very fast so that both electronic configurations are effectively in equilibrium.

One might well expect a triplet to be more likely to undergo 1,4-addition than a singlet, since the intermediate diradical might not be restricted to 1,2-closure. Even with triplets, however, acyclic dienes yield only 1,2-adducts[158, 161].

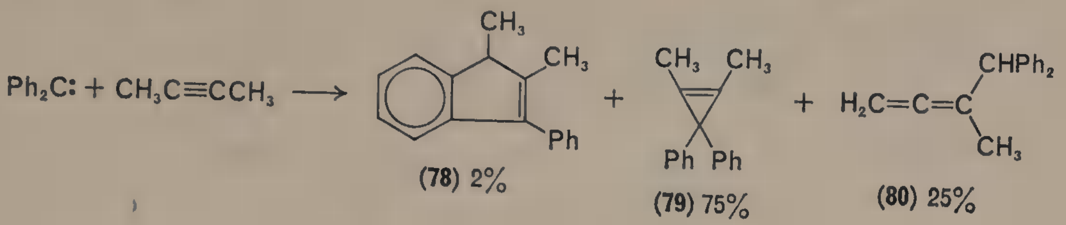




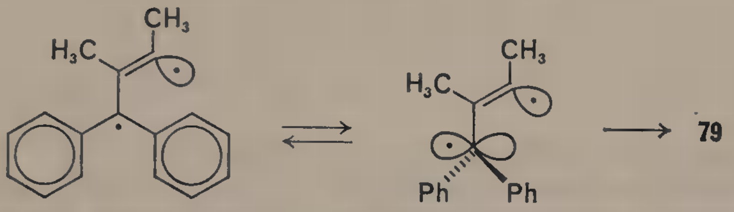
Triplet diphenylcarbene reacts with alkynes by addition and abstraction, and each of the reactions is a two-step process. With monosubstituted acetylenes, indenes are the sole products as shown. Addition of diphenylcarbene to the less substituted



end of the acetylenes generates **76**, which may or may not be initially the triplet carbene shown, but in any event it should quickly relax to yield **77**. In the reaction of diphenylcarbene with dimethylacetylene, the main products are the cyclopropene (**79**) and the allene (**80**). Compound **80** is probably the product of hydrogen abstraction reflecting the unavailability of an unsubstituted end of the acetylene for attack by diphenylcarbene. However, both **78** and **79** are formed through addition to give **81**. The added methyl group causes a new effect: the most obvious difference between **81** and **76** involves the methyl-aromatic ortho-hydrogen interaction indicated in **81**.

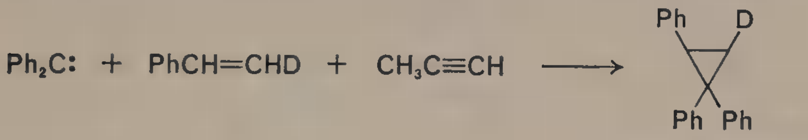


(**78**) 2% (**79**) 75% (**80**) 25%



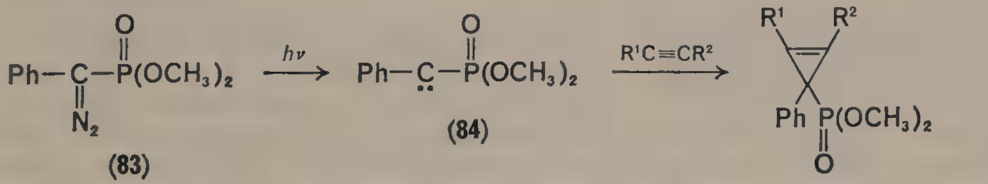
(**81**) (**82**)

Competition between *cis*-β-deuterostyrene and methylacetylene for the irradiation product of diphenyldiazomethane gave mainly addition to styrene and only traces of indene. This is reasonable, since styrene is a much better triplet trap than propene. Phenylacetylene competes more successfully and 25% of the products in a competition reaction with styrene are derived from addition to the acetylene.



cis/*trans* = 59/41

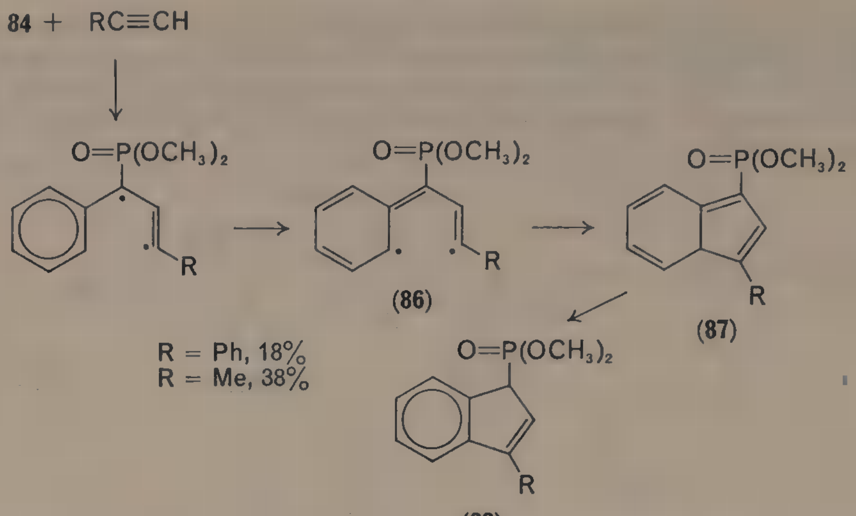
(Dimethoxyphosphoryl)phenylcarbene (**84**), produced photolytically from **83**, reacts with alkynes to give satisfactory yields of dimethyl 1-phenyl-2-cyclopropenylphosphonates (**85**)[162]. With monosubstituted alkynes, ring closure to dimethyl-3-indenylphosphonates (**88**) competes with the formation of **85**. The carbene **84**



(**83**) (**84**) (**85**)

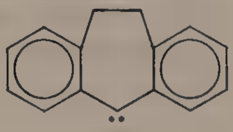
$R^1 = R^2 = Ph$, 61%
$R^1 = R^2 = Me$, 55%
$R^1 = Ph, R^2 = Me$, 41%
$R^1 = Me, R^2 = H$, 59%

apparently attacks the unsubstituted alkyne carbon atom with formation of the diradical **86** which yields first **87** and then **88**.



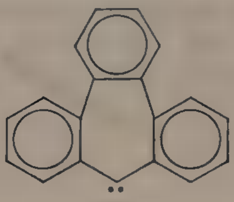
(86) **(87)** **(88)**

Moritani and coworkers[163] found that cyclopropanes were not formed by attack of **89** on 2-butene but that some products of abstraction–recombination could be found. The similarity between carbene **89** and diphenylcarbene may seem odd since **89** appears flat, at least on paper, and diphenylcarbene has been shown[164] to be bent and twisted. Carbenes **90** and **91** are even less flexible and both give products

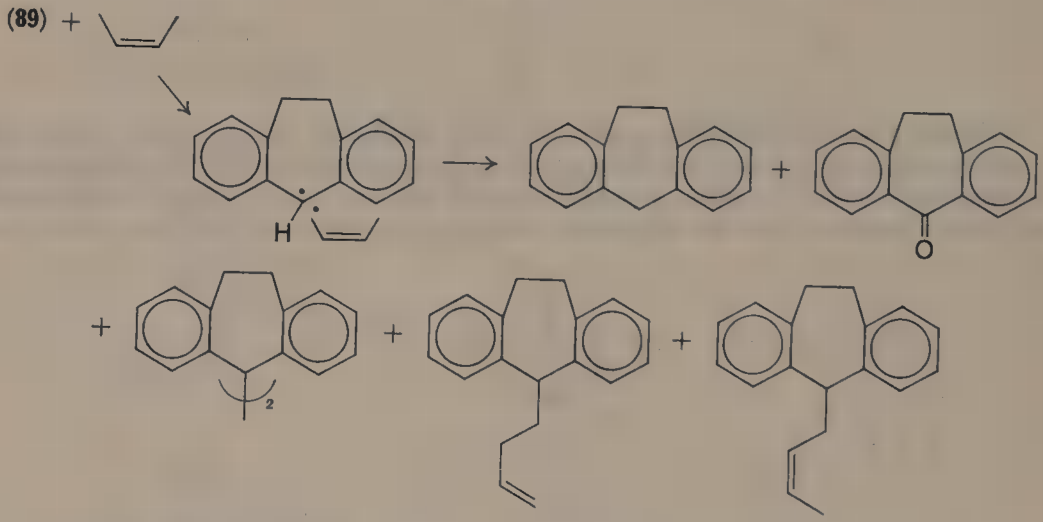


(89)

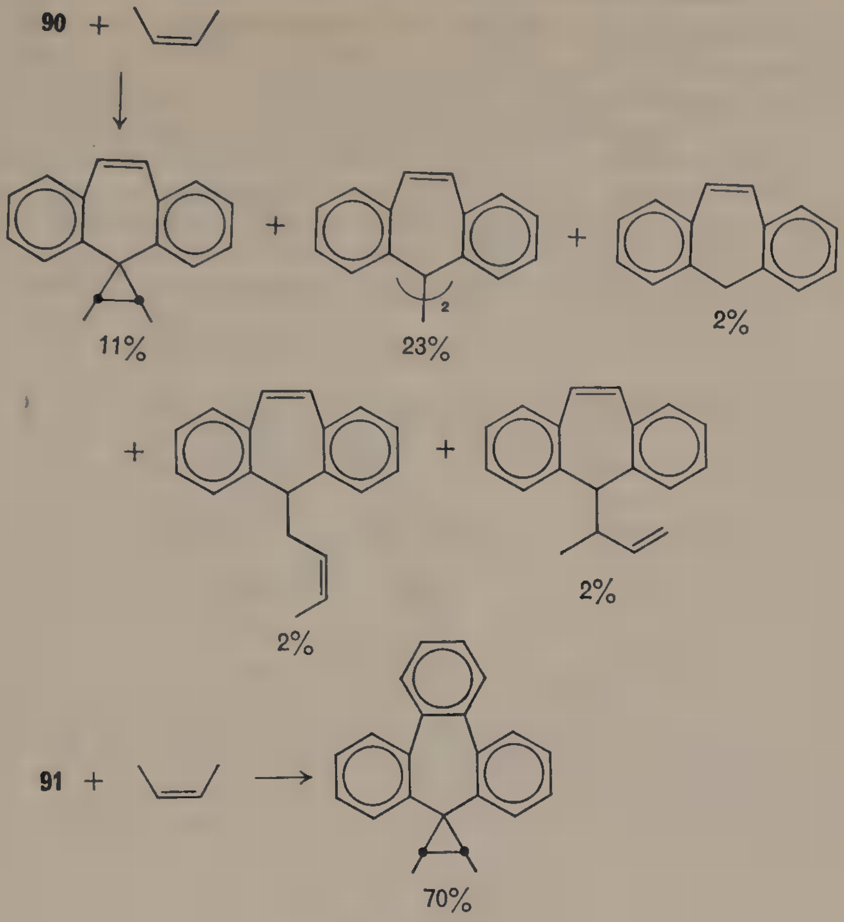
(90)

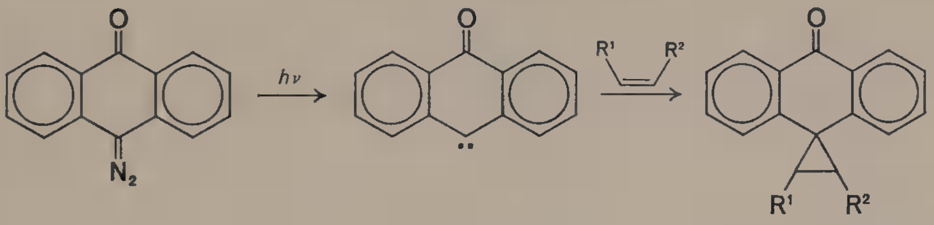


(91)



of addition to olefins[165, 166]. Remarkably the cyclopropanes are formed in a stereospecific fashion. Carbene **90** gives a spectrum of products which seems to implicate a mixture of spin states. Irradiation of diazoanthrone in cyclohexane again led to products of hydrogen abstraction, with no cyclopropane being formed[167]. Olefins not containing allylic hydrogen did form adducts, however[168].





R¹ = R² = H, 39%
R¹ = Ph, R² = H, 93%

3. Fluorenylidene

Fluorenylidene, generated by photolysis from 9-diazofluorene, unlike diphenylcarbene, adds to π-systems without the complication of large amounts of hydrogen abstraction. Fluorenylidene adds easily to a variety of olefins[169]. With *cis*-2-butene as the solvent, *cis*-dimethylspirocyclopropane-9-fluorene and its *trans* isomer are formed in a ratio of 1·95, while irradiation in *trans*-2-butene gives the same products in a ratio of 0·06. This memory effect becomes much smaller when the reaction mixture is diluted with hexafluorobenzene as an inert solvent. At the highest dilution,

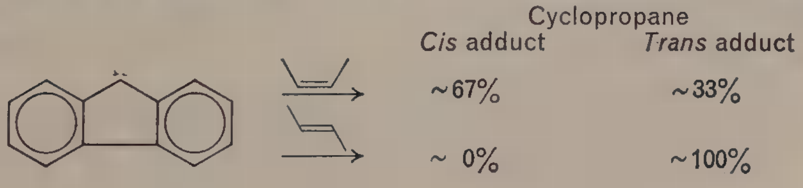
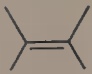
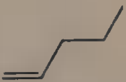
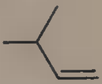
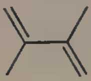
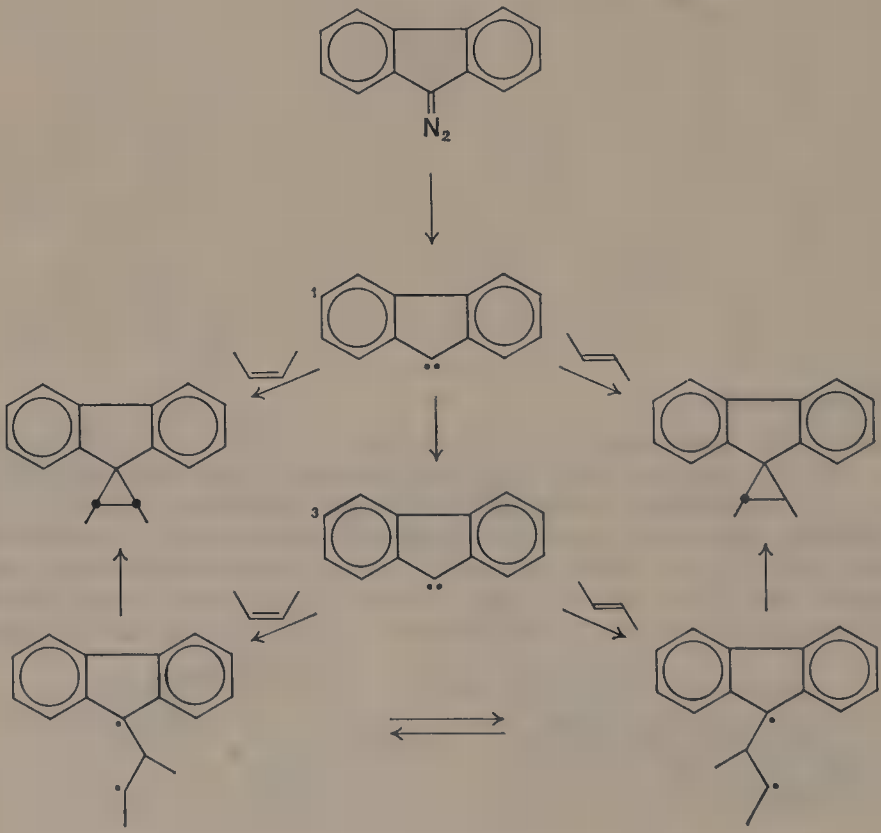


TABLE 15. Relative rates of fluorenylidene addition to olefins

Olefin	90% C_6F_6	Pure olefin
	0·37	0·66
	1·00	1·00
	1·70	0·47
	0·86	0·38
	0·40	0·43
	0·69	0·56
	9·00	3·5



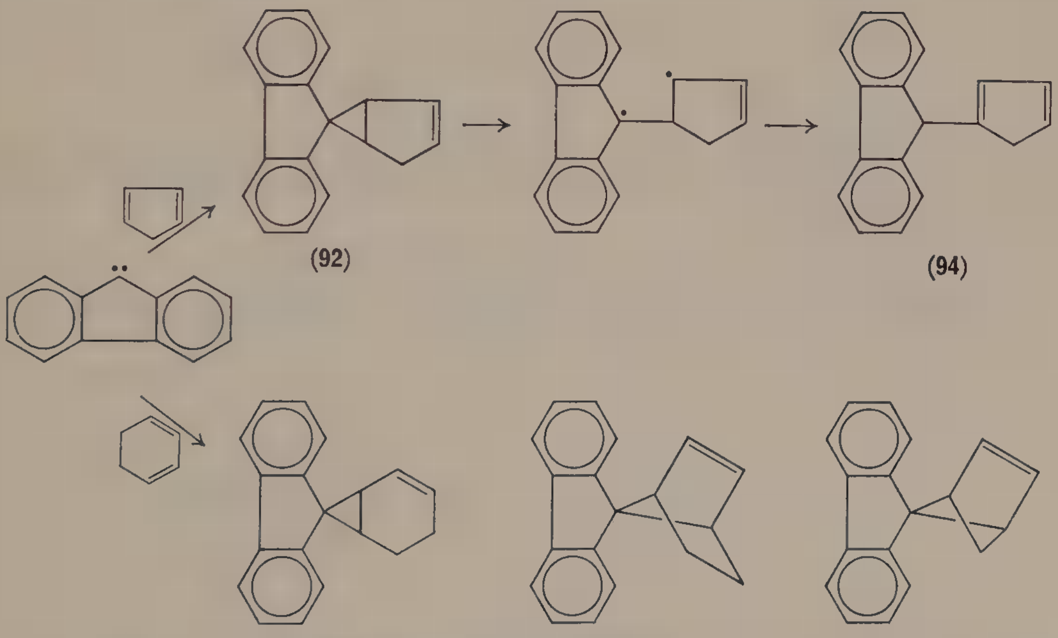
when the solution was approximately 0·1 M in olefin, the corresponding ratios were 0·25 and 0·14. These observations fit a mechanism involving stereospecific addition of a metastable singlet fluorenylidene and a competing addition from the triplet ground state occurring with complete loss of stereospecificity.

It is possible selectively to filter out the triplet state by allowing it to react with a triplet trap such as butadiene, with which the triplet seems to react particularly fast. As can be seen from Table 16, the more butadiene is added, the more stereospecific the addition becomes. Of course at high butadiene concentrations very little product is observed from the reaction with the 2-butene, and precise numbers become very difficult to obtain.

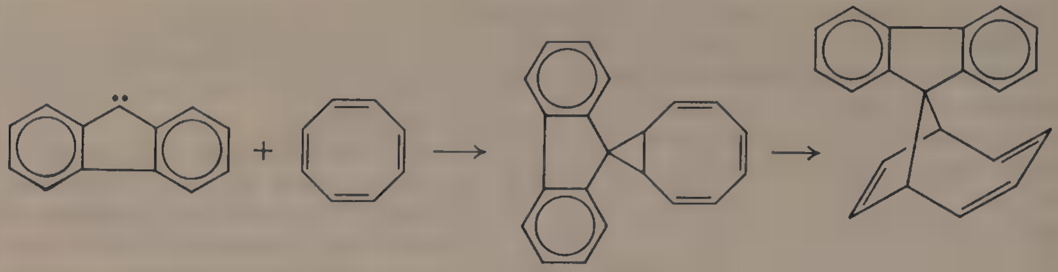
TABLE 16. Reaction of fluorenylidene with *cis*-2-butene in the presence of 1,3-butadiene

Butadiene (mmol)	*cis*-2-Butene	*Cis*/*trans* ratio of cyclopropane
0	10·0	2·1
3·0	6·0	10·1
11·5	3·0	49

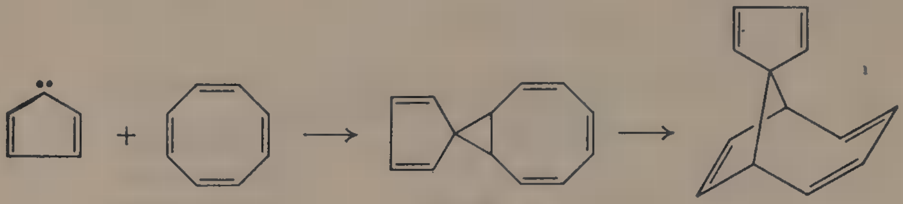
Fluorenylidene was found to add to cyclopentadiene to give only **92** and to add to cyclohexadiene to give **95**. No trace of the hypothetical 1,4-adducts **93** and **96** could be found. Diphenylcarbene also gives 1,2-adducts with cyclopentadiene[170]. The reactions of fluorenylidene and cyclopentadienylidene[171, 172] with cyclooctatetraene are normal and no 1,4-addition products are found. The further rearrangements of the initially formed adducts **97** and **98** have been studied.


(92) (94)

(95) (96) (93)



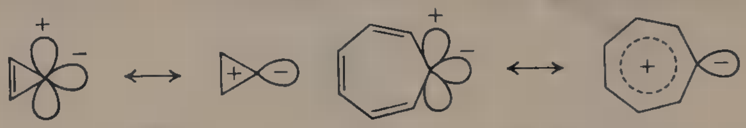
(97)



(98)

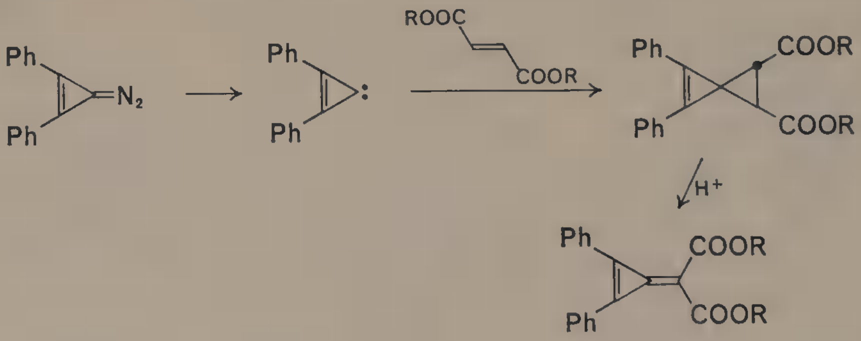
4. Cyclopropenylidene, cycloheptatrienylidene and cyclopentadienylidene

For cyclopropenylidene (**99**) and cycloheptatrienylidene (**100**), it was hoped that the singlet carbene would derive important stabilization from the aromaticity expressed by the resonance hybrids which are shown below:

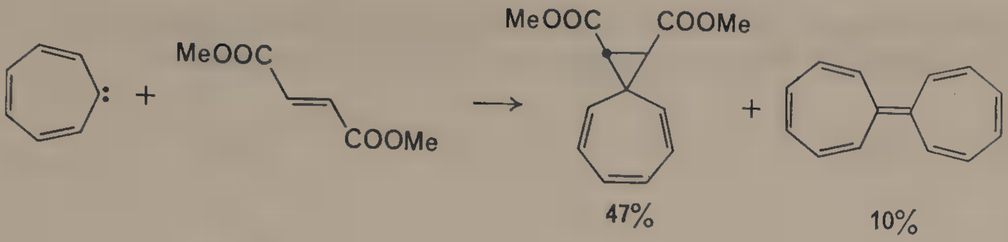


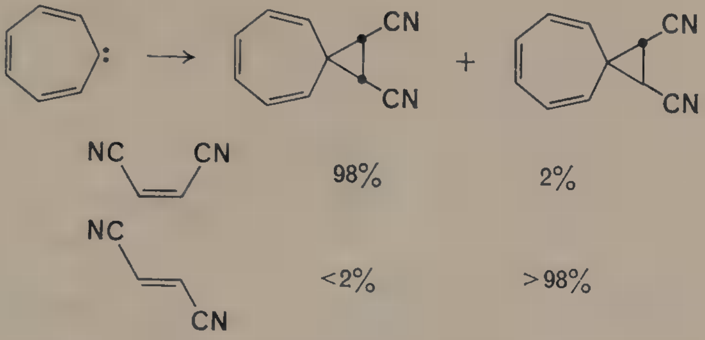
(99) **(100)**

Important contributions by these forms would be shown by nucleophilic behaviour and, indeed, only olefins with electron-poor π-bonds have proved to be suitable substrates for these systems[173].



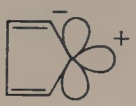
When tropylidene is generated at lower temperatures, heptafulvalene is the only product. It is not captured by simple alkenes, but it does add stereospecifically to electron-poor olefins such as dimethyl fumarate or maleate, and to mixture of *para*-substituted styrenes in such a way that ρ can be deduced to be $+1{\cdot}05$. These findings suggest that tropylidene is a nucleophilic singlet, the electron-donating character being imparted by resonance contribution form **100**.

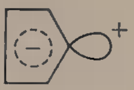




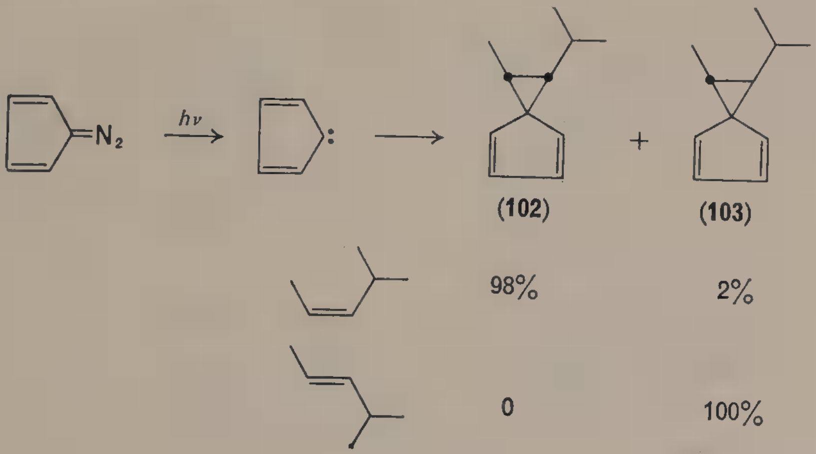
The ground state of cyclopentadienylidene is known to be a triplet in which one unpaired electron is localized in plane sp^2 orbital, while the other electron is in the π-system[174]. The singlet state of the carbene may be expressed as the resonance hybrid **101**. Recent calculations indicate that the configurations **(101a)** and **(101b)** are within 0·2 eV [175]; the resulting extensive configuration interaction will lead to mixing and the singlet is therefore best represented as the entire resonance hybrid **101**.


(101a)

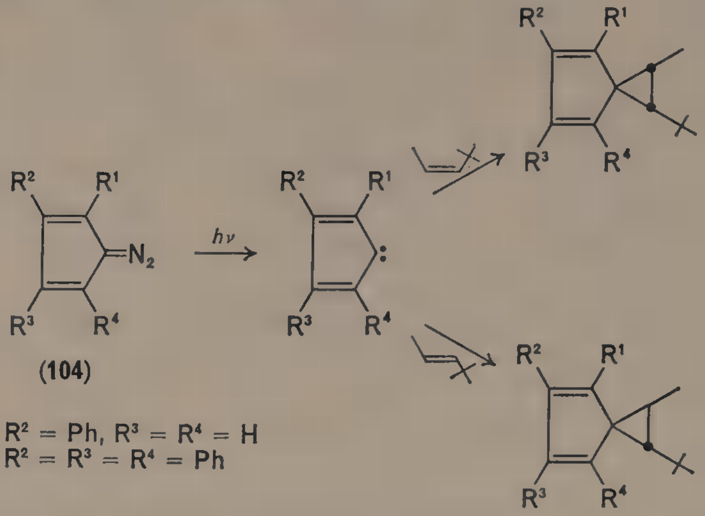

(101b)


(101c)

Photolysis of diazocyclopentadiene in *trans*- and *cis*-4-methyl-2-pentene led to spiro[2.4]heptadienes **102** and **103**, respectively, in good yields. The addition is nearly, but not completely, stereospecific. Addition of either hexafluorobenzene or



perfluorobutane has little effect on the stereochemistry. The reacting state seems to be the singlet, although the ground state is known to be the triplet.

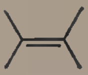
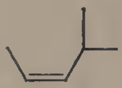
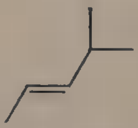


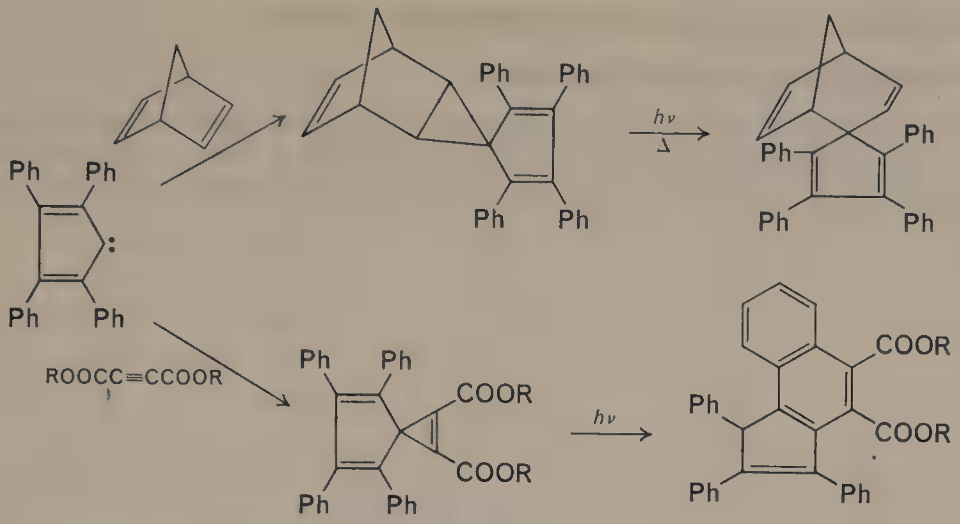
(104)

a: R¹ = R² = Ph, R³ = R⁴ = H
b: R¹ = R² = R³ = R⁴ = Ph

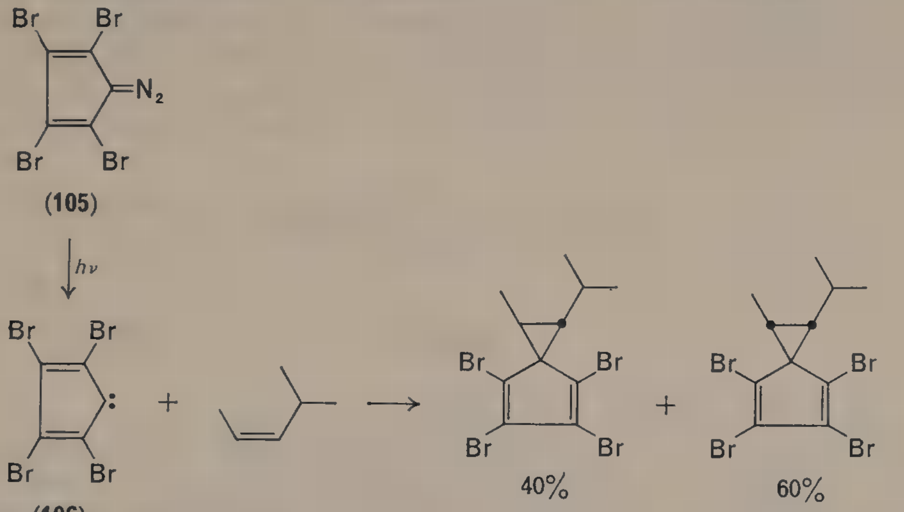
A variety of phenyl-substituted cyclopentadienylidenes has been examined. The properties do not seem much changed by phenyl substitution[176]. Norbornadiene gives an initial adduct which rearranges further on photolysis[177]. Alkynes give cyclopropenes which though isolable rearrange further[178, 179].

TABLE 17. Relative rates of addition of carbenes **106** and **107**

Olefin	Carbene **106**	Carbene **107**
	0·29	1·23
	1·00	1·00
	1·35	—
	—	0·19
	—	0·21
	—	0·24
	1·25	0·21
	0·93	3·0



The photolytic addition of **105** to the double bond of *cis*-4-methyl-2-pentene proceeded non-stereospecifically[180]. The properties of **106** can best be described as arising from the triplet state. The steric requirement of **106** is quite large and hence

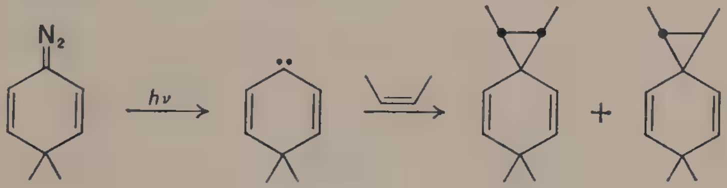


(105)

(106)

might allow many non-reactive collisions to occur, and thus give the carbene time to undergo intersystem crossing. In addition, heavy atoms are known to enhance the probability of spin-forbidden transitions through coupling of spin and orbital angular momenta.

4,4-Dimethylcyclohexadienylidene undergoes additions similar to that of the five-membered ring compound[181] (Table 17).

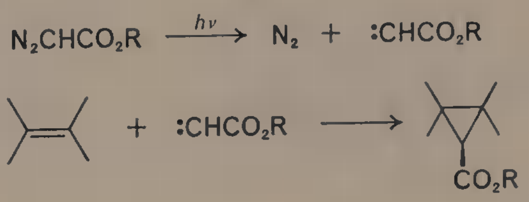


(107)

E. Photolysis of Diazocarbonyl Compounds in Olefins

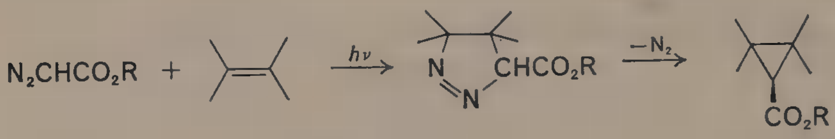
1. Intermolecular addition reactions

Diazo esters react with olefins by two distinct paths to produce cyclopropanes. Diazoacetic ester might lose nitrogen under the influence of heat or light to produce a carboalkoxycarbene which adds to the olefin or to the acetylene giving a cyclopropane or cyclopropene carboxylate.



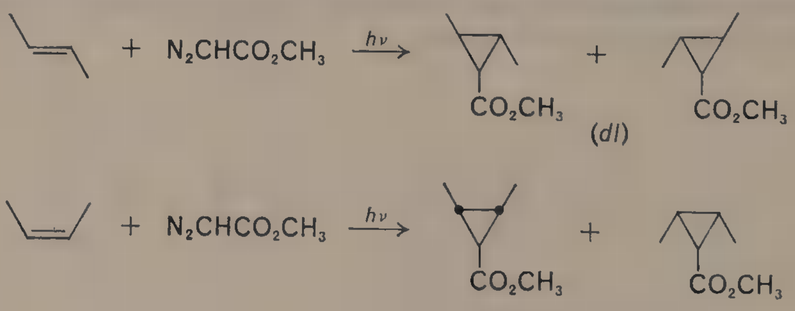
PATH A

Alternatively, the diazoacetic ester might react with the olefin to form a pyrazoline which loses nitrogen to produce the cyclopropane carboxylate. In non-photochemical reactions of double or triple bonds conjugated with a carbonyl, imine or nitrile group, 1,3-dipolar addition of the diazo group usually occurs to give a pyrazoline or pyrazole which is stable under the reaction conditions.

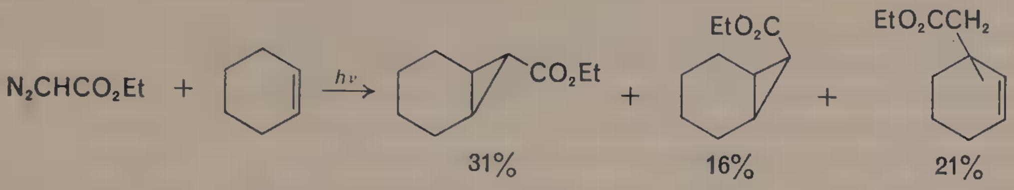


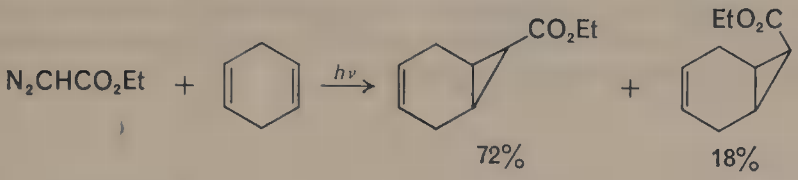
PATH B

Carboalkoxycarbenes are involved in reactions above 100 °C and in photochemical reactions. Carboalkoxycarbenes behave as electrophilic species. With *cis*- and *trans*-2-butene, photochemically produced carboalkoxycarbene adds in a stereospecifically *cis* manner. Thus, Doering and Mole[182] showed that methyl diazoacetate and *cis*-2-butene gave a mixture of two *meso* cyclopropanecarboxylic esters, whereas *trans*-2-butene gave only the corresponding racemic mixture:



Addition to cyclic or asymmetric double bonds gives the less hindered adduct[183–185]:



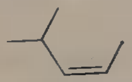
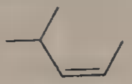


An attempt to compare singlet and triplet states of photolytically generated carboalkoxycarbenes has been made by Jones and his collaborators[186, 187].

Direct photolysis of dimethyl diazomalonate has been shown by these investigators to afford a reactive intermediate whose chemical properties differ markedly from those of the corresponding species produced via benzophenone-sensitized photodecomposition of the same diazo ester. It is thought that the reacting species produced in the direct and sensitized photodecompositions are singlet and triplet biscarbomethoxycarbenes, respectively. The results with *cis*- and *trans*-4-methyl-2-pentene are shown in Table 18. Since the addition is only 90–92% stereoselective, (*cis*) rather than 100% stereospecific, it is possible that in the direct photolysis the carbene is not formed exclusively in one spin state, but predominantly in one state

TABLE 18. Product distribution in the reactions of dimethyl diazomalonate with *cis*-4-methyl-2-pentene and *trans*-4-methyl-2-pentene

(108a) (108b)

Conditions	108a (%)	108b (%)	Yield (%)
hν + 	92	8	39·8
hν + 	10	90	24·3
hν + Ph₂CO + 	10	90	43·0
hν + Ph₂CO + 	14	86	—

and to a lesser extent in the other. In an attempt to induce intersystem crossing from the singlet to the triplet, the photolysis of methyl diazomalonate in *cis*-4-methyl-2-pentene was studied in varying concentrations of hexafluorobenzene. Only when very large amounts of hexafluorobenzene are added does the amount of *trans*-cyclopropane increase significantly. Indeed, initially, the amount of *cis*-cyclopropane increases slightly. A likely source of this increase is excited methyl diazomalonate, which could produce *trans*-cyclopropane by addition to the double bond followed by loss of nitrogen. As hexafluorobenzene is added fruitless collisions could deactivate the excited diazo compound to the ground state, producing more *cis*-cyclopropane until enough has been added so that all excited diazo compound has been deactivated and intersystem crossing begins.

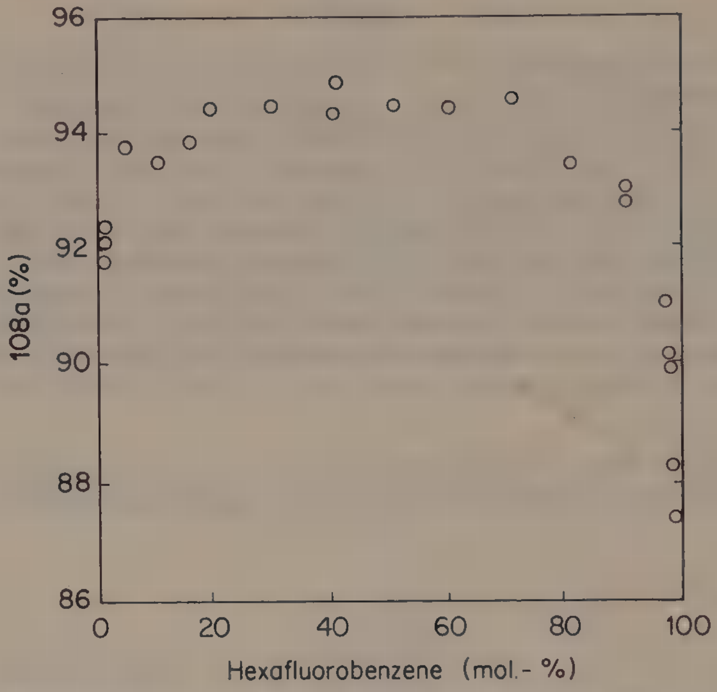
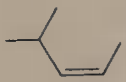


FIGURE 14. Addition of dimethyl diazomalonate to *cis*-4-methyl-2-pentene in hexafluorobenzene. [Reprinted with permission from Jones, *J. Amer. Chem. Soc.*, **94**, 7469 (1972). Copyright by the American Chemical Society.]

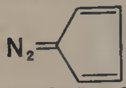
In a recent study of the benzophenone-sensitized photolysis of dimethyl diazomalonate in the presence of *cis*-4-methyl-2-pentene, the ratio of products (**108a**)/(**108b**) was larger in the presence of dimethyl sulphide than in its absence[188]. Singlet carbenes generally act as electrophiles, although the bulkier ones are subject to steric hindrance. In contrast to the large amount of data reported on singlet relative rates, only fragmentary information is available for triplets. Diphenylcarbene is reported to add to 1,3-butadiene and 1,1-diphenylethylene 100-times faster than to *cis*-2-butene[189]. This comparison is unsatisfactory since diphenylcarbene reacts with *cis*-2-butene primarily by hydrogen abstraction, not addition[190]. Table 19 shows that in the sensitized photolysis there is a three- to four-fold increase in the relative rate of addition to dienes over monoolefins, and there is a decrease in the relative rates of addition to certain olefins, e.g. to 2,3-dimethyl-2-butene and to *cis*-4-methyl-2-pentene.

TABLE 19. Relative rates of addition of carbenes produced in direct and sensitized photolysis of dimethyl diazomalonate

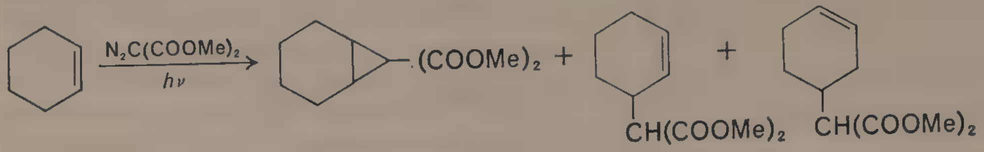
Olefin	Direct	Sensitized
	0·88	0·33
	1·00	1·00
	0·47	0·46
	0·48	0·48
	0·55	0·15
	0·23	0·13
	1·3	4·4
	—	4·5

Relative rate constants for addition of several carbenes to a series of allylic compounds were determined by means of competitive experiments[191]. Results summarized in Table 20 show that polar selectivities of carbenes are generally low but correlate with the polar nature of substituents in the carbenes. The selectivities of singlet carbenes were even lower than those of the corresponding triplet carbenes. These facts strongly support a mechanism of addition with singlet carbenes which does not involve any rate-determining process leading to polar intermediates, but involves transition states having slight contributions from polar structures.

TABLE 20. Competitive reaction of carbene with allylic compounds, $CH_2{=}CHCH_2R$

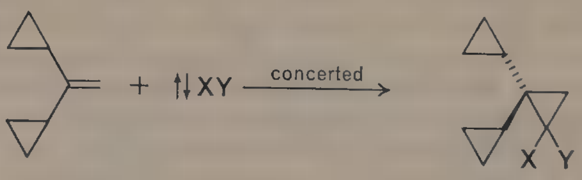
Carbene precursor	Mode of decomposition	R				
		$SiMe_3$	n-Pr	OMe	Cl	CN
$N_2CHCOOMe$	$h\nu$	2·07	1·47	1·23	1·00	0·97
$N_2CHCOOMe$	$h\nu + Ph_2CO$	2·55	1·55	0·95	1·00	0·66
$N_2C(COOMe)_2$	$h\nu$	1·85	1·50	0·93	1·00	0·66
$N_2C(COOMe)_2$	$h\nu + Ph_2CO$	3·66	2·15	1·25	1·00	1·13
N_2CHPh	$h\nu$	1·13	1·06	1·00	—	0·80
	$h\nu$	1·99	1·79	1·20	1·00	0·92
$NaOH + CHCl_3$		80·14	14·04	3·44	1·00	0·75

However, Wulfman[192], recently tried to establish the existence of bismethoxycarbonyl carbenoids by analysing the activation parameters for both catalytic and photolytic processes, but the data cast strong doubt on the existence of free carbenes during the cyclopropanation of olefins and during insertions into the allylic C—H bonds by the alleged singlet carbene. They are forced to conclude that a free singlet carbene is not an intermediate during the non-sensitized photolysis of dimethyl diazomalonate. The cyclopropane and the allylic C—H insertion products may be formed via the photoexcited diazo compound forming a complex with the olefin.

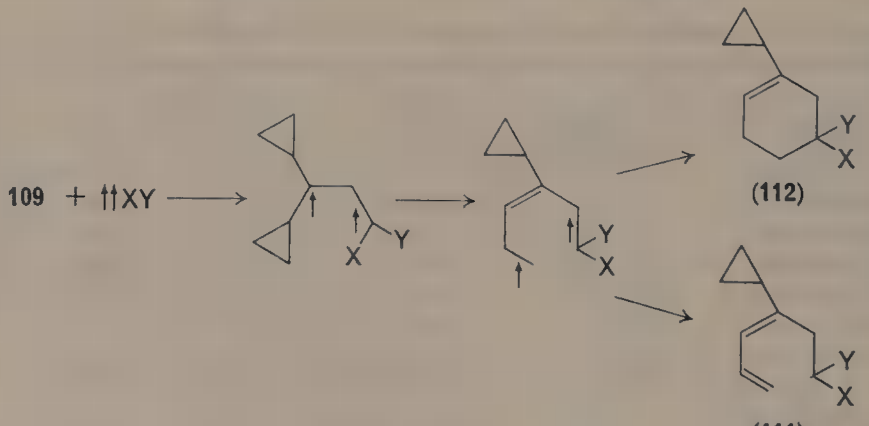


Conditions	Temperature (°C)	3-CH Insertion / Cyclopropane	4-CH Insertion / Cyclopropane
Pure	0	0·47	0·05
	54	0·46	0·11
90 mol.-% C_6F_6	0	0·46	0·23
	54	0·47	0·39
Sensitized $Ph_2C{=}O$	0	0·13	0·11
	54	0·19	0·10

An alternative criterion was proposed recently by Shimizu and Nishida[193], who used 1,1-dicyclopropylethylene (**109**) as the substrate. Here addition of a singlet carbene can proceed in the usual concerted manner to afford **110**, whereas the existence of a triplet carbene is revealed by the observation of rearranged products **111** and **112** as shown below.



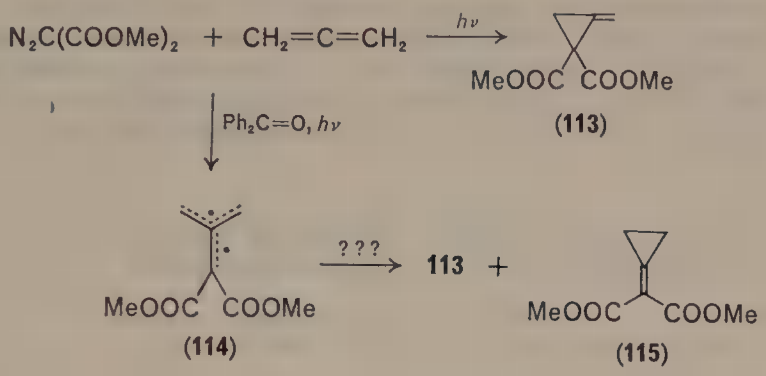
(109) **(110)**

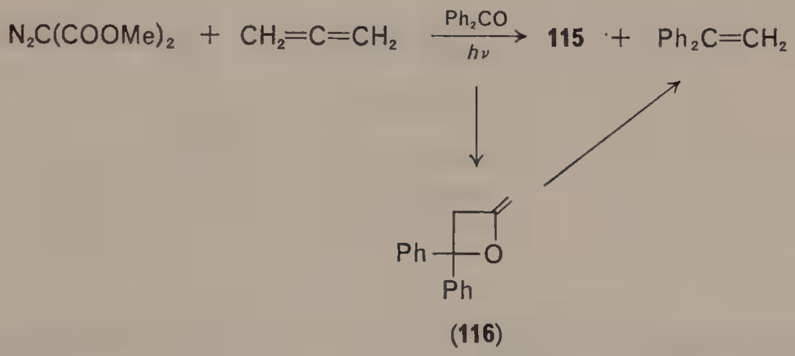


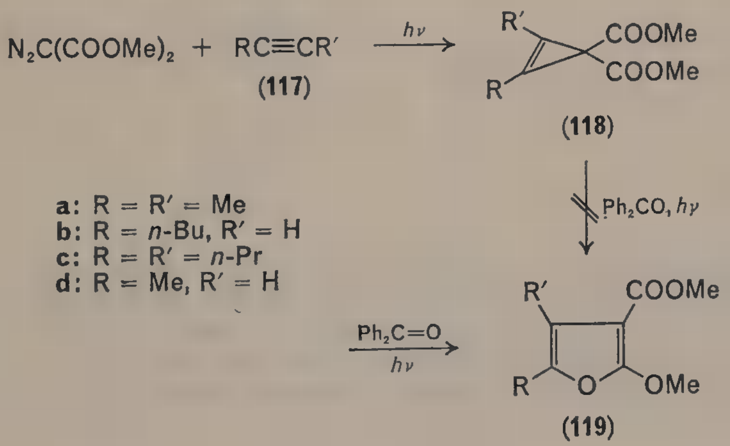
(112)

(111)

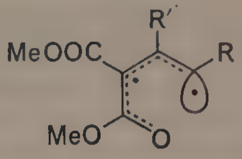
Unsensitized decomposition of dimethyl diazomalonate in allene gives **113** as the only isolable product[186]. One might have speculated that the sensitized reaction, proceeding through a triplet, would lead to trimethylenemethane (**114**), and then to **113** and **115**. A similar scrambling of label has been seen in the gas phase addition of dideuteromethylene to allene but the likely explanation for the scrambling involves hot molecule rearrangements, not spin state. The sensitized decomposition gave only **113** and 1,1-diphenylethylene in the ratio 12 : 1. The latter product probably arises via the oxetane (**116**). Hendrick[194] has observed furan formation in the reactions of triplet biscarbomethoxycarbene with alkynes. The direct photolysis of methyl diazomalonate in 2-butyne afforded the expected cyclopropene **118** in 36% yield. Only trace amounts of other products, assumed to be insertion products, were detectable.







a: R = R' = Me
b: R = *n*-Bu, R' = H
c: R = R' = *n*-Pr
d: R = Me, R' = H



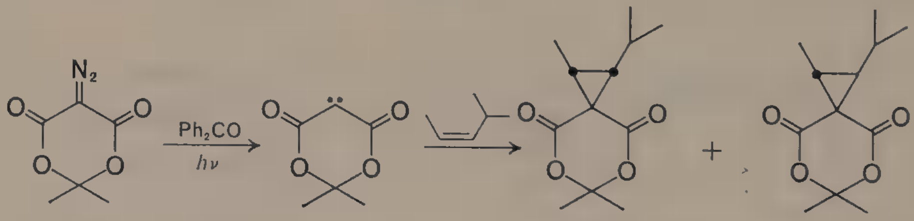
(120)

In sharp contrast, sensitization of the photolysis in 2-butyne with an equimolar amount of benzophenone gave as the major product the furan **119** in 43% yield, accompanied by only 9% yield of **118**. The course of the triplet carbene reaction can be ascribed to cyclization of the diradical **120**. It is interesting to note that the substitution of bulky groups on the acetylene results in increased closure to cyclopropene but not nearly so dramatically as in the case of diphenylcarbene.

Table 21. Relative yields of **118** and **119** from decompositions of dimethyl diazomalonate in acetylenes **117a–d**

117	Mode of decomposition	**118**	**119**
a	*hν*	99	1
a	*hν* + Ph_2CO	16	84
b	*hν*	99	1
b	*hν* + Ph_2CO	10	90
c	*hν*	99	1
c	*hν* + Ph_2CO	25	75
c	$CuSO_4$, reflux	99	1
d	*hν* + Ph_2CO	1	99

In the photolyses of the diazo compound **121**, related to Meldrum's acid, direct irradiation in olefins produced very little product of any kind, while in the sensitized decomposition adducts can be isolated in relatively good yields. The stereochemistry of the sensitized decomposition is exactly what one would expect from a triplet intermediate. These results are summarized in Table 22 [186].



(121)

Photolysis of ethyl bromo-, iodo- and chloro-diazoacetate affords the bromo-, iodo- and chloro-ethoxycarbenes, which add *cis* stereospecifically to olefins and insert to C—H bonds of alkanes, though less readily than the carboethoxycarbene. The photosensitized decomposition of ethyl bromo- and chloro-diazoacetate in olefins leads to addition products with essentially complete *cis*-stereospecificity (97%)[195].

TABLE 22. Decomposition of **121** in olefins

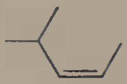
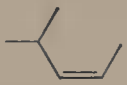
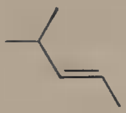
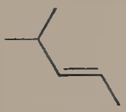
Olefin	Conditions	Yield (%)	*Cis* (%)	*Trans* (%)
	*hν*	2	—	—
	*hν* + Ph_2CO	26	14	86
	*hν*	2	—	—
	*hν* + Ph_2CO	26	15	85
	*hν*	Very small	—	—
	*hν* + Ph_2CO	17	4	96
	*hν*	Very small	—	—
	*hν* + Ph_2CO	—	6	94

TABLE 23. Relative yield of dicyanocarbene addition

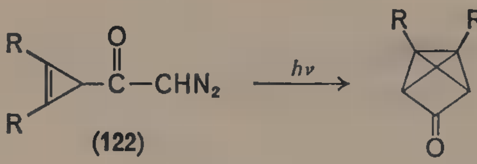
Olefins	Addition/Insertion	Dilution	*cis*-Cyclopropane (%)	*trans*-Cyclopropane (%)
	92/8	Neat	92	8
	94/6	1 : 100	60	40
	98/2	1 : 100	30	70
	88/12	Neat	6	94
	94/6	1 : 10	22	78
	98/2	1 : 100	30	70

Addition of dicyanocarbene to olefins is largely but not completely stereospecific. Addition of cyclohexane as diluent evidently induces intersystem crossing since the stereochemistry of addition becomes independent of the configuration of the starting 2-butene at 100 : 1 (cyclohexane : olefin).

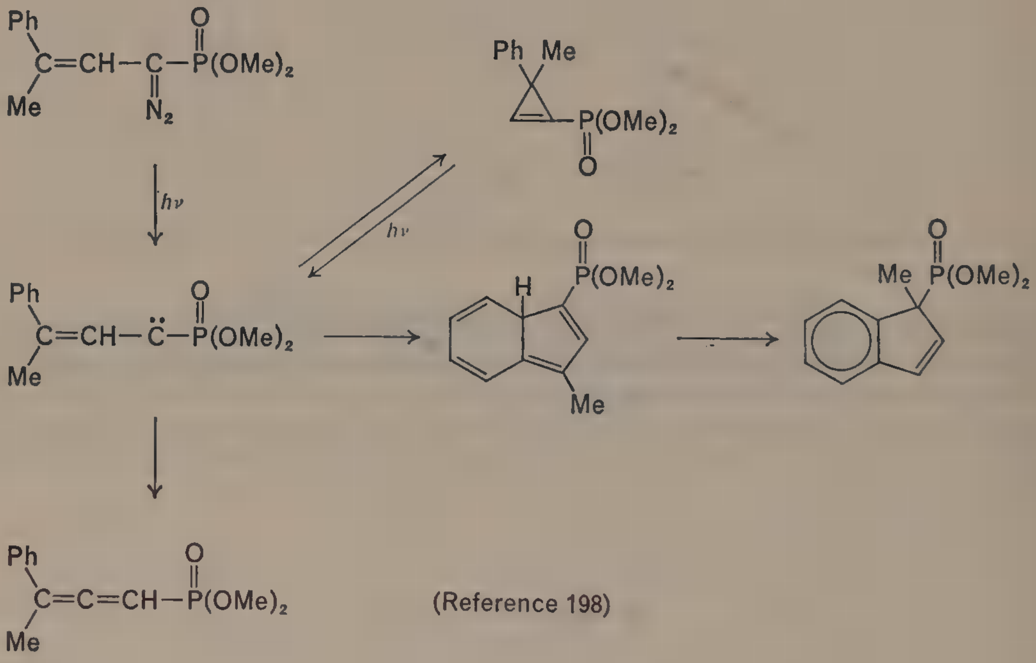
Addition to acetylenes gives cyclopropenes, and the carbon–hydrogen insertion reaction is common (tertiary/secondary/primary = 12/4·6/1) [196].

2. Intramolecular reactions

Intramolecular reaction of diazoketones also give cyclic compounds. 3-Diazomethylketocyclopropenes (**122**) are the only unsaturated ketones so far where light-effected intramolecular addition produces the tricyclo[1.1.1.0^{4,5}]pentane skeleton[197].

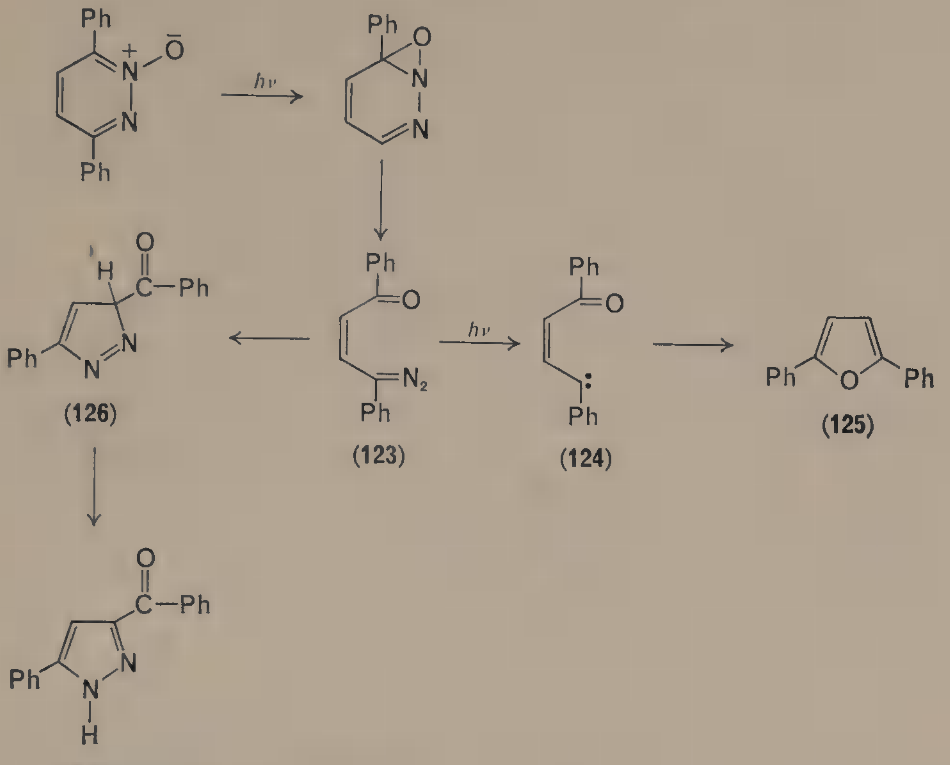


(122)

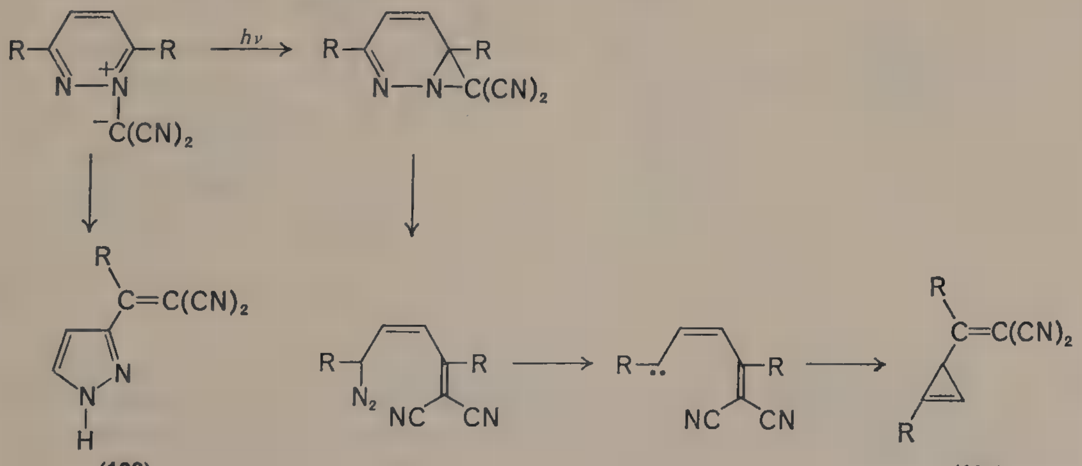


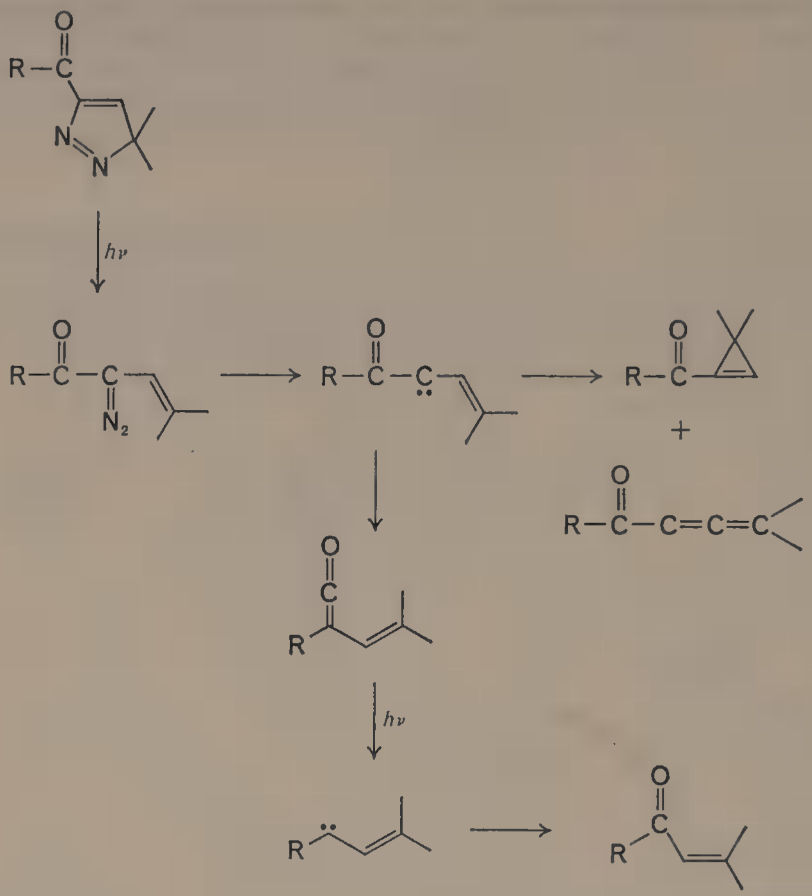
(Reference 198)

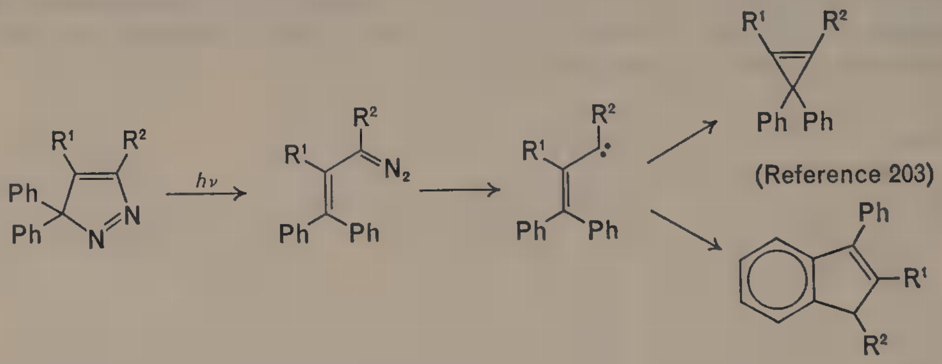
The intermediate diazoketone (**123**) obtained in the photolysis of 1,2-diazine *N*-oxide has two competitive pathways open to it[199]. One pathway is the intramolecular 1,3-dipolar cycloaddition resulting in the formation of benzoyl-5-phenylpyrazole (**127**) via the tautomeric 3*H*-pyrazole (**126**); this thermal isomerization is expected to be even faster than the known isomerization of vinyldiazomethane to pyrazole[200]. The other pathway involves photodecomposition of the diazoketone to a carbene which reacts intramolecularly to yield 2,5-diphenylfuran. Since there are competing thermal and photochemical reactions it would be expected that irradiation with more intense light source or lowering the temperature during irradiation would increase the photochemical reaction, i.e. the conversion to 2,5-diphenylfuran.



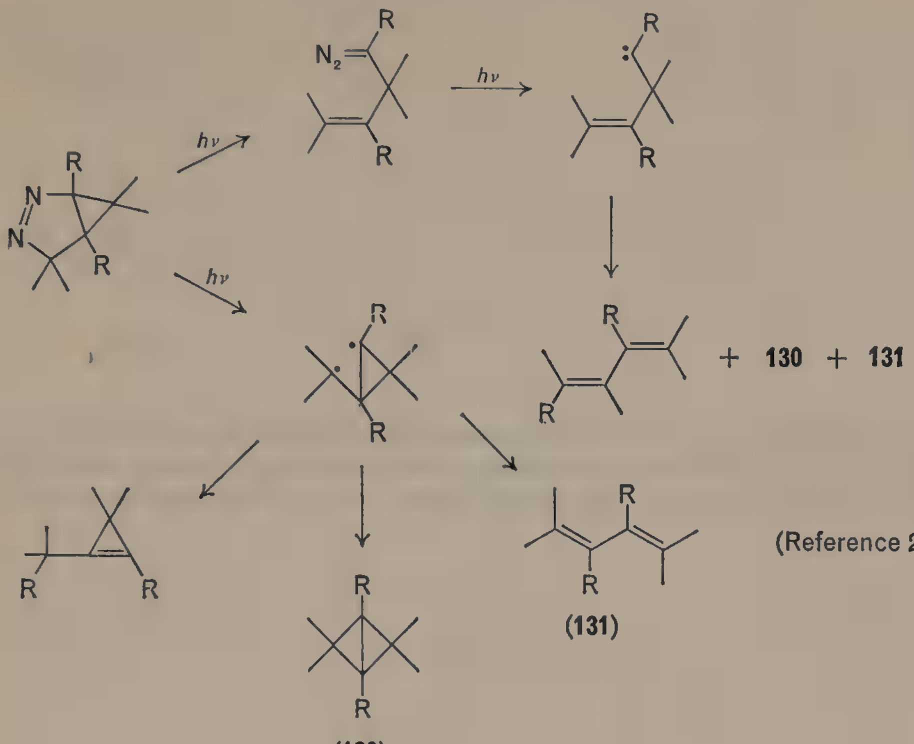
Irradiation of pyridazinium dicyanomethylylide gave 3-(2,2-dicyanovinyl)-pyrazoles (**128**) and 3-(2,2-dicyanovinyl)cyclopropenes (**129**) [201], probably through a mechanism similar to that operating in the photolysis of pyridazine *N*-oxide. Photolysis of 3-acylpyrazolines yields an α,β-unsaturated ketocarbene, which rearranges mainly into ketene. However, intramolecular addition of the α,β-ethylenic ketocarbene has been observed[202].







(Reference 203)



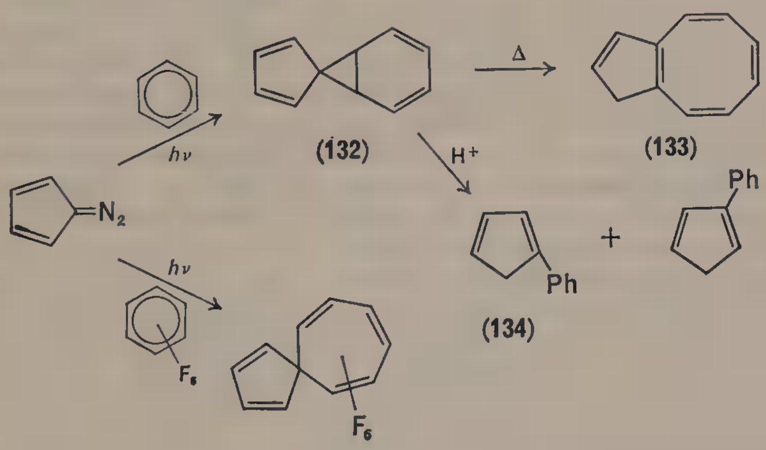
(130)

(131)

(Reference 204)

F. Photolysis of Diazo Compounds in Aromatic Compounds

Photolysis of diazocyclopentadiene in benzene solution afforded a crystalline, rather sensitive, adduct of a spironorcaradiene structure. Thermal rearrangement of **132** led to **133**, while a mixture of phenylcyclopentadienes resulted from acid-catalysed rearrangement[205]. Hexafluorobenzene gives an adduct of a spiro cycloheptatriene structure[206]. Similarly, a norcaradiene-type adduct was isolated from the

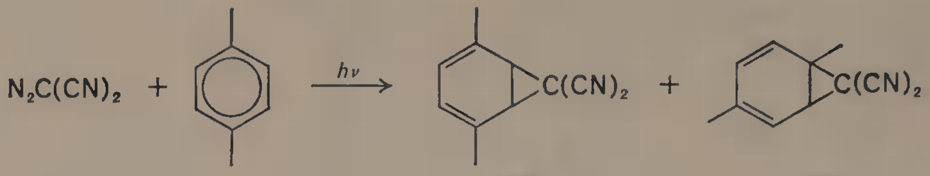


(132)

(133)

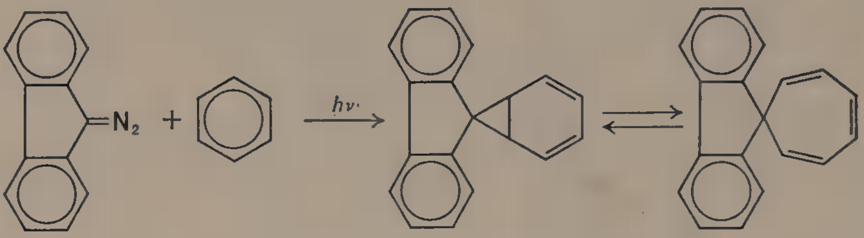
(134)

photolysis of 1-diazo-4,4-dimethylcyclohexa-2,5-diene in benzene[207]. Photolysis of dicyanodiazomethane in benzene gave, as the sole product in 82% yield, 7,7-dicyanonorcaradiene[208]. *p*-Xylene afforded two isomeric products, **135** and **136**. The



(135) (136)

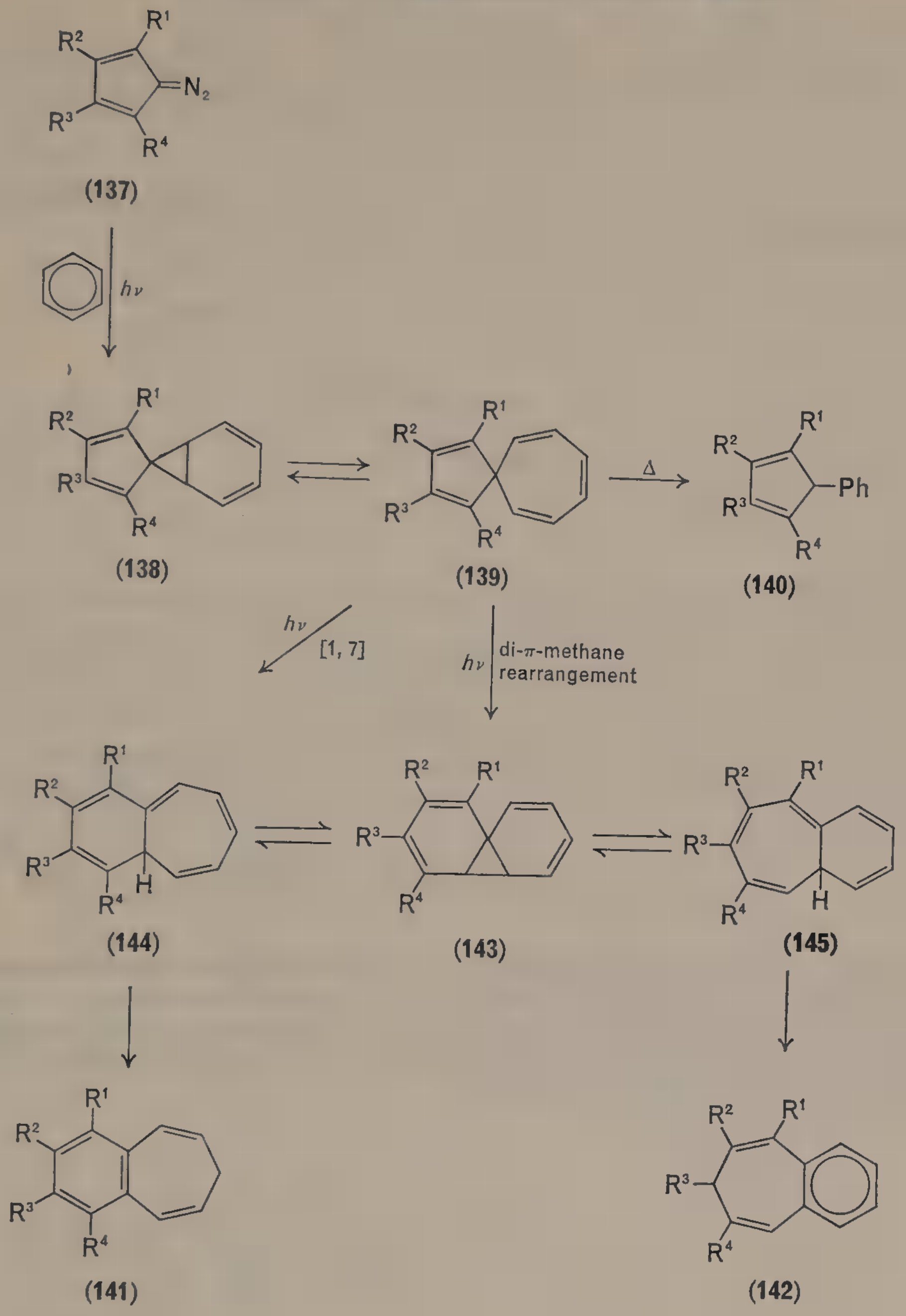
photolysis of diazofluorenylidene in benzene afforded the equilibrating norcaradiene–cycloheptatriene system[209]. Tetraphenylcyclopentadienylidene reacts with benzene to give a product, presumably the norcaradiene, which rearranges further to **(140)**



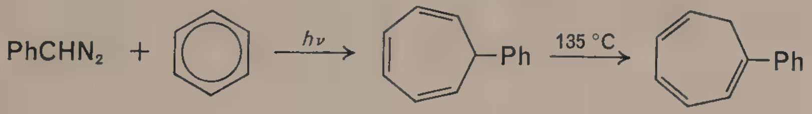
and **(141)**. The final product **(141)**, which arises via ring expansion of the five-membered ring, is somewhat unusual, since ring expansion of the seven-membered ring usually occurs[210]. Spironorcaradienes **138** (in equilibrium with their valence isomers **139**) can be isolated if the photolysis is carried out with a long wavelength filter ($\lambda > 360$ nm).

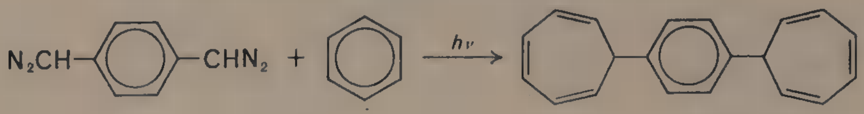
With pyrex filter ($\lambda > 290$ nm) the mixture **138** ⇌ **139** rearranges to benzocycloheptatrienes **(141)** and their 5*H* isomers. Two possible mechanisms have been proposed for this rearrangement[211]; a symmetry-allowed [1,7]-sigmatropic shift (to **143**), or a di-π-methane rearrangement (to **143**). The successful isolation of **142**, provides strong evidence for the intermediacy of novel bisnorcaradiene **(143)**.

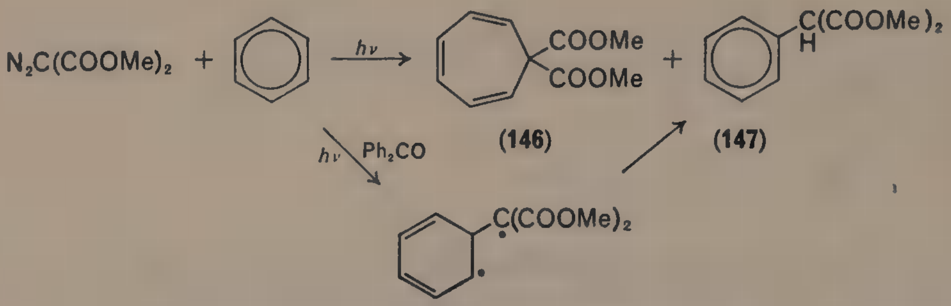
7-Phenylcycloheptatriene was obtained by photolysis of phenyldiazomethane in benzene solution[212]. Similarly, 1,4-bis(diazomethyl)benzene was converted into 1,4-bis(cycloheptatrienyl)benzene[213]. Benzene also acts as an acceptor for bis-carbomethoxycarbene, a report to the contrary notwithstanding[214]. Photolysis of methyl diazomalonate in benzene gave **146** and **147** in a ratio of 2·7 : 1. The photosensitized reaction gave the same two products in the ratio of 1·6 : 1. The increased amount of the phenylmalonate **(147)** is consistent with a mechanism involving a diradical which can either close to the norcaradiene related to **146** or undergo hydrogen shift to **147** [186, 215]. Photolysis of ethyl diazoacetate by means of pyrex-filtered light afforded **148** in reasonable yield and 80–90% purity[216, 217]. Short wavelength u.v. irradiation caused extensive isomerization of **148** to cycloheptatriene-3-, -4-carboxylate and bicyclo[3.2.0], and [2.2.1]heptadiene carboxylate[218]. A Hammett treatment showed that the reaction was an electrophilic aromatic attack. The ρ value of $-0{\cdot}38$ suggested that not much positive charge had developed in the ring at the transition[219].



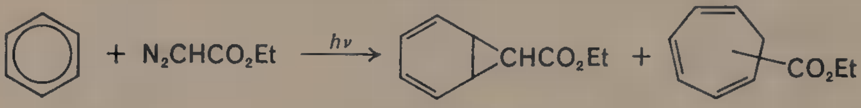
		(141)	(142)	(140)
$R^1 = R^2 = R^3 = R^4 = Ph$	2·5 °C	82%	18%	
	100 °C	10%	43%	47%
$R^1 = R^4 = Ph$, $R^2 = R^3 = H$	40 °C	69%	31%	
$R^1 = R^2 = R^3 = R^4 = Cl$	40 °C	7%		







(146) **(147)**



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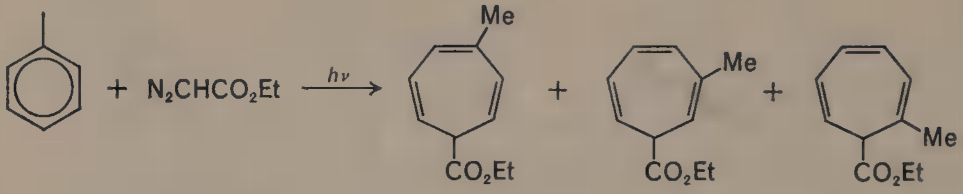
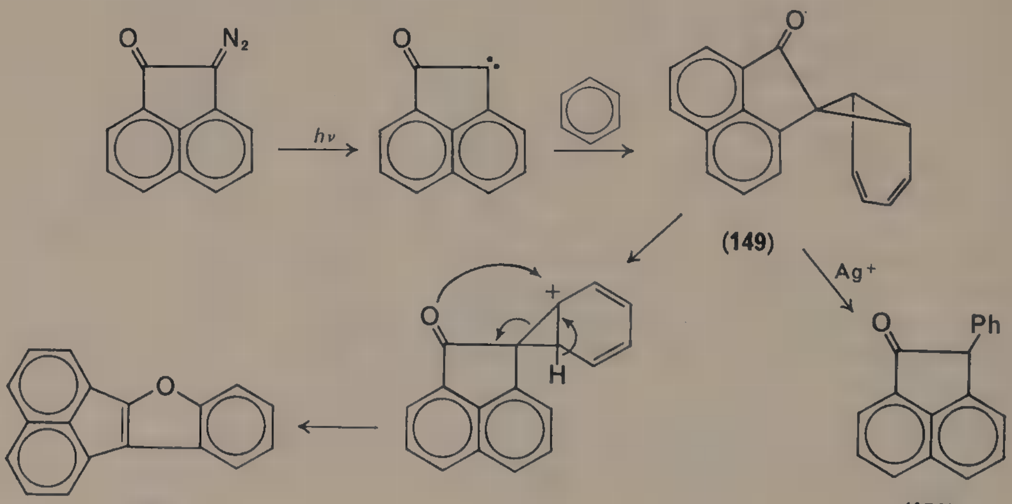
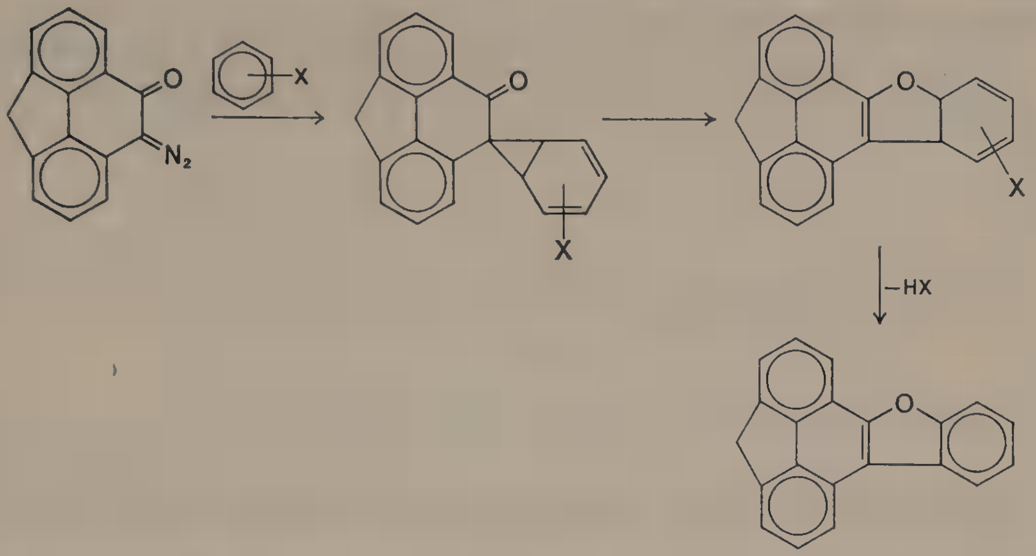


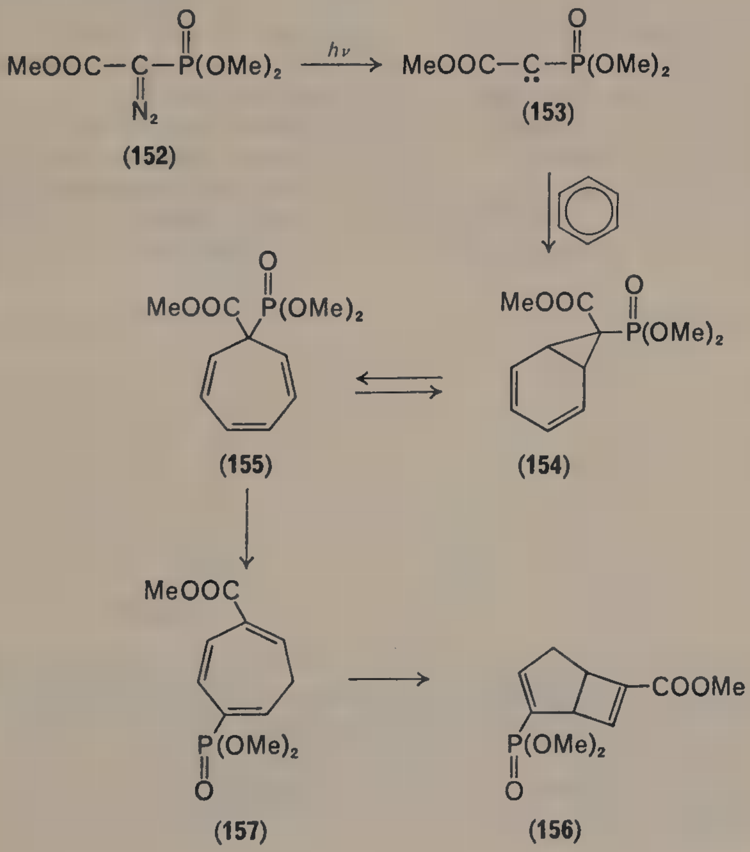
Photolysis of 2-diazoacenaphthen-1-one in benzene gives spiro[acenaphthen-1,7′-*cis*-norcara-2′,4′-diene]-2-one (**149**) which rapidly isomerizes to 2-phenylacenaphthen-1-one (**150**) under silver perchlorate catalysis[220], and gives acenaphtho-[1,2-*b*]benzofuran (**151**, X = H) in the presence of dicyanobenzoquinone. Other aromatic receptors give similar results[221].



(151) **(150)**

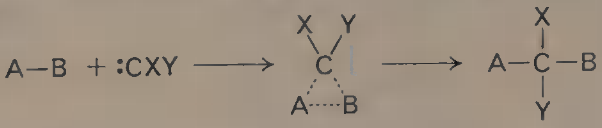


(Dimethoxyphosphoryl)(methoxycarbonyl)carbene (**153**) and benzene afford products that depend on the duration of the irradiation[222]. If the photolysis of **152** is interrupted before the reaction is complete, the equilibrium system **154** ⇌ **155** is produced. More prolonged irradiation leads next to a sequence of shifts of ester groups and of H atoms, producing the cycloheptatriene **157**. On still further irradiation, the photostable bicyclo[3.2.0]heptadiene (**156**) is formed from **157** by electrocyclic ring closure[223].

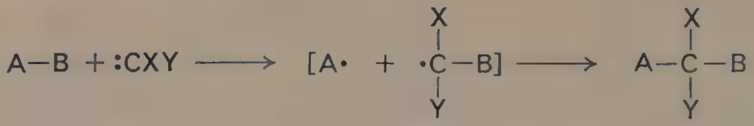


G. Insertion Reactions

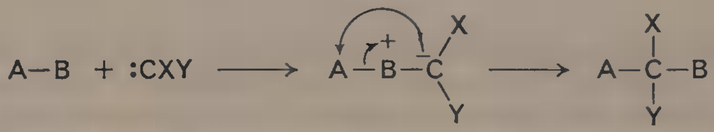
The term 'insertion' is reserved for reactions where cleavage of the A—B bond and formation of the A—C and B—C bonds occur in concert. The alternative



stepwise process, abstraction followed by recombination, may afford insertion type products via diradical processes:



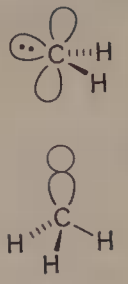
When B is a heteroatom containing one or more unshared pairs of electrons, a third mechanistic possibility may be operative involving intermediate ylide formation:



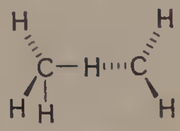
1. C—H insertion of carbene in saturated hydrocarbons

The insertion of singlet methylene into hydrogen has been subjected to a very detailed analysis[224]. The results indicate that insertion can take place over a wider range of initial conditions and by a much more complex pathway than static 'minimum energy path' analysis would suggest. The reaction of methylene with hydrogen has also been the subject of other calculations[225].

EHM calculations for concerted insertion of singlet methylene into a C—H bond of methane[226] indicate a nearly linear transition state, the methylene approaching the C—H bond in the direction shown in **158**. The hydrogen is transferred from methane to methylene while the C—C distance (2·5 Å) changes little; this is then followed by collapse to give ethane, with no evidence for a discrete radical intermediate in the process.



(158)



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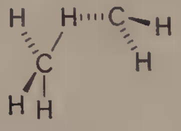
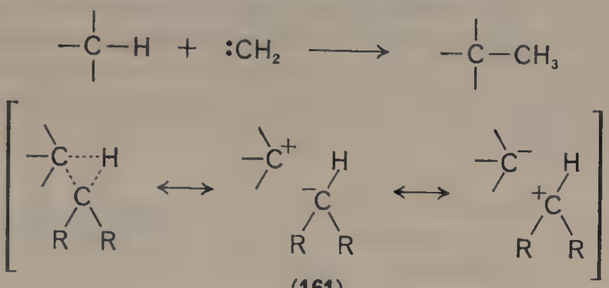


(160)

MINDO/2 calculations on the reaction of singlet and triplet methylene with methane predict[227] that the singlet can approach along the axis of a C—H bond of methane, either in an eclipsed (**159**) or in a staggered conformation (**160**). The triplet can also approach along the C—H axis, or midway between two C—H bonds of methane; the latter approach is predicted to lead to insertion by the triplet. Insertion of methylene has been analysed by Zimmerman, using his 'MO following' concept[228].

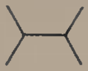
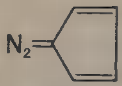
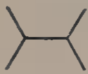
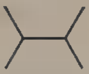
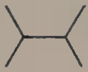
Doering and Knox[229] proposed the charge separation hypothesis for the rationalization of the selectivity of various substituted carbenes toward primary,



(161)

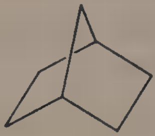
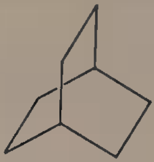
secondary and tertiary carbon–hydrogen bonds, as well as for the selectivity sequence $(CH_3OOC)_2CN_2 > CH_3OOCCHN_2 \gg CH_2N_2$.

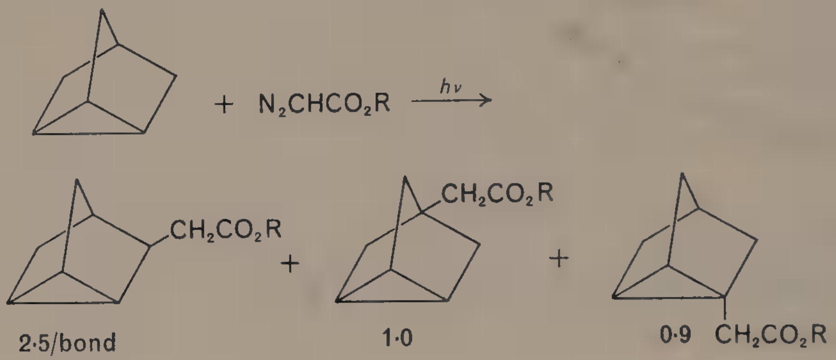
TABLE 24. Relative insertion rates of carbenes into C—H bonds under photolytical conditions

Carbene precursor	Alkane	Secondary/primary	Tertiary/primary
N_2CH_2		1·2	1·5
N_2CH_2		—	1·2
N_2CHCF_3		1·0	—
N_2CHCF_3		—	1·3
		—	7·3
N_2CHPh		6·3	—
N_2CHPh		8·3	—
$N_2CHCOOMe$		—	3·1
$N_2CHCOOMe$		—	2·9
$N_2CHCOOMe$		2·3	—
$N_2C(COOMe)_2$		4·8	—
$N_2C(COOMe)_2$		—	13·1
$N_2C(COOEt)_2$		8·4	—
$N_2C(COOEt)_2$		—	12·5
$N_2C(COOEt)_2$		—	21·1

Evidence supporting the postulated charge separation in the transition state comes from the reactivity of bridgehead hydrocarbons. Methylene reacts with bicyclo[2.2.1]heptane to give all of the possible C—H insertion products in essentially statistical amounts[230]. The product mixtures obtained with methoxycarbonylcarbene and biscarbomethoxycarbene, however, reflected lower reactivities for the bridgehead positions. The bridgehead C—H bonds of nortricyclene were found to be even less reactive toward ethoxycarbonylcarbene[231].

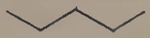
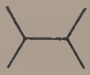
TABLE 25. Relative rates of reaction with bicyclic hydrocarbons

Diazo compound	Hydrocarbon	1-Position	All others	Tertiary/secondary
N_2CHCO_2R		1·0	6·7	0·7
$N_2C(COOR)_2$		1·0	27·3	0·2
N_2CHCO_2R		1·0	6·0	1·0
$N_2C(COOR)_2$		1·0	6·7	0·7

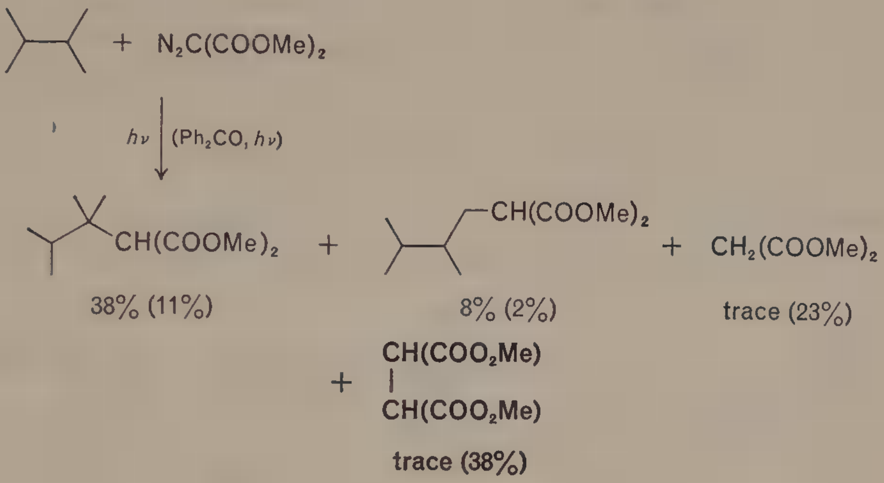


Generally, the sensitized decomposition of diazomalonate affords a slightly more selective intermediate than does direct photolysis. Yields of insertion products are much lower in the sensitized decomposition. Rough composite values for the

TABLE 26. Relative rate of insertion of biscarbomethoxycarbene into carbon–hydrogen bonds[186]

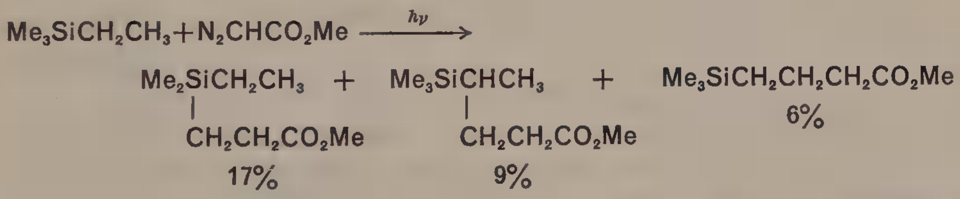
Hydrocarbon	Ratio	Singlet	Triplet
	Secondary/primary	5·4	6·9
	Secondary/primary	4·8	5·2
	Tertiary/primary	39	52
	Tertiary/primary	13	20

tertiary–secondary–primary ratios of singlet and triplet biscarbomethoxycarbenes are 15–40 : 5 : 1 and 20–50 : 6 : 1, respectively. This fits in general the data of Ring and Rabinovitch[232, 233] on the abstraction of hydrogen by triplet methylene, although the effects seem to be smaller. A hydrogen abstraction–recombination process would be expected to give new products derived from the radicals generated by abstraction. Such products do appear as shown below, with the yields of the sensitized reaction shown in brackets:



Direct irradiation produces only insertion products while the sensitized decomposition gives more of the products expected from free radical dimerization and hydrogen abstraction.

The photolysis of methyl diazoacetate in trimethylethylsilane gave three major products[234]. The rates show that an α-secondary C—H bond (2·5) is more reactive than a primary α-C—H bond (1·0), which in turn is less reactive than a primary β-C—H bond (1·2). The differences may be explained by steric hindrance to carbene insertion. A competition reaction showed that the reactivities of C—H bonds towards carbomethoxycarbene insertion are higher in trimethylethylsilane than in 2,2-dimethylbutane [$k(\text{Si})/k(\text{C}) = 1{\cdot}8$], possibly as a result of the inductive effect of the silicon substituent.



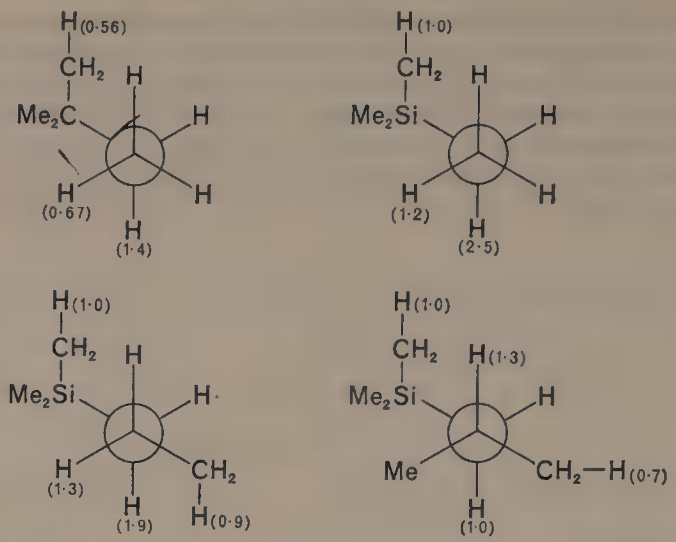
$$\mathrm{Me_3SiCH_2CH_3 + N_2CHCO_2Me} \xrightarrow{h\nu}$$

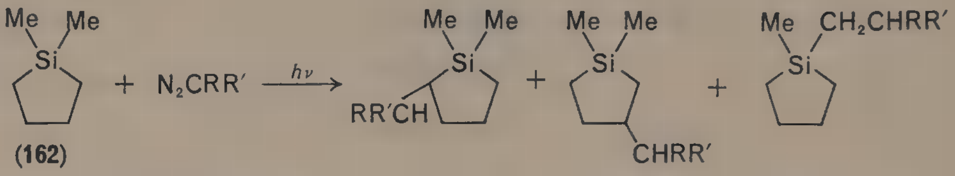
$$\underset{17\%}{\mathrm{Me_2\underset{|}{Si}CH_2CH_3}\atop \mathrm{CH_2CH_2CO_2Me}} + \underset{9\%}{\mathrm{Me_3Si\underset{|}{C}HCH_3}\atop \mathrm{CH_2CH_2CO_2Me}} + \underset{6\%}{\mathrm{Me_3SiCH_2CH_2CH_2CO_2Me}}$$

The relative rate of the carbene insertion into the primary γ-C—H bond in trimethyl(*n*-propyl)silane and in trimethyl(*iso*-butyl)silane showed it to be less reactive than that of the primary β-C—H bond of trimethylethylsilane, probably because of the diminished effect of the silyl group.

The photolysis of methyl diazoacetate and dimethyl diazomalonate in 1,1-dimethyl-1-silacyclopentane (**162**) gave carbene insertion products into the secondary α- and β-C—H bonds as well as into primary C—H bonds in comparable extent.

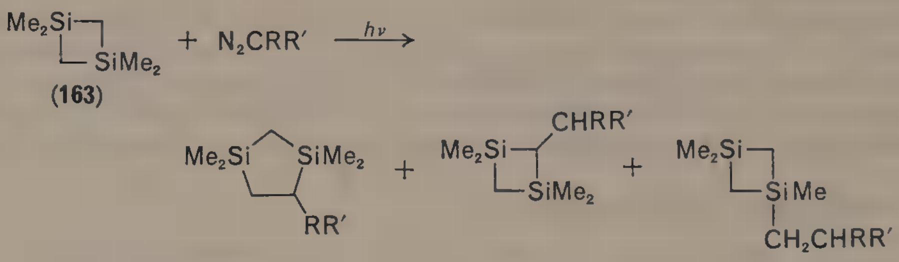
The reaction of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (**163**) gave carbene insertion into the Si—C bond, as has been observed with dichlorocarbene[235] as well as insertion into primary and secondary C—H bonds in comparable rates.





(162)

R = H, R′ = CO₂Me	1·6	2·0	1·0/bond
R = R′ = CO₂Me	7·0	11·9	1·0/bond

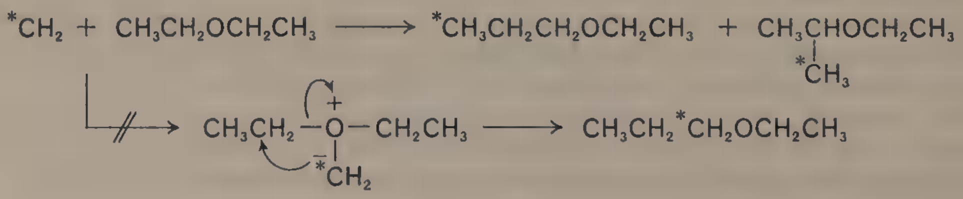


(163)

R = H, R′ = CO₂Me	14%	33%	55%
R = R′ = CO₂Me	5%	50%	45%

2. C—H insertion of carbene in ethers

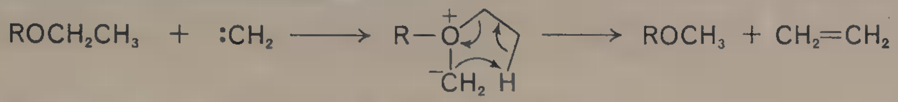
The insertion of singlet methylene into the C—H bonds of ethyl ether was reported as long ago as 1942, but the intervention of an ylide mechanism was ruled out only recently. Thus, attack of ^{14}C-labelled methylene on ether gave only end-labelled propyl ethyl ether[236]:



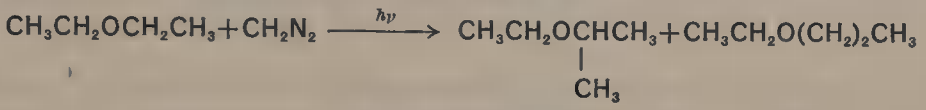
$$^{*}CH_2 + CH_3CH_2OCH_2CH_3 \longrightarrow {}^{*}CH_3CH_2CH_2OCH_2CH_3 + CH_3\underset{^{*}CH_3}{\underset{|}{C}}HOCH_2CH_3$$

$$\not\longrightarrow CH_3CH_2-\overset{+}{\underset{\underset{^{*}CH_2}{|}}{O}}-CH_2CH_3 \longrightarrow CH_3CH_2{}^{*}CH_2OCH_2CH_3$$

Thus, methyl ethers often are obtained probably from ylides in decomposition of ethereal solutions of diazomethane[236]:

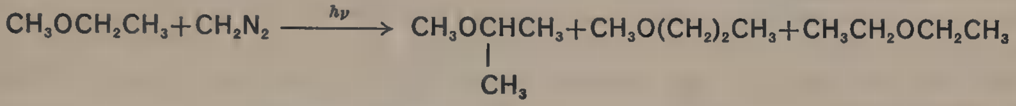


The oxygen atom of aliphatic ethers has a small promoting effect on methylene insertion which is accompanied by minor side reactions which may be explained by an attack of methylene on oxygen. Triplet methylene abstracts hydrogen almost exclusively from the α position, giving rise to products of apparent α-insertion[237-239]:



$$CH_3CH_2OCH_2CH_3 + CH_2N_2 \xrightarrow{h\nu} CH_3CH_2O\underset{\underset{CH_3}{|}}{C}HCH_3 + CH_3CH_2O(CH_2)_2CH_3$$

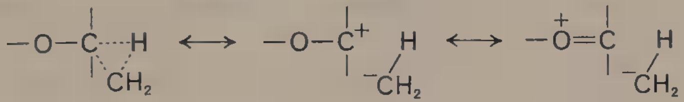
1·23 1·00
(in liquid phase)



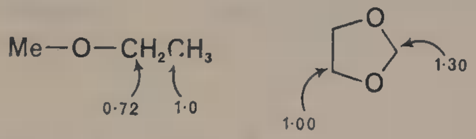
$$CH_3OCH_2CH_3 + CH_2N_2 \xrightarrow{h\nu} CH_3O\underset{\underset{CH_3}{|}}{C}HCH_3 + CH_3O(CH_2)_2CH_3 + CH_3CH_2OCH_2CH_3$$

In gas phase 1·49 1·00 1·13
In liquid phase 1·30 1·00 1·00

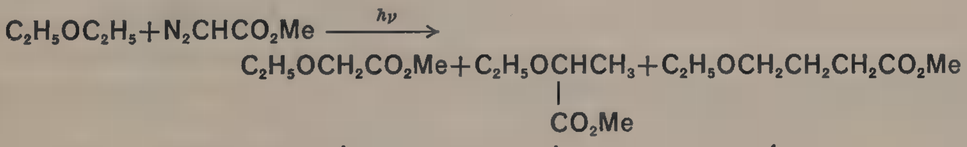
The small preference for insertion into the α-C—H bonds of ethers was rationalized in terms of polar resonance structures of the transition state.



In contrast to expectations based on this concept, the O—CH_2—O hydrogens of methylal were found to be less reactive than the CH_3—O hydrogens. The reverse relation holds with 1,3-dioxolane. These results suggest that the conformation of ethers and acetals may be an important factor in determining the relative rates of methylene insertion[240].

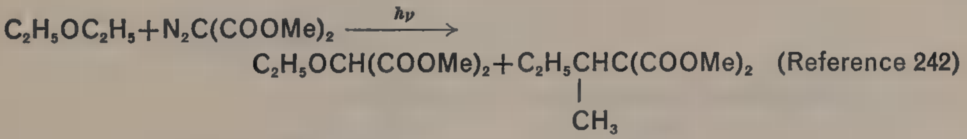


Insertion of carboalkoxycarbene into the C—H bonds of ethers competes less efficiently with cleavage at the *O*-alkyl bond than does the insertion of methylene. When methyl diazoacetate was photolysed[241] in the presence of diethyl ether, methyl ethoxyacetate, methyl β-ethoxybutyrate and γ-ethoxybutyrate were produced in the ratio of 4 : 4 : 1.



$$C_2H_5OC_2H_5 + N_2CHCO_2Me \xrightarrow{h\nu} C_2H_5OCH_2CO_2Me + C_2H_5O\underset{\underset{CO_2Me}{|}}{C}HCH_3 + C_2H_5OCH_2CH_2CH_2CO_2Me$$

4 : 4 : 1

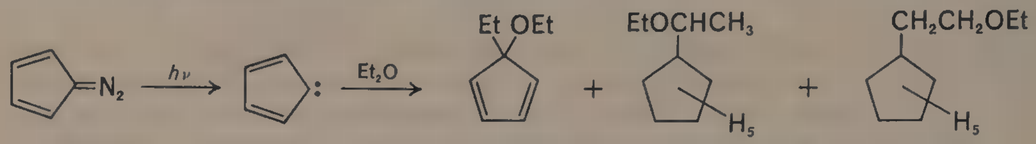


$$C_2H_5OC_2H_5 + N_2C(COOMe)_2 \xrightarrow{h\nu} C_2H_5OCH(COOMe)_2 + C_2H_5\underset{\underset{CH_3}{|}}{C}HC(COOMe)_2$$

(Reference 242)

39% yield 27% yield

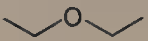
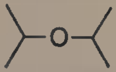
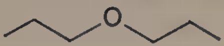
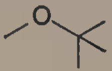
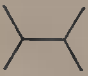
Cyclopentadienylidene inserts into both α-C—H and β-C—H bonds of diethyl ether, producing **164** and **165** in 27 and 2% yields, respectively. The correction by statistical factor shows that the reaction occurred 19-times faster at an α-C—H bond than at a β-C—H bond[243]. Competition experiments, in which mixtures of an ether and either cyclohexane or 2,3-dimethylbutane were allowed to react with cyclopentadienylidene, gave some indication that both resonance and inductive effects of the oxygen atom influenced the rate of the insertion reaction of the carbene. As in the other carbene reaction, cyclopentadienylidene inserts into C—H bonds most favourably when a partial positive charge on the carbon atom involved can be stabilized. The inductive and resonance effects of the alkoxy group can be seen in the results shown in Table 27.



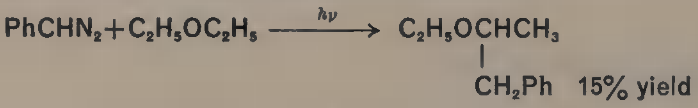
C—O insertion α-C—H insertion β-C—H insertion

(164) **(165)**

TABLE 27. C—H insertion in the photolysis of diazocyclopentadiene in ethers

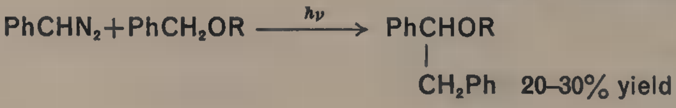
Ether	α-C—H insertion	β-C—H insertion	γ-C—H insertion
	5·9	0·32	
	6·2	0·55	
	6·2	2·3	0·9
	2·7	0·58	
	4·2	1·3	
	1·0 (standard, primary C—H insertion)		
	3·9 (secondary C—H insertion)		

A variety of phenylcarbene precursors gave the same α-C—H insertion in alkyl ethers[244].



$$PhCHN_2 + C_2H_5OC_2H_5 \xrightarrow{h\nu} C_2H_5OCH(CH_2Ph)CH_3$$

15% yield

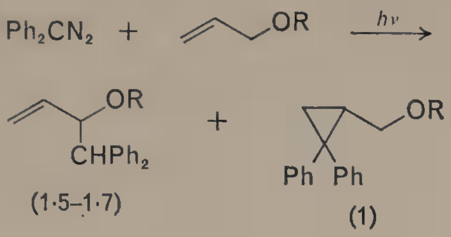


$$PhCHN_2 + PhCH_2OR \xrightarrow{h\nu} PhCH(CH_2Ph)OR$$

20–30% yield

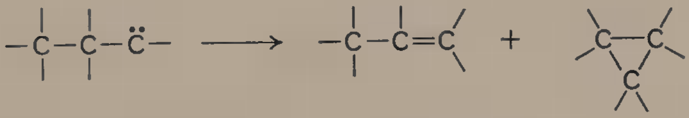
With allylic ethers, diphenylcarbene prefers insertion into the allylic C—H bond over addition to the C=C double bond by about 1·5–1·7 to 1, and with benzyl alkyl ethers, it inserts readily into the benzyl C—H bond.

Photodecomposition of diphenyldiazomethane in the presence of aldehyde afforded the insertion product of diphenylcarbene into the aldehyde C—H bond[245].

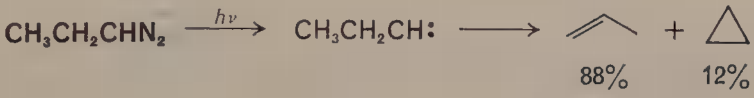


H. Intramolecular Reactions

Alkyl and dialkylcarbenes react predominantly by self-insertion into β- and γ-C—H bonds to give olefins and cyclopropanes.

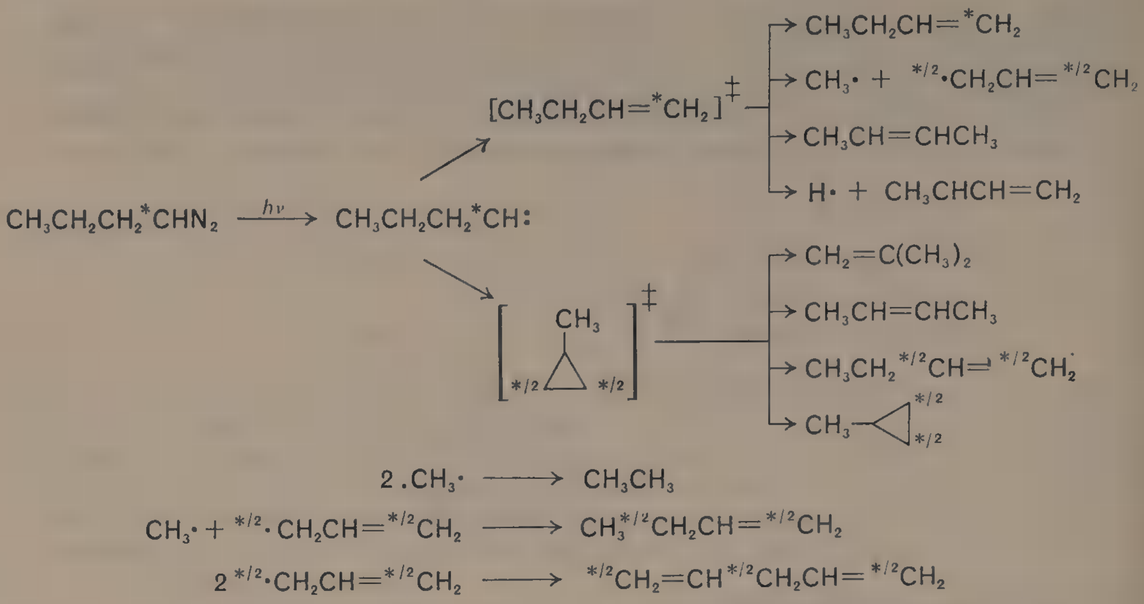


The photolysis of diazoethane in the gas phase produced ethylene and acetylene as the major products. The ratio of ethylene to acetylene increased linearly with pressure[246]. The photolysis of CD_3CHN_2 showed that acetylene is formed from excited ethylene and not from CD_3CH:, directly[247]. Ethylcarbene illustrates two common reactions of alkylcarbenes, 1,2-shift and 1,3-C—H insertion[248].



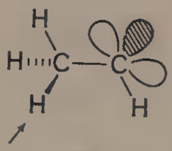
Carbon-14-labelled diazo-*n*-propane decomposes into nitrogen and singlet *n*-propylcarbene[249], which rearranges[250–252] either to butene or to methylcyclopropane, both in a vibrationally excited state. The latter either decompose or are collisionally deactivated. The radical produced may recombine to give stable products. The yield of the product formed by collisional stabilization of 'hot' species should increase with increasing pressure as indeed was observed while the fragmentation products (ethane, hexa-1,5-diene) should show opposite behaviour.

The 1,2-hydrogen shift in methylcarbene was subjected to detailed analysis[253]. In conformation **166**, the hydrogen atoms adjacent to the vacant p orbital can migrate with little or no activation, but movement of the third hydrogen is much less favourable; in cases where rotation about the carbon–carbon bond is inhibited,



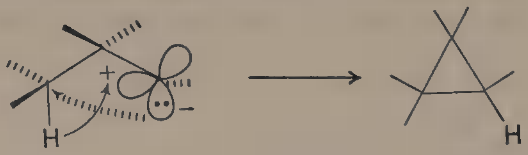
SCHEME 8

for example, the axial hydrogen atom adjacent to the centre should migrate preferentially:

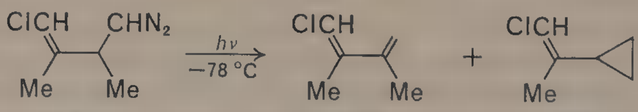


(166)

The 1,3-shift insertion can be formulated as follows:

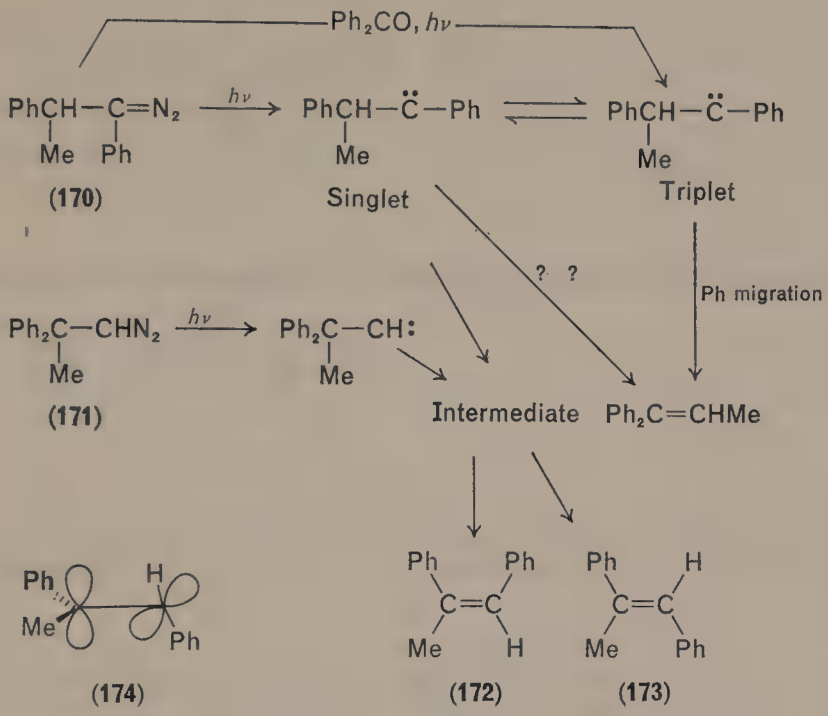


The photolysis of **167** led to formation of the butadiene (**168**) and as major product, the vinylcyclopropane (**169**)[254].

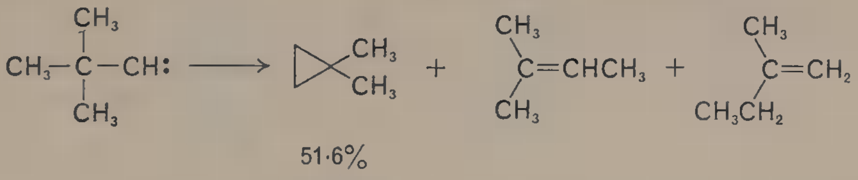


(167) **(168)** 48% **(169)** 52%

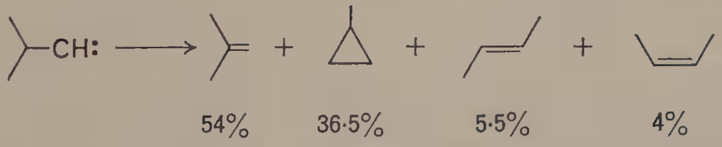
Hydrogen migration is a very efficient intramolecular trapping process for phenylmethylcarbene[255]. It was proposed that in the photolysis of **170** migration of the phenyl group takes place in the triplet carbene, whereas hydrogen migration occurs exclusively in the singlet[256]. The diazo compounds **170** and **171** give the same ratio of stereoisomers of 1,2-diphenylpropene (**172** and **173**) by migration of different groups: this points to the existence of a common intermediate. It is suggested that



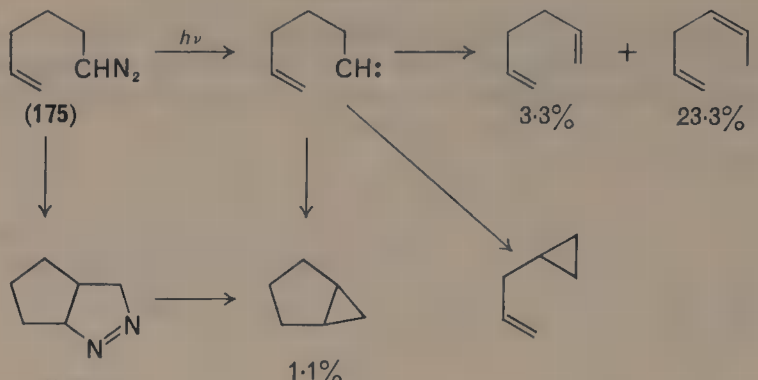
this intermediate might best be formulated as the phantom singlet state **174** of α-methylstilbene. 1,2-Alkyl shift (C—C insertion) can also occur[257]:



Clearly, the more complicated the alkyl substituents in alkylcarbenes, the more products are expected from intramolecular insertion. A relatively simple example is the following:



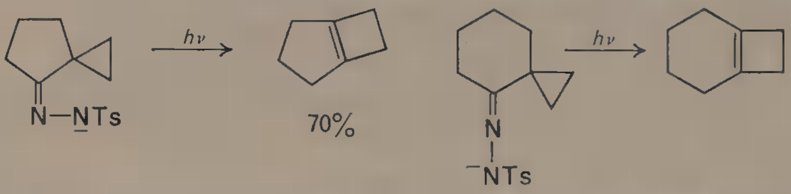
Kirmse and Grassmann[258] found that 1,2-hydrogen shift dominates in alkylcarbenes. Some intramolecular cycloaddition may arise from decomposition of **176**, but this was slow compared to that of **175**. Saturated bicyclic systems undergo ring expansion as well as C—C insertion. Ring expansion also occurs in spiro systems and some unusual olefins have been synthesized by Kirmse and Pook[259] and



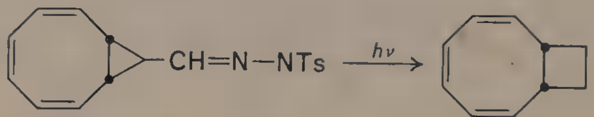
(175)

(176)

later by Wiberg[260]. It seems remarkable that no hydrogen shift was observed:



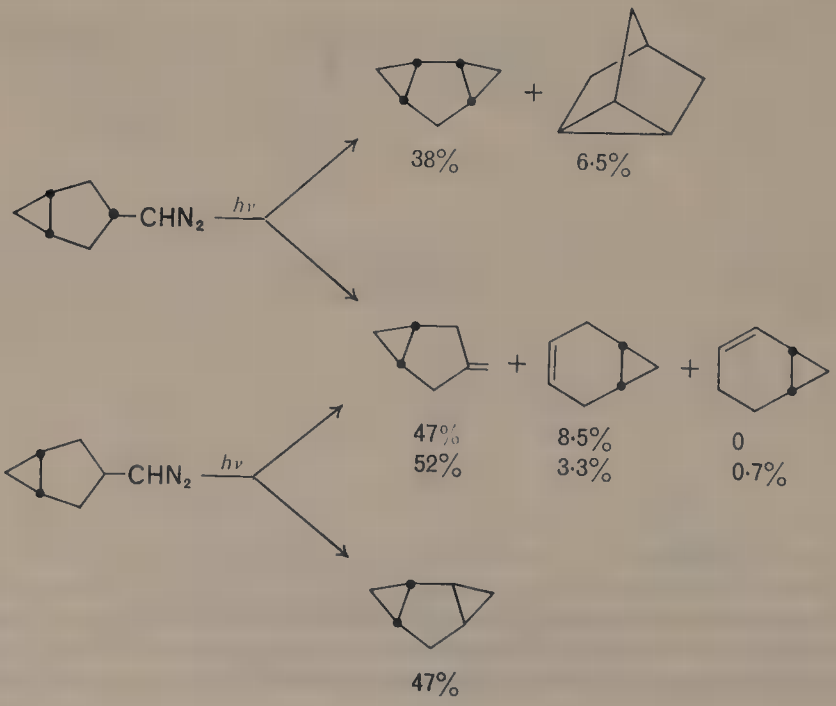
Masamune and coworkers isolated the ring-expanded product **178** on the photolysis of **177**[261]. Photolysis of *cis*- and *trans*-3-diazomethylbicyclo[3.1.0]hexane gave a



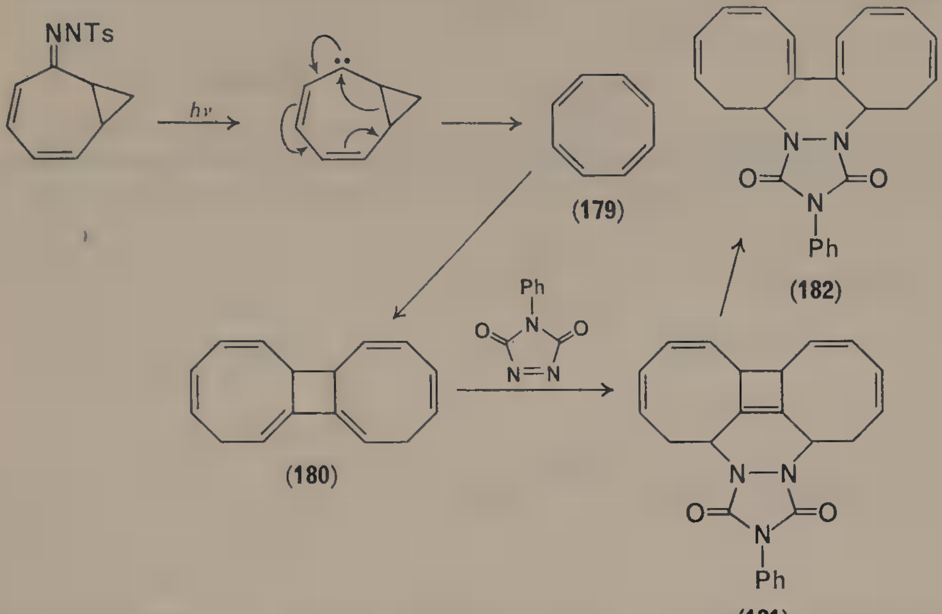
(177)

(178)

variety of products of carbon–hydrogen insertion but little ring expansion[262]:



Photoirradiation of the sodium salt of 2,3-homotropone *p*-toluenesulphonylhydrazone in tetrahydrofuran afforded a hydrocarbon **(180)** as the sole product in 70% yield, which is a dimer of 1,2,4,6-cyclooctatetraene **(179)** [263]. The compound **180** reacted smoothly with *N*-phenyltriazoline-1,4-dione at room temperature to afford, probably via **181**, the 1,1-adduct **182** in 65% yield. The intramolecular insertion of (2-*n*-butylphenyl)diazomethane **(183)** was found to proceed with fairly indiscriminate attack on the α, β, γ and δ-C—H bonds, both when the irradiation is effected directly or via photosensitization[264]. This is interpreted in terms of an equilibrium between the singlet **191** and the triplet **192**, equilibration being more rapid than the ensuing processes leading to intramolecular insertion (i.e. **184–187**), intermolecular C—H insertion (i.e. to form **188**) and hydrogen migration (i.e. to form **189** and **190**). Kirmse studied reactions of methoxy alkylcarbenes.

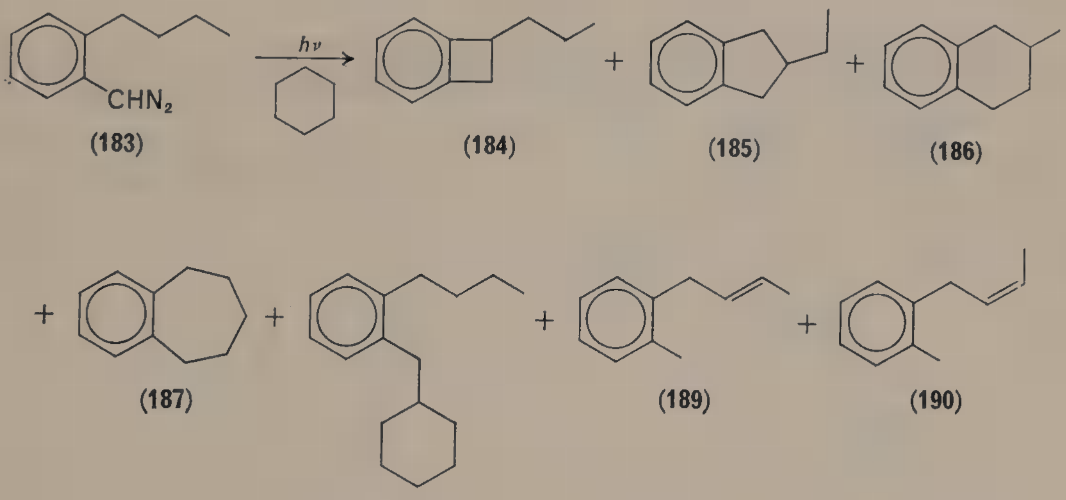


(179)

(180)

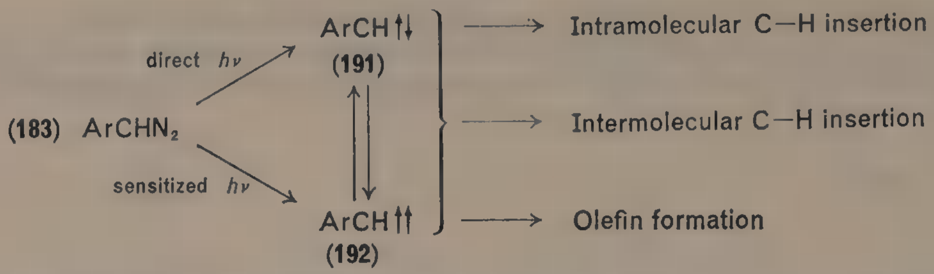
(181)

(182)

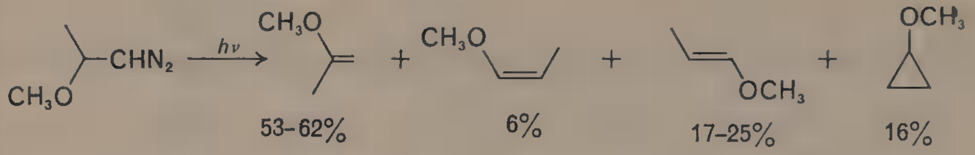


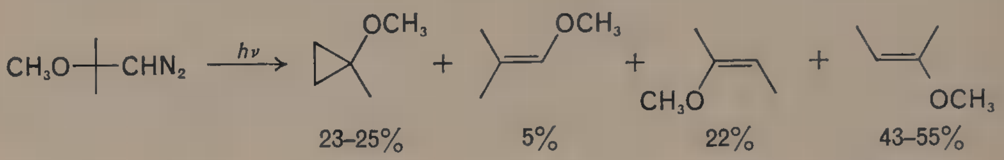
(183) (184) (185) (186)

(187) (188) (189) (190)

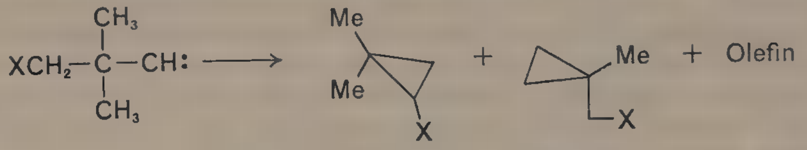


A methoxy group accelerates the shift of adjacent groups while itself being slow to move compared to hydrogen and also to alkyl[265, 266].



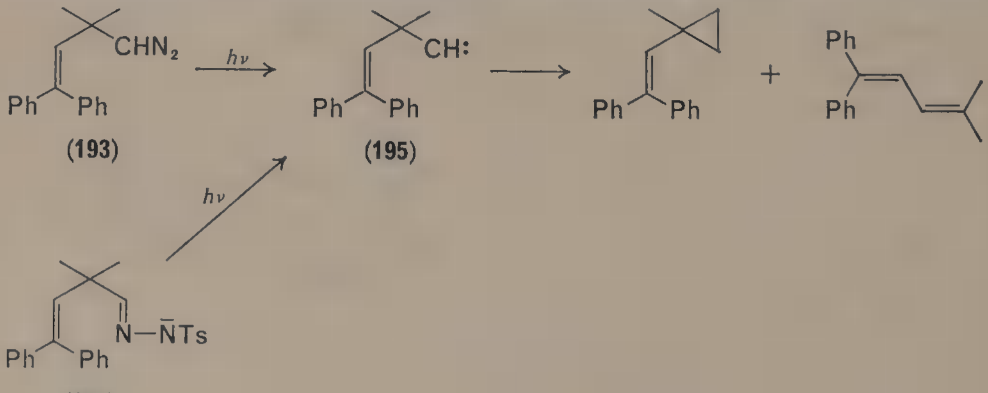


Substitution in the γ-position by a variety of groups X makes insertion more difficult. The data indicate a largely inductive effect of X. Stabilization of partial charge by resonance does not appear to be an important factor[267]. The small contribution of resonance suggests concerted hydrogen transfer and C—C bonding in the γ-C—H insertion.



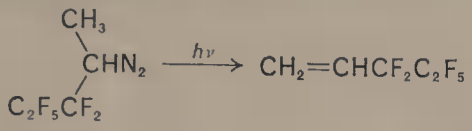
X = OMe	1·5%	60–80%	15–35%
X = NMe₂	6–8%	92–94%	
X = Ph	9–13%	60–70%	

Direct irradiation of **193** and the tosylhydrazone anion **194** gave C—H insertion and vinyl group migration. Rearrangement of **195** might afford diphenyldimethyl-



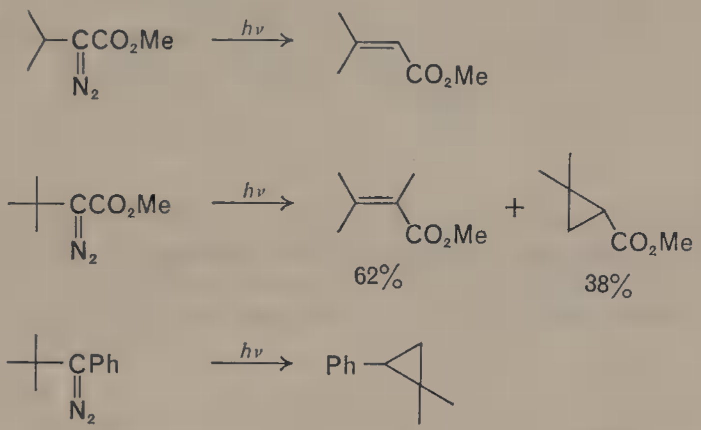
(193) (195) (194)

butadiene[268]. Hydrogen shift was shown to be favoured over fluorine or fluoroalkyl shift[269]:

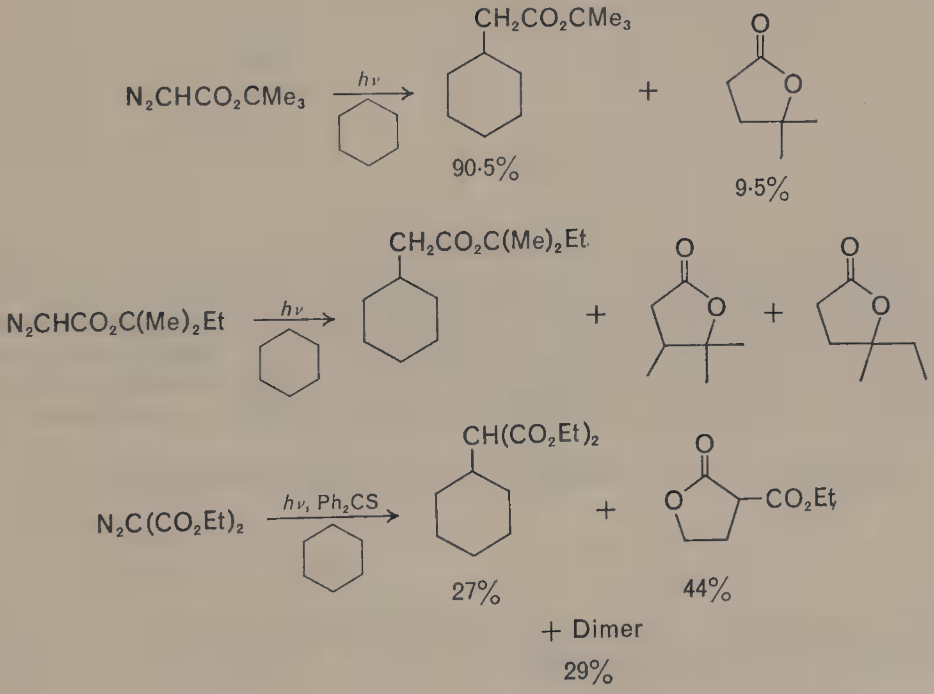


$$CH_3(C_2F_5CF_2)CHN_2 \xrightarrow{h\nu} CH_2{=}CHCF_2C_2F_5$$

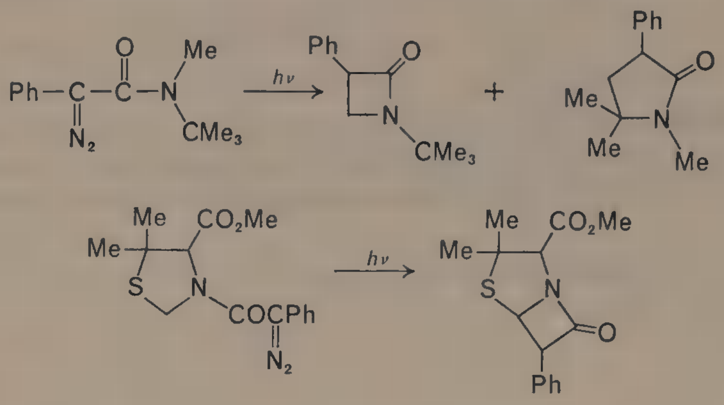
β-C—H insertion and alkyl migration predominate with alkyl(alkoxycarbonyl)-carbenes[270]. In contrast to β,β-dimethyl-α-diazobutyrate, *t*-butyl phenyldiazomethane prefers self-insertion to give cyclopropane rather than methyl shift[271].



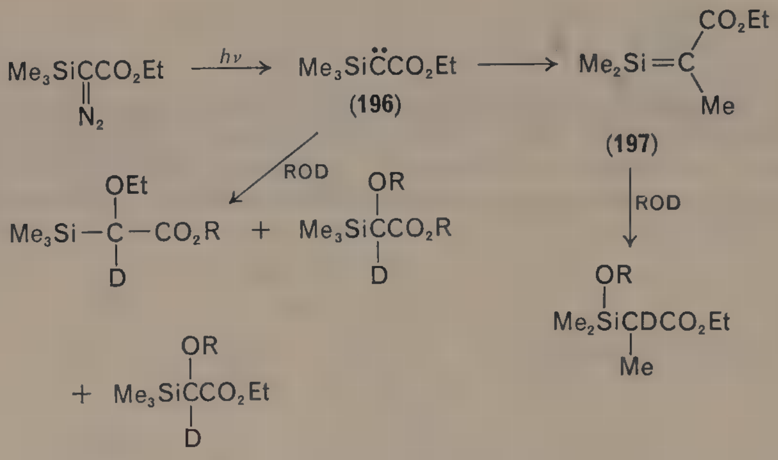
Photolysis of ethyl diazoacetate, even in the vapour phase, did not produce butyrolactone. *t*-Butyl and *t*-amyl diazoacetate, however, afforded small amounts of lactones on photolysis in cyclohexane[272]. Diethyl diazomalonate gave both intermolecular and intramolecular reactions in the presence of thiobenzophenone[273].



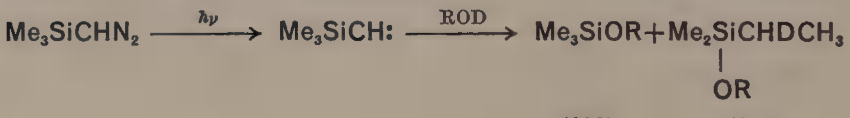
Several diazoamides were found to undergo intramolecular insertion into β-C—H bonds of the N-alkyl groups with formation of β-lactams[274, 275]. This method was applied in a synthesis of methyl 6-phenylpenicillanate.



The 1,2-alkyl shift in carbenes has been used to generate highly unstable olefins as transient intermediates. α-Silylcarbene (**196**) rearranges in alcohols to the ester (**197**) containing an unstable silicon–carbon double bond which is then attacked by the solvent[276]. When trimethylsilyldiazomethane was photolysed with a high



pressure mercury lamp in various alcohols, two major products are obtained. Product **198** may be produced by a nucleophilic attack of alcohol on the silicon centre to release the diazomethane. The photolysis of silyldiazomethane in ethanol-d_1 showed that the deuterium was only introduced into the α-carbon of the ethyl group. The formation of **199** might be accounted for by 1,2-methyl migration producing a silicon–carbon double bond followed by addition of alcohol to the latter. While



$$\mathrm{Me_3SiCHN_2} \xrightarrow{h\nu} \mathrm{Me_3SiCH:} \xrightarrow{\mathrm{ROD}} \mathrm{Me_3SiOR} + \underset{\mathrm{OR}}{\underset{|}{\mathrm{Me_2Si}}}\mathrm{CHDCH_3}$$

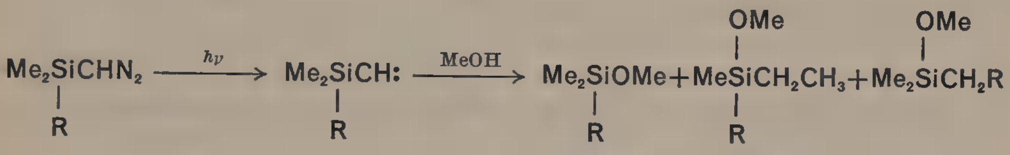
(**198**) (**199**)

methoxy(trimethyl)silane is the major product in methanol, 1,2-methyl migration becomes more rapid in *t*-butanol[277, 278].

TABLE 28. Photolysis of trimethylsilyldiazomethane in alcohols

ROH	198 (%)	199 (%)	Total yield (%)
MeOH	83	17	96
EtOH	47	53	96
i-PrOH	35	65	66
t-BuOH	0	100	45

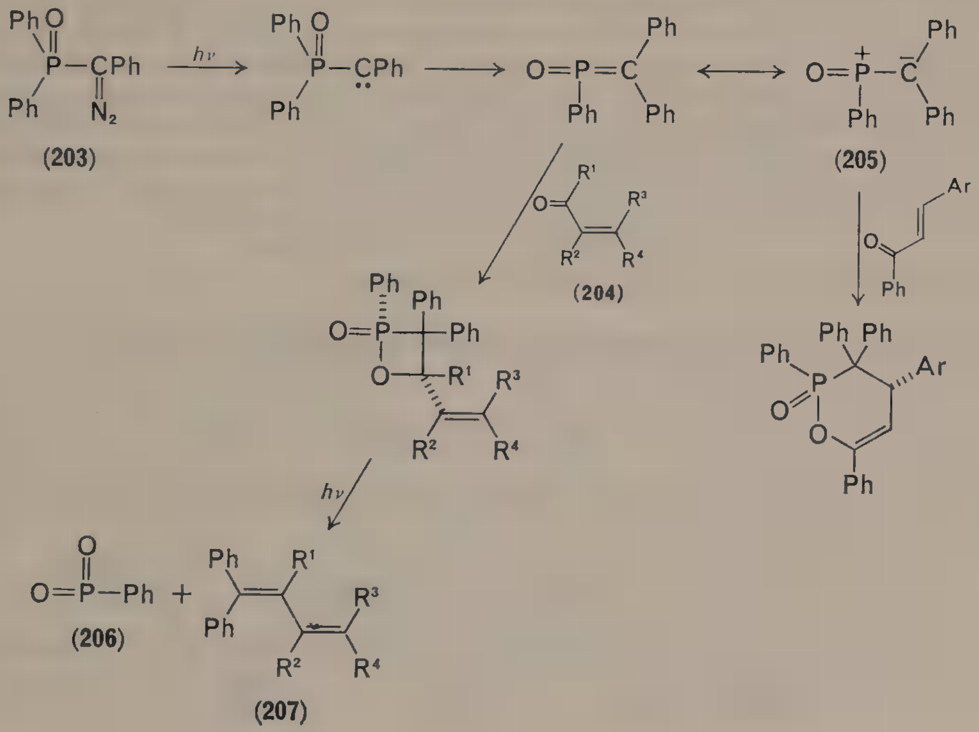
Similarly, the photolysis of dimethylphenyl- and dimethylbenzyl-silyldiazomethane in methanol gave three major products, **200**, **201** and **202**. Relative yields of **201** and **202** indicate that the migratory aptitude of the methyl group is larger than that of the phenyl or the benzyl group, even though statistical factors are considered. This tendency is quite different from that observed in cases when the migrating group is bound to carbon and not to silicon[277]:



$$\underset{\mathrm{R}}{\mathrm{Me_2SiCHN_2}} \xrightarrow{h\nu} \underset{\mathrm{R}}{\mathrm{Me_2SiCH}}: \xrightarrow{\mathrm{MeOH}} \underset{\mathrm{R}}{\mathrm{Me_2SiOMe}} + \overset{\mathrm{OMe}}{\underset{\mathrm{R}}{\mathrm{MeSiCH_2CH_3}}} + \overset{\mathrm{OMe}}{\mathrm{Me_2SiCH_2R}}$$

	(200)	**(201)**	**(202)**
R = Ph	52%	39%	9%
R = CH$_2$Ph	49%	43%	8%

Photolysis of **203** in **204** gives **206** and **207**, which probably arise from the intermediate **205** [279].

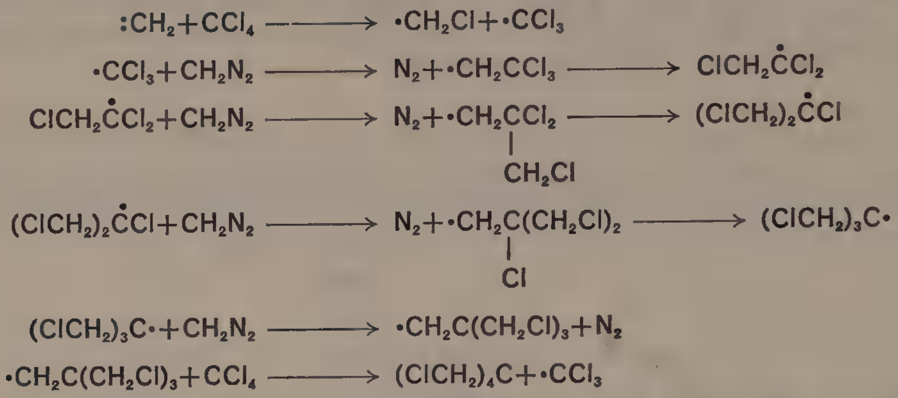


I. Photolysis of Diazo Compounds in Compounds Containing Hetero Atoms

In this section we treat especially attacks by carbenes at C—X bonds where X is a substituent having a lone-pair of electrons. This mechanism involves intermediate ylide formation prior to abstraction–recombination.

I. Reaction with polyhalomethanes

The reaction of diazomethane with polyhalomethanes in the liquid phase proceeds by a radical chain mechanism, which is initiated by halogen abstraction. The fast migration of chlorine in the intermediate radical is thought to prevent chain transfer at an early stage, and to produce **208**, the major product from carbon tetrachloride. The high quantum yield and the inhibiting effect of radical scavengers provide further support for the chain mechanism[280]. The course of free radical reactions of



$$:CH_2+CCl_4 \longrightarrow \cdot CH_2Cl+\cdot CCl_3$$

$$\cdot CCl_3+CH_2N_2 \longrightarrow N_2+\cdot CH_2CCl_3 \longrightarrow ClCH_2\dot{C}Cl_2$$

$$ClCH_2\dot{C}Cl_2+CH_2N_2 \longrightarrow N_2+\cdot CH_2\underset{\underset{\textstyle CH_2Cl}{|}}{C}Cl_2 \longrightarrow (ClCH_2)_2\dot{C}Cl$$

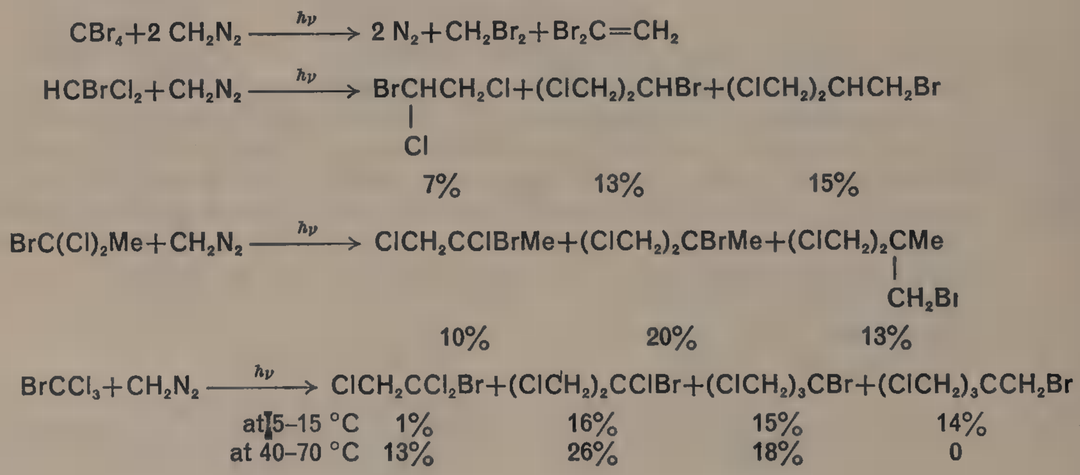
$$(ClCH_2)_2\dot{C}Cl+CH_2N_2 \longrightarrow N_2+\cdot CH_2\underset{\underset{\textstyle Cl}{|}}{C}(CH_2Cl)_2 \longrightarrow (ClCH_2)_3C\cdot$$

$$(ClCH_2)_3C\cdot+CH_2N_2 \longrightarrow \cdot CH_2C(CH_2Cl)_3+N_2$$

$$\cdot CH_2C(CH_2Cl)_3+CCl_4 \longrightarrow (ClCH_2)_4C+\cdot CCl_3$$

(208)

diazomethane with polyhaloalkanes depends upon the reactivity of the organic halide, the stability of the intermediate and on the reaction conditions. With unreactive halides, polymethylene is the dominant product (cf. 2-chloro-2-methylpropane[280]); with halides of low reactivity (cf. bromochloromethane), mixtures of products of the general formula $ClCH_2(CH_2)_xBr$ are obtained[281]. The highly reactive polybromo- and polyiodo-methanes give dibromo- or diiodo-methane and related alkenes via β-elimination of bromine or iodine atoms from intermediate radicals[282], while the light-promoted reaction of halides of comparable reactivity give products of attack of intermediate free radicals upon the polyhaloalkanes:



$$CBr_4+2\,CH_2N_2 \xrightarrow{h\nu} 2\,N_2+CH_2Br_2+Br_2C{=}CH_2$$

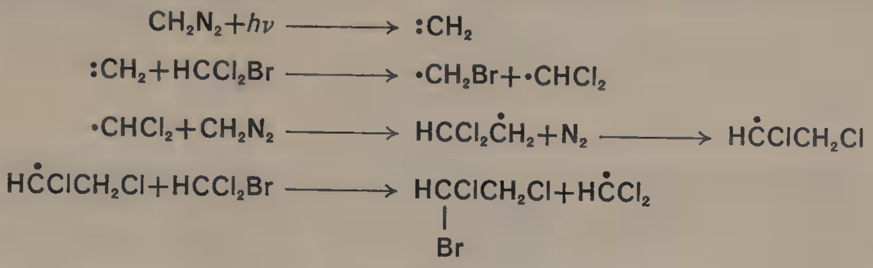
$$HCBrCl_2+CH_2N_2 \xrightarrow{h\nu} \underset{7\%}{Br\underset{\underset{\textstyle Cl}{|}}{C}HCH_2Cl}+\underset{13\%}{(ClCH_2)_2CHBr}+\underset{15\%}{(ClCH_2)_2CHCH_2Br}$$

$$BrC(Cl)_2Me+CH_2N_2 \xrightarrow{h\nu} \underset{10\%}{ClCH_2CClBrMe}+\underset{20\%}{(ClCH_2)_2CBrMe}+\underset{13\%}{(ClCH_2)_2\underset{\underset{\textstyle CH_2Br}{|}}{C}Me}$$

$$BrCCl_3+CH_2N_2 \xrightarrow{h\nu} ClCH_2CCl_2Br+(ClCH_2)_2CClBr+(ClCH_2)_3CBr+(ClCH_2)_3CCH_2Br$$

	ClCH₂CCl₂Br	(ClCH₂)₂CClBr	(ClCH₂)₃CBr	(ClCH₂)₃CCH₂Br
at 5–15 °C	1%	16%	15%	14%
at 40–70 °C	13%	26%	18%	0

The following is the postulated mechanism in the reaction of diazomethane with bromodichloromethane:



$$CH_2N_2+h\nu \longrightarrow :CH_2$$
$$:CH_2+HCCl_2Br \longrightarrow \cdot CH_2Br+\cdot CHCl_2$$
$$\cdot CHCl_2+CH_2N_2 \longrightarrow HCCl_2\dot{C}H_2+N_2 \longrightarrow H\dot{C}ClCH_2Cl$$
$$H\dot{C}ClCH_2Cl+HCCl_2Br \longrightarrow H\underset{\substack{|\\ Br}}{C}ClCH_2Cl+H\dot{C}Cl_2$$

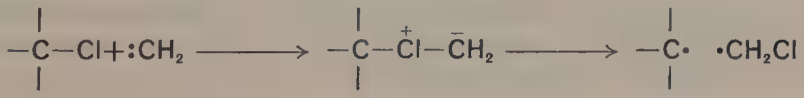
The gas-phase reactions of methylene with methyl chloride and methylene chloride take place predominantly by chlorine and hydrogen abstraction. In the case of methyl chloride, both abstraction processes give rise to the same intermediates, methyl and chloromethyl radicals. At higher pressures the major products are ethane, chloroethane and 1,2-dichloroethane[283]. These products are consistent with the following set of reactions:

TABLE 29. Reaction products of $:CH_2$ with CH_3Cl

Pressure (cm)	Yield (%)				
	C_2H_6	C_2H_5Cl	$C_2H_4Cl_2$	C_2H_4	C_2H_3Cl
150	29	45	26	—	—
76	28	44	28	trace	—
32	31	31	26	12	trace
12	34	13	25	26	2
4·8	32	5	24	33	6
0·9	17	—	13	50	20

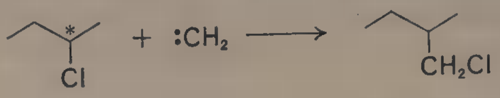
$$:CH_2+CH_3Cl \longrightarrow \cdot CH_3+\cdot CH_2Cl$$
$$\cdot CH_3+\cdot CH_3 \longrightarrow C_2H_6$$
$$\cdot CH_3+\cdot CH_2Cl \longrightarrow CH_3CH_2Cl$$
$$\cdot CH_2Cl+\cdot CH_2Cl \longrightarrow ClCH_2CH_2Cl$$

The products above could also be consistent with C—H abstraction as the initial reaction of $:CH_2$. This possibility was checked by experiments with dichloromethane where C—H abstraction would yield ethane, 1,1-dichloroethane, 1,1,2-trichloroethane, chloroethane and 1,1,2,2-tetrachloroethane in addition to 1,2-dichloroethane. Only 1,2-dichloroethane was produced in significant quantities. Further evidence for the abstraction mechanism was obtained by adding a small percentage of oxygen, when ethane, chloroethane and 1,2-dichloroethane were virtually eliminated from the reaction products. Mechanisms involving the formation of an ylide intermediate, however, cannot be eliminated:



$$-\underset{|}{\overset{|}{C}}-Cl+:CH_2 \longrightarrow -\underset{|}{\overset{|}{C}}-\overset{+}{Cl}-\overset{-}{C}H_2 \longrightarrow -\underset{|}{\overset{|}{C}}\cdot \quad \cdot CH_2Cl$$

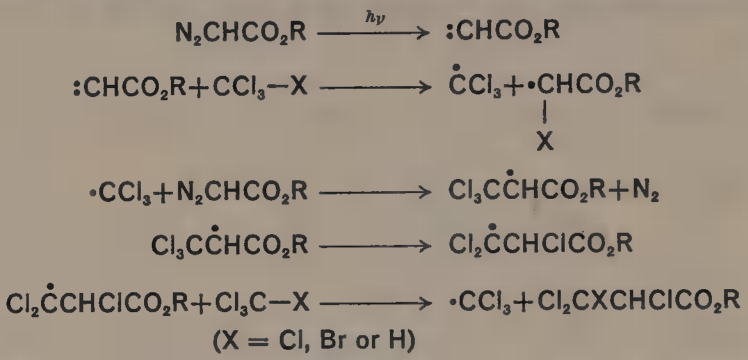
Doering has found that the reaction of methylene with the carbon–chlorine bond of optically active 2-chlorobutane proceeds with a high degree of racemization[284]:



(90% racemic)

These experiments indicate the possibility of an ylide intermediate followed by radical cleavage and recombination. More recently, the use of CIDNP has implicated the singlet state in chlorine abstraction and the triplet state in hydrogen abstraction[285, 286].

It was suggested that reactions of alkyl diazoacetates with polyhalomethanes may proceed via a free radical chain mechanism[287]. Urry and Wilt found that photolytic reactions of methyl diazoacetate with chloroform, carbon tetrachloride and bromotrichloromethane produced the corresponding methyl polyhalopropionates[288, 289]. A free radical chain mechanism was postulated on the basis of the identity of the products and by analogy to the reaction with diazomethane. Recently, arguments against the operation of a radical chain mechanism in the photolytic reaction of diazoacetate with carbon tetrachloride, chloroform and methylene chloride have appeared. When ethyl diazoacetate was decomposed in each of these substrates in the presence of radical chain initiators (such as benzoyl peroxide), different products were obtained from those reported earlier by Urry and Wilt. These results suggest[290] that the photochemical decomposition of ethyl diazoacetate affords a different species than that produced when the diazo ester is decomposed in radical fashion. The preferred mechanism to account for the formation of the methyl propionates involves carbene attack at halogen with consequent ylide formation, followed by S_Ni type displacement of the halogen involved in ylide formation:



$$N_2CHCO_2R \xrightarrow{h\nu} :CHCO_2R$$

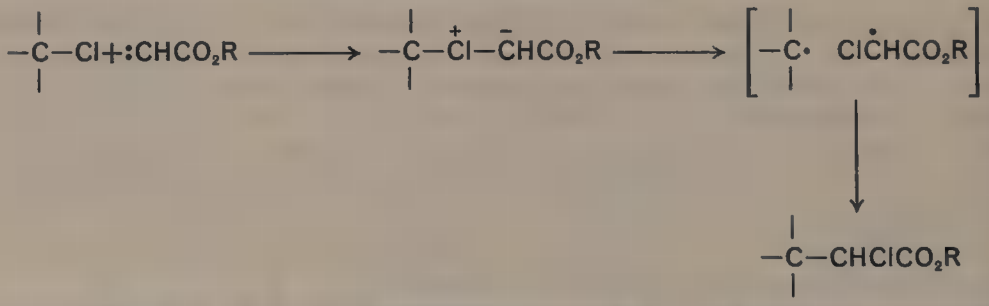
$$:CHCO_2R + CCl_3{-}X \longrightarrow \dot{C}Cl_3 + \cdot\underset{\substack{|\\ X}}{C}HCO_2R$$

$$\cdot CCl_3 + N_2CHCO_2R \longrightarrow Cl_3C\dot{C}HCO_2R + N_2$$

$$Cl_3C\dot{C}HCO_2R \longrightarrow Cl_2\dot{C}CHClCO_2R$$

$$Cl_2\dot{C}CHClCO_2R + Cl_3C{-}X \longrightarrow \cdot CCl_3 + Cl_2CXCHClCO_2R$$

(X = Cl, Br or H)

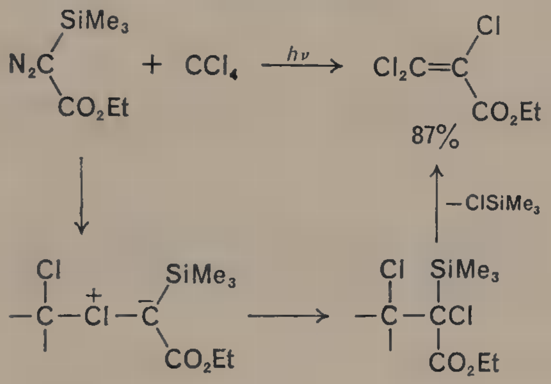


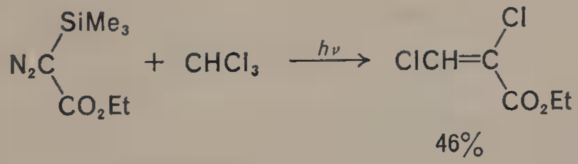
$$-\overset{|}{\underset{|}{C}}-Cl + :CHCO_2R \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{+}{Cl}-\overset{-}{C}HCO_2R \longrightarrow \left[-\overset{|}{\underset{|}{C}}\cdot \quad Cl\dot{C}HCO_2R\right] \longrightarrow -\overset{|}{\underset{|}{C}}-CHClCO_2R$$

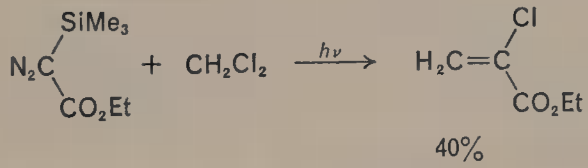
The photolysis of ethyl trimethylsilyldiazoacetate in polyhalomethanes afforded ethyl acrylate derivatives[291], considered to be formed from a chloronium ylide intermediate followed by cleavage and recombination.

TABLE 30. The photolysis of diazo ester in polyhalomethanes

Diazo ester	Halide	Products	Yield (%)
N_2CHCO_2Et	CCl_4	$CCl_3CHClCO_2Et$	42
	$CHCl_3$	$CCl_2HCHClCO_2Et$	58
		$ClCH_2CO_2Et$	15·2
	CH_2Cl_2	$CClH_2CHClCO_2Et$	42·4
		$ClCH_2CO_2Et$	3·7
$N_2C(CO_2Me)_2$	CCl_4	$CCl_3CCl(CO_2Me)_2$	49·8
		$(MeO_2C)_2C{=}C(CO_2Me)_2$	13·2
	$CHCl_3$	$CHCl_2CCl(CO_2Me)_2$	43·3
		$(MeO_2C)_2C{=}C(CO_2Me)_2$	8·6
		$H_2C(CO_2Me)_2$, $HClC(CO_2Me)_2$	trace
	CH_2Cl_2	$CH_2ClCCl(CO_2Me)_2$	44·5
		$(MeO_2C)_2C{=}C(CO_2Me)_2$	4·6
		$H_2C(CO_2Me)_2$	4·9
		$HClC(CO_2Me)_2$	5·1

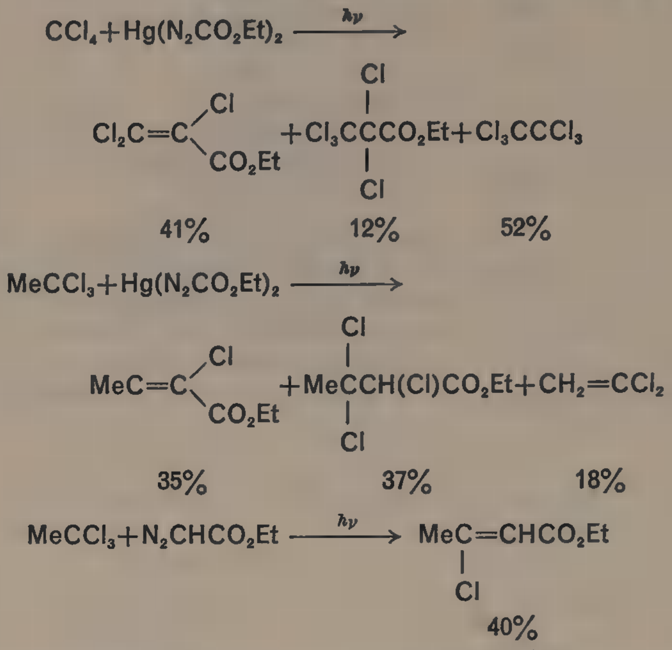






CIDNP studies have confirmed the cage recombination of radical pairs from the decomposition of halonium ylide intermediate, but are inconsistent with radical chain mechanism[292–294].

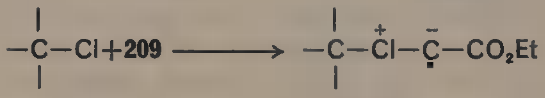
Photolysis of diethyl mercurybisdiazoacetate with chloroalkanes may yield chlorocarboethoxycarbene ($Cl{-}\ddot{C}{-}CO_2Et$) by chlorine abstraction, with the resulting products then arising from reaction of either carboethoxycarbene or chlorocarboethoxycarbene with the chloroalkane[295]. However, the marked differences in reaction products from diethyl mercurybisdiazoacetate as compared with those from ethyl diazoacetate give strong support for the absence of carboethoxycarbene in the photolysis of the mercurybisdiazoacetate. The results suggest that carbyne **209** may be produced from mercurybisdiazoacetate in yields from 63 to 83%:



By analogy with the suggested mechanism for the carbon–halogen insertion reaction of carbenes, one can speculate about a novel ylide-radical intermediate **(210)** in the reaction of **209** with chloroalkanes:

$$\mathrm{Hg(N_2CCO_2Et)_2 \xrightarrow{h\nu} 2\,N_2 + Hg + 2\,\cdot\ddot{C}CO_2Et}$$

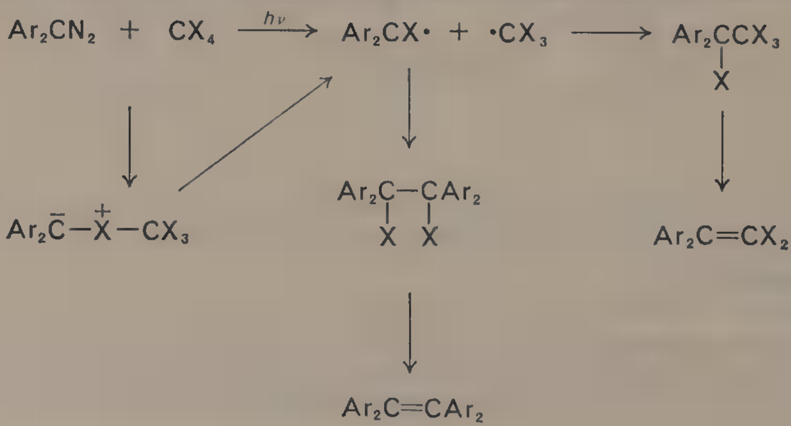
(209)



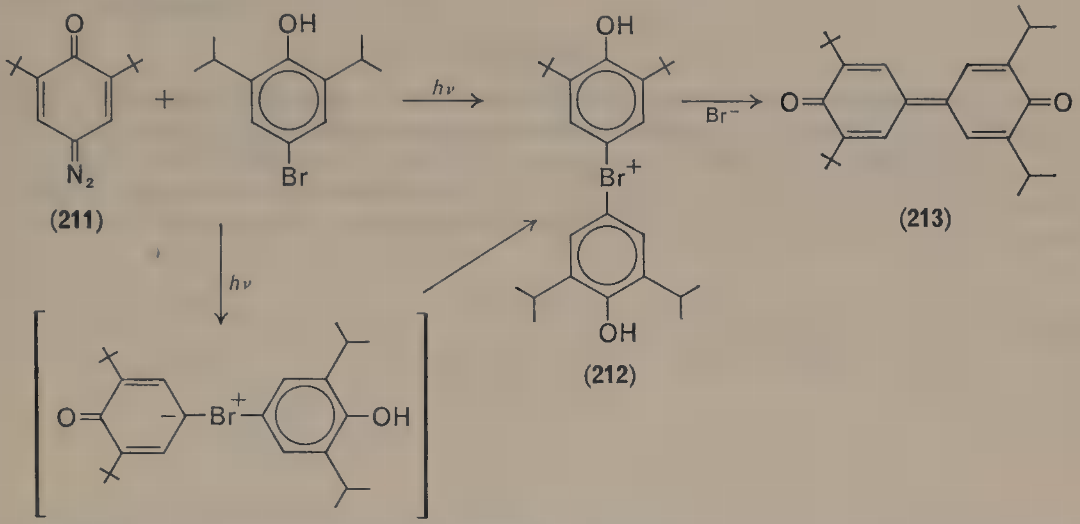
$$\mathrm{-\overset{|}{\underset{|}{C}}-Cl + \mathbf{209} \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{+}{Cl}-\overset{-}{\underset{\cdot}{C}}-CO_2Et}$$

(210)

Halogen abstraction and recombination of the radicals thus produced appears to be the major path of diarylcarbene reactions with polyhalomethanes[296, 297]. On the other hand, ylide formation plays an important part in the formation of

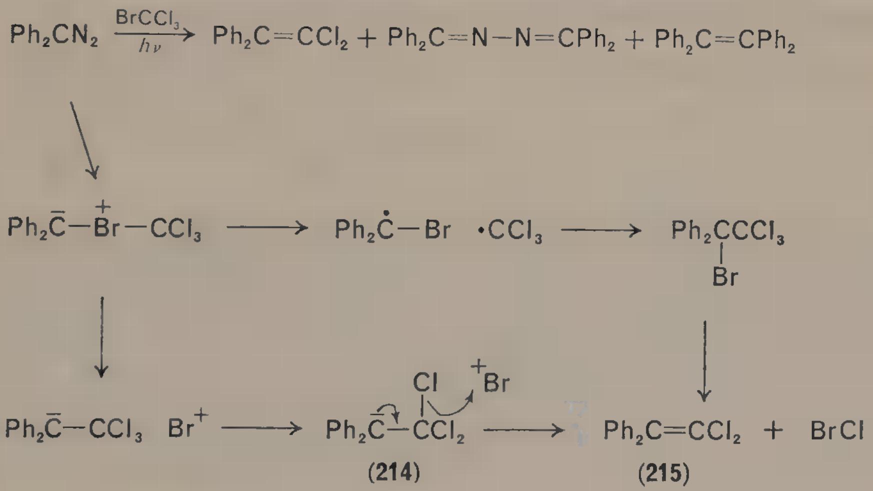


diphenoquinones by photolysis of **211** in the presence of halogen compounds[298]. The isolation of the bromonium salt **212** lends support to the ylide intermediate which is converted into the diphenoquinone **213** by triethylamine.



(211) (212) (213)

The reaction between singlet diphenylcarbene and bromotrichloromethane could also lead to the formation of the transition state **214** which could then eliminate bromine chloride to give **215**.



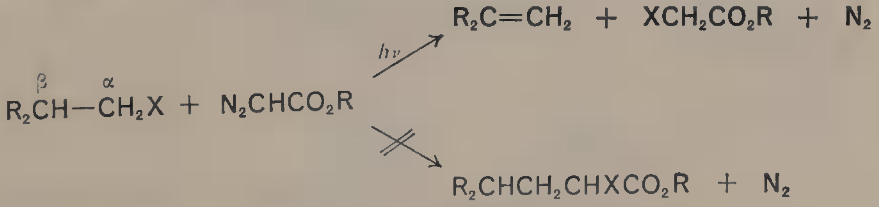
$$Ph_2CN_2 \xrightarrow[h\nu]{BrCCl_3} Ph_2C{=}CCl_2 + Ph_2C{=}N{-}N{=}CPh_2 + Ph_2C{=}CPh_2$$

$$Ph_2\bar{C}{-}\overset{+}{Br}{-}CCl_3 \longrightarrow Ph_2\dot{C}{-}Br \quad \cdot CCl_3 \longrightarrow Ph_2\underset{\displaystyle Br}{\underset{|}{C}}CCl_3$$

$$Ph_2\bar{C}{-}CCl_3 \quad Br^+ \longrightarrow Ph_2\bar{C}{-}\overset{\displaystyle Cl \quad {}^{+}Br}{\overset{|}{C}Cl_2} \longrightarrow Ph_2C{=}CCl_2 + BrCl$$

(214) (215)

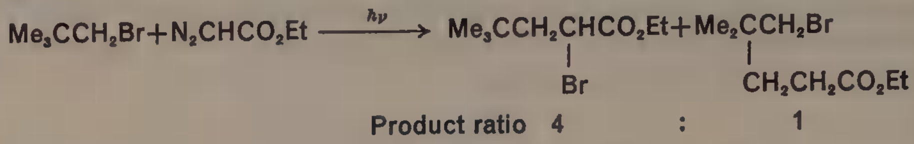
Generally, alkyl halides appear to react whenever possible with carboalkoxycarbene to give olefins via HX elimination, when there is a β-carbon–hydrogen bond present as indicated below:



$$\overset{\beta}{R_2CH}{-}\overset{\alpha}{CH_2X} + N_2CHCO_2R \xrightarrow{h\nu} R_2C{=}CH_2 + XCH_2CO_2R + N_2$$

$$\overset{\beta}{R_2CH}{-}\overset{\alpha}{CH_2X} + N_2CHCO_2R \not\longrightarrow R_2CHCH_2CHXCO_2R + N_2$$

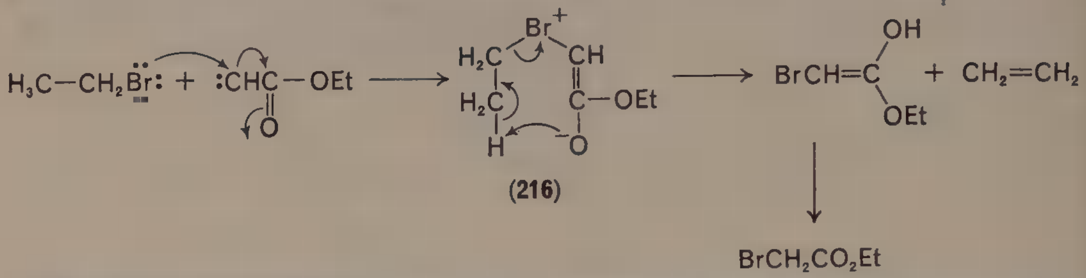
In neopentyl bromide, carbon–bromine insertion predominates over carbon–hydrogen insertion by a factor of 4. It is especially interesting to note that no rearranged products were observed in this reaction[299]:



$$\mathrm{Me_3CCH_2Br + N_2CHCO_2Et \xrightarrow{h\nu} \underset{\displaystyle Br}{Me_3CCH_2CHCO_2Et} + \underset{\displaystyle CH_2CH_2CO_2Et}{Me_2CCH_2Br}}$$

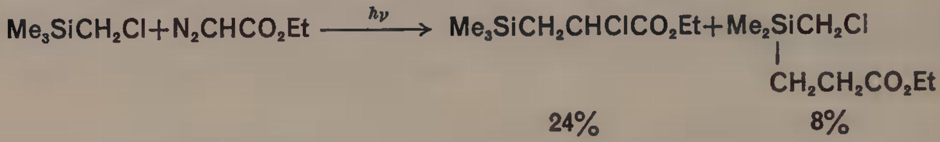
Product ratio 4 : 1

This argues against the operation of a mechanism whereby an intermediate ylide breaks down to form the carbon–bromine insertion product via dipolar abstraction of bromine with subsequent recombination of ionic fragments. The reaction is therefore envisaged as an initial attack of singlet carbene on the halogen atom to give an ylide intermediate **216** followed by β-elimination. Insertion into the C—Cl bond of chlorotetramethylsilane by singlet biscarbomethoxycarbene or carboethoxycarbene may proceed via a chloronium ylide which undergoes homolytic fission at the original C—Cl bond and recombination[300]:



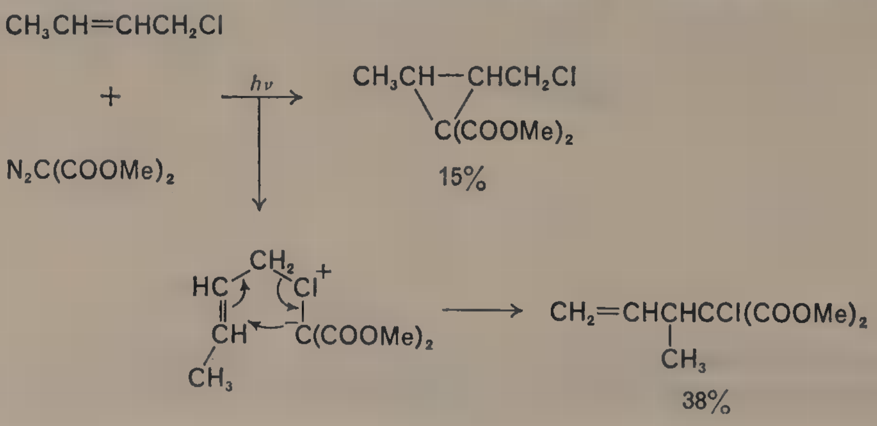
(216)

$$\mathrm{Me_3SiCH_2Cl + N_2C(COOMe)_2 \xrightarrow{h\nu} Me_3SiCH_2CCl(COOMe)_2}$$



$$\mathrm{Me_3SiCH_2Cl + N_2CHCO_2Et \xrightarrow{h\nu} \underset{24\%}{Me_3SiCH_2CHClCO_2Et} + \underset{\displaystyle \underset{8\%}{CH_2CH_2CO_2Et}}{Me_2SiCH_2Cl}}$$

A chloronium ylide intermediate has recently been suggested to account for the reactions of carboethoxycarbene and biscarbomethoxycarbene with allylic halides. Direct photolysis of dimethyl diazomalonate yields singlet biscarbomethoxycarbene which reacts with allyl chloride to give 53% of allyl chloromalonate and 23% of the cyclopropane derivative[301]. With γ-methylallyl chloride the formation of α-methylallyl chloromalonate and the cyclopropane was observed, but no γ-methylallyl chloromalonate was observed. The formation of 'insertion' products may be explained by the formation of a halonium ylide followed by a symmetry allowed, thermal [2,3]sigmatropic rearrangement[302]. With allyl bromide, an excellent yield



was obtained by the insertion of biscarbomethoxycarbene into the carbon–bromine bond, whereas only a trace of addition product was formed (Table 31).

The most marked change between direct and sensitized photolysis is in the ratio of the insertion and addition products.

TABLE 31. The photolysis of diazocarbonyl compounds in allyl halides

Diazo compound	Halides	Insertion (%)	Addition (%)
DM[a]		53 (5)[d]	23 (88)[d]
DM		25 (trace)	22 (86)
DM		38 (trace)	15 (49)
DM		38 (4)	6 (30)
DA[b]		21 (7)	18 (69)
DA		15 (3)	7 (22)
SA[c]		38 (20)	13 (55)

[a] Dimethyl diazomalonate.
[b] Ethyl diazoacetate.
[c] Ethyl trimethylsilyldiazoacetate.
[d] Benzophenone sensitized decomposition.

The proposed mechanism for the formation of insertion products through halonium ylide intermediates may be supported by the following evidence. In direct photolysis, the insertion reaction with allyl chloride was about 1–2·5 times and with the bromide about 8 times faster than the addition. Since the reactivities of the double bonds toward the attacking carbene species are not considered to be very different in these two allylic substrates, the change in the ratio of insertion to addition may be due to the difference in nucleophilicity between chlorine and bromine atoms. This consideration is also supported by results obtained in competition experiments using pairs of allylic compounds (Table 32). From these

TABLE 32. Competitive reaction of singlet and triplet biscarbomethoxycarbene with allylic compounds

Olefin	Mode of product	Singlet	Triplet
	Addition	1·00	1·00 (standard)
	Insertion	2·3	0·07
	Addition	1·0	1·0
	Insertion	8·5	0·3
	Addition	1·2	1·0
	Insertion	6·3	0·5

results it was concluded that singlet carboalkoxycarbene produced via direct photolysis of diazo ester preferentially attacks the halogen atom in allylic halides to afford predominantly C—X bond insertion products, whereas the corresponding triplet carbenes generated by benzophenone-sensitized photolysis preferentially add to the carbon–carbon double bonds in these substrates.

Support for this interpretation of the differing behaviour of the carboalkoxycarbenes produced via direct photolyses *vs* sensitized photolyses of diazo ester was obtained by the observation of a solvent effect on the insertion/addition ratio in the photolytic reaction of dimethyl diazomalonate. It can immediately be seen that the ratio of the insertion to addition products decreases with dilution with methylene halides or cyclohexane[303]. This was interpreted as indicating collision-induced conversion of singlet to triplet. In the heavily diluted runs the yields are severely reduced, and the scavenging by methylene halide leaves a mixture of carbenes richer in the triplet.

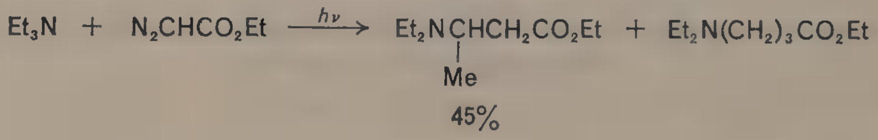
TABLE 33. The effect of added solvents on the photodecomposition of dimethyl diazomalonate in allyl chloride

Solvent		Insertion/Addition	Yield (%)
None		2·35	76
None + Ph_2CO		0·056	93
C_6H_{12}	10%	3·39	64
	50%	2·52	26
	90%	1·95	5
CH_2Cl_2	10%	2·38	60
	50%	2·20	35
	90%	1·17	10
CH_2Br_2	50%	1·60	14
	90%	0·06	4
CH_2I_2	10%	1·94	27

2. Reaction with nitrogen compounds

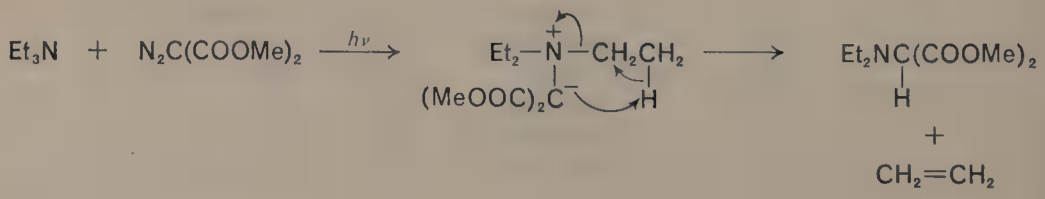
Insertion into carbon–hydrogen bonds is the predominant reaction of methylene[304] and of ethoxycarbonylcarbene[305, 306] with triethylamine. Products possibly resulting from β-elimination within the hypothetical nitrogen ylide are formed only to a minor extent:

$$Et_3N + N_2CH_2 \xrightarrow{h\nu} Et_2NMe + Et_2NCHMe_2$$

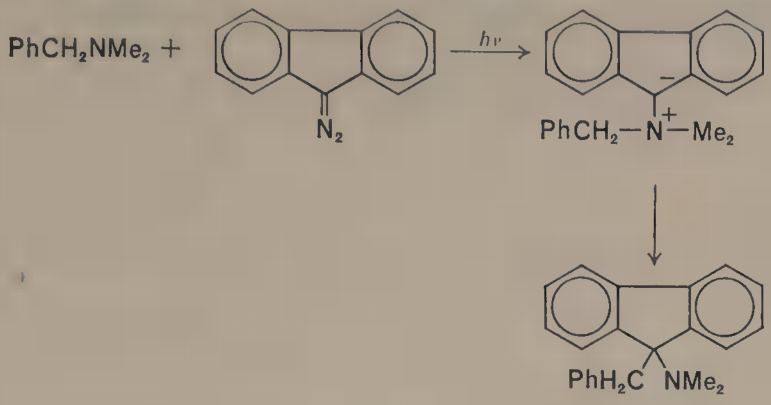


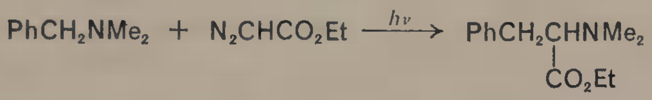
$$Et_3N + N_2CHCO_2Et \xrightarrow{h\nu} Et_2N\underset{\underset{\textstyle Me}{|}}{C}HCH_2CO_2Et + Et_2N(CH_2)_3CO_2Et$$

45%



Benzyldimethylamine reacts with ethyl diazoacetate and with diazofluorene by apparent insertion of the carbene into the *N*-benzyl bond[307]:

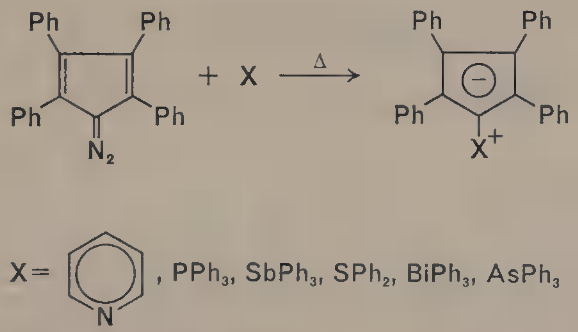




$$PhCH_2NMe_2 + N_2CHCO_2Et \xrightarrow{h\nu} PhCH_2\underset{\displaystyle CO_2Et}{\underset{|}{C}}HNMe_2$$

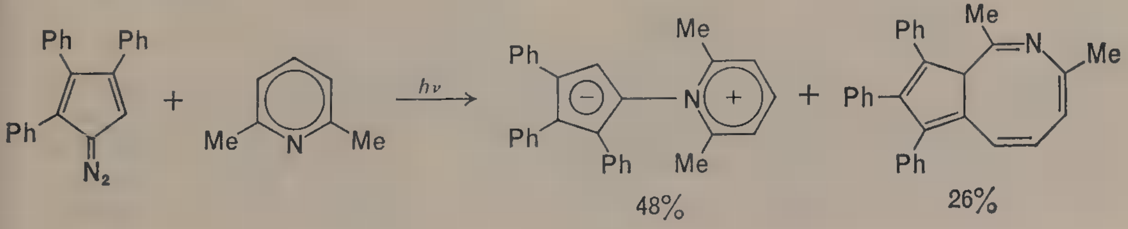
Most likely these products arise from a Stevens rearrangement of the ylide intermediate.

Relatively little is known about the isolation of stable nitrogen ylides in these reactions. Substituted pyridinium tetraphenylcyclopentadienylides were produced in almost theoretical yields on refluxing tetraphenyldiazocyclopentadiene in pyridine, the picolines or 2,6-lutidine under an atmosphere of nitrogen for 10 min [308–311]:

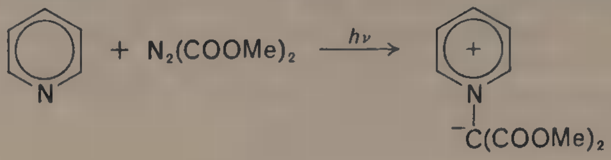


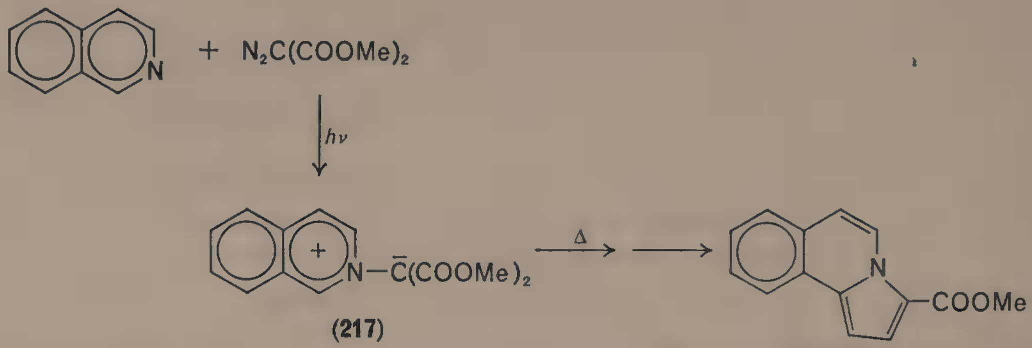
Cyclopentadienylides of other hetero atoms were similarly readily obtainable by decomposition of diazo compounds with reagents containing these elements.

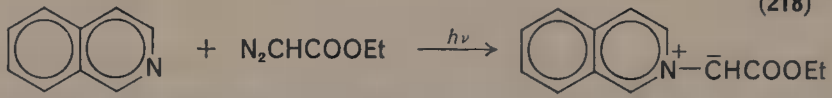
The triphenyldiazocyclopentadiene was irradiated under nitrogen in the 2,5-dimethylpyridine with a high-pressure mercury lamp through a pyrex filter. Recrystallization afforded the 2,5-dimethylpyridiniumtriphenylcyclopentadienylide in 48% yield[312]:



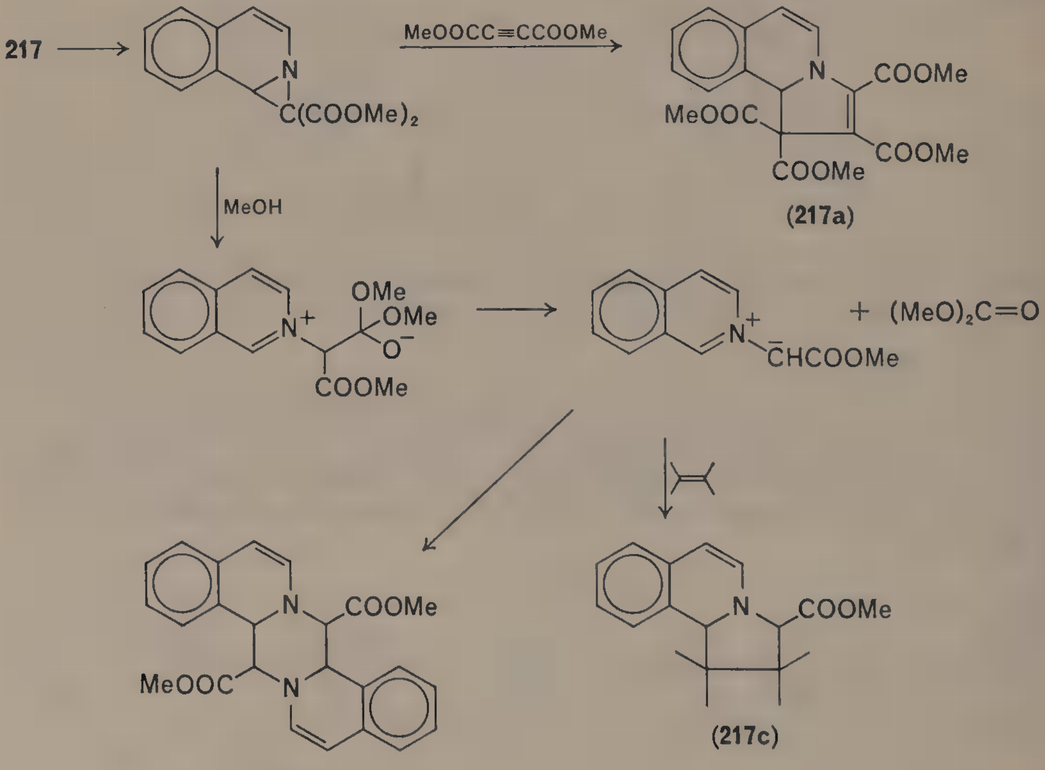
Pyridinium and isoquinolinium biscarbomethoxymethylides could be isolated from the photodecomposition of dimethyl diazomalonate in pyridine and isoquinoline[313]. Isoquinolinium carboethoxymethylide has also been obtained by photodecomposition of ethyl diazoacetate in the presence of isoquinoline[314].



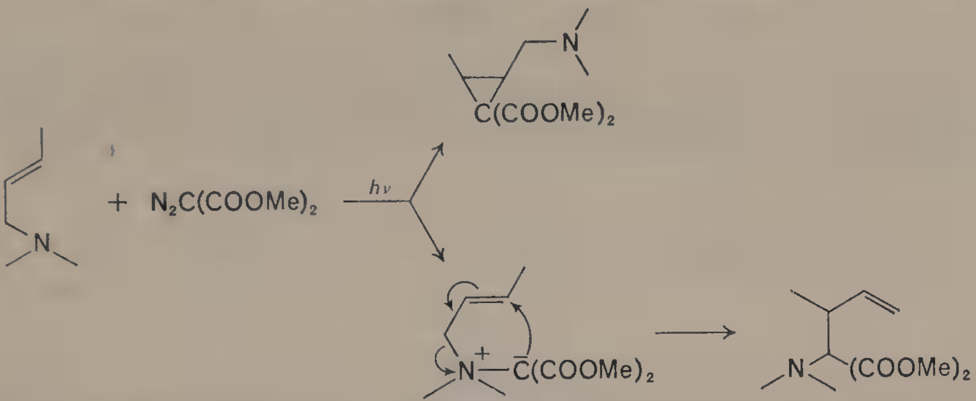

(217) **(218)**



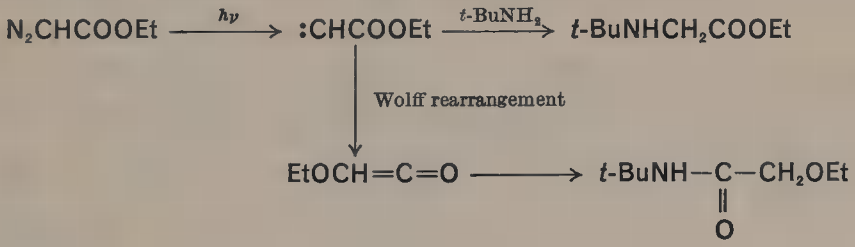
Isoquinolium dialkoxycarbonyl ylides (**217**) and dimethyl acetylene dicarboxylate react in methanol to give the 1,10-*b*-dihydropyrrole[2,1-*a*]isoquinolines (**217a**);


(217a) **(217b)** **(217c)**

217 in methanol alone yields the more reactive monoalkoxycarbonyl ylide and dialkyl carbonate, the former dimerizes to **217b** or reacts *in situ* with olefins to yield 1,2,3,10-*b*-tetrahydropyrrolo[2,1-*a*]isoquinolines (**217c**)[316]. The isolation of stable pyridinium ylides suggests also the intervention of nitrogen ylides in reactions in which one group bound to nitrogen is unsaturated. Here the ylide cannot be isolated but rearranges *in situ*[317]. Very similar results were reported for the reaction of carbomethoxycarbene with allyl chloride and allyl sulphides:



The study of reactions of carbenes with nitrogen–hydrogen bonds is practically virgin territory. In one such study, the reaction of carboethoxycarbene with *t*-butylamine has been reported to afford the nitrogen–hydrogen bond insertion product along with a product resulting from Wolff rearrangement (see Section J) of the carbene[318]:

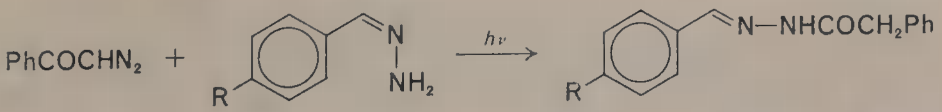


$$\begin{tikzcd} N_2CHCOOEt \arrow[r, "h\nu"] & :CHCOOEt \arrow[r, "t\text{-BuNH}_2"] \arrow[d, "\text{Wolff rearrangement}"] & t\text{-BuNHCH}_2COOEt \\ & EtOCH{=}C{=}O \arrow[r] & t\text{-BuNH}-\underset{\underset{\displaystyle O}{\|}}{C}-CH_2OEt \end{tikzcd}$$

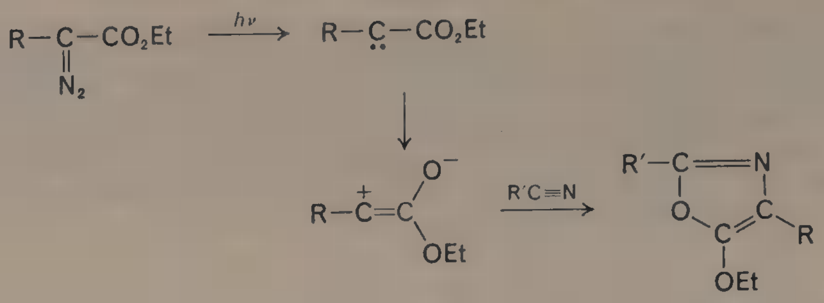
The photolysis of a hydrazine or a hydrazone with ω-diazoacetophenone in dry tetrahydrofuran yields the corresponding phenylacetylhydrazine or phenylacetylhydrazone in fairly good yields[319], probably via Wolff rearrangement. The benzhydrylamines produced from diphenyldiazomethane were accompanied by tetraphenylethane suggesting hydrogen abstraction as another possibility[320]:

$$PhCOCHN_2 + RNHNH_2 \xrightarrow{h\nu} PhCH_2CONHNHR$$

$$(R = H, Ph, CH_2Ph)$$

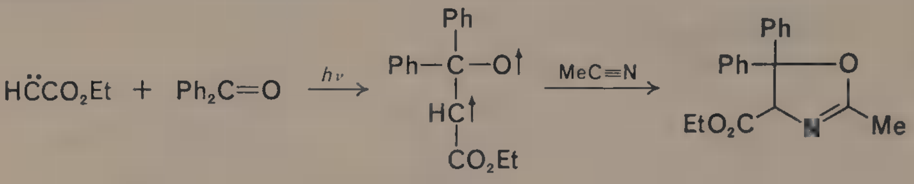


The photolysis of ethyl diazoacetate and of ethyl diazomalonate in acetonitrile gave oxazoles. It seems likely that the carboethoxycarbene formed by decomposition of the diazo ester undergoes 1,3-dipolar addition to the nitrile to form the oxazole **219** directly. The photolysis of ethyl diazoacetate in the presence of benzophenone gave an oxazoline incorporating the elements of carboethoxymethylene, benzophenone and acetonitrile, presumably by the addition of triplet carboethoxymethylene



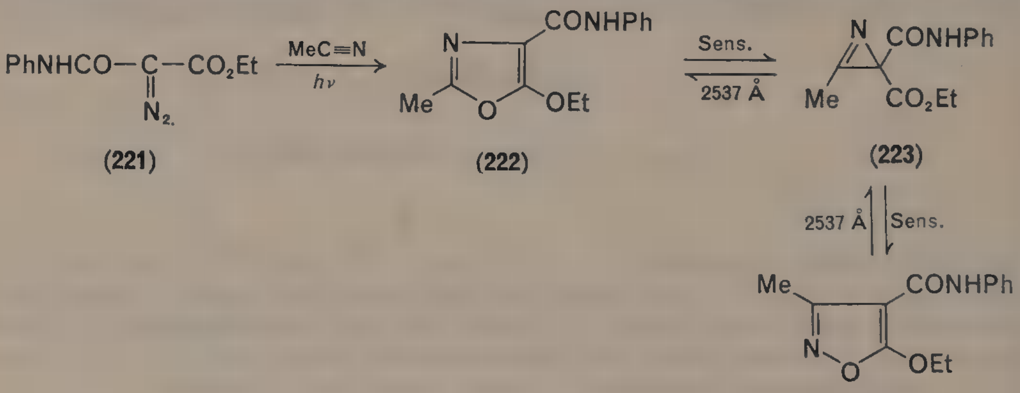
(219)

to benzophenone and further addition of the diradical intermediate **220** to acetonitrile[321].



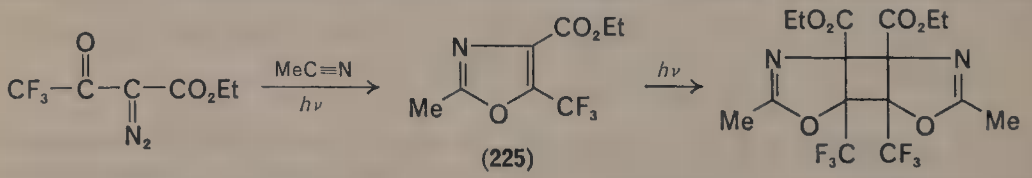
(220)

Irradiation of diazoacetate (**221**) in acetonitrile gave the oxazole **222** initially which in the presence of benzophenone rearranges to the isoxazole **224**. The azirine **223** has been proposed as the intermediate but could not be detected. When molecular oxygen, a triplet quencher, is introduced into the reaction vessel, the conversion of **222** to the isoxazole **224** is completely inhibited. The photolysis of trifluoroacetyldiazoacetate in acetonitrile gives **225** in 50% yield. The photolysis of the latter



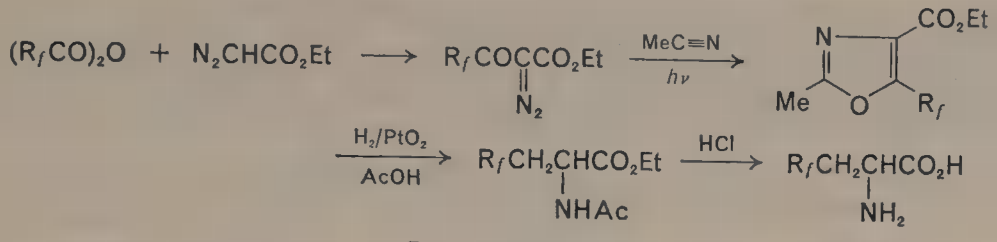
(221) **(222)** **(223)** **(224)**

affords a 10% yield of the dimeric species **226** which is thought to arise from a formal [2+2] cycloaddition of two oxazole rings. Weygand and coworkers have



(225) **(226)**

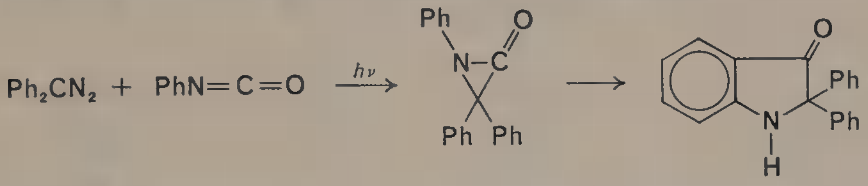
developed a general procedure for preparing β-perfluoroalkylalanines from perfluoroalkyloxazole synthesized by the 1,3-dipolar addition of perfluoroalkyl diazoacetic esters to acetonitrile. Over-all yields of **227** are 35–50%[322].



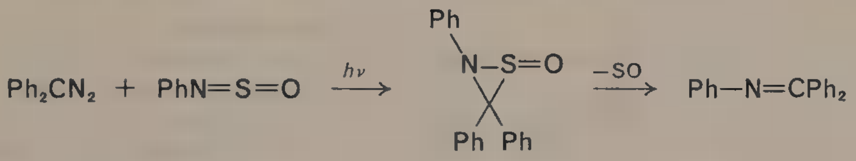
$R_f = CF_3, C_2F_5, C_3F_7$

(227)

Diphenyldiazomethane and phenylisocyanate react under influence of u.v. light to afford 2,2-diphenylindoxyl[323], presumably via diphenylcarbene addition to the C=N bond and rearrangement of the α-lactam intermediate:



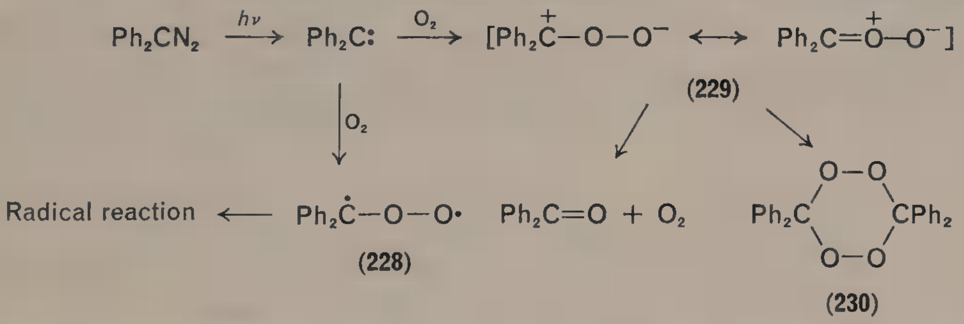
Irradiation of *N*-sulphurylaniline and diphenyldiazomethane gave *N*-diphenylmethyleneaniline as the major product[324]. There is evidence that S=O was evolved:



3. Reaction with oxygen compounds

a. *Molecular oxygen.* The photolysis of diphenyldiazomethane in the presence of oxygen afforded benzophenone, which became the major product under suitable conditions[325]. The isolation of the cyclic peroxide from the photooxidation of diphenyldiazomethane suggests a carbonyl oxide as the intermediate[326].

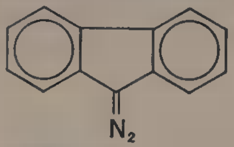
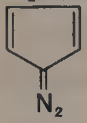
Experiments with $^{18}O_2$ indicate that no decomposition of **230** to give oxygen and benzophenone occurred under the conditions of the photooxidation. The processes leading to benzophenone appear to proceed in a parallel fashion rather than consecutively[327]. When the photooxidation was carried out in the presence of acetaldehyde, propionaldehyde or benzaldehyde, the ozonides of 1,1-diphenylpropene, 1,1-diphenyl-1-butene or triphenylethylene, respectively, could be isolated[328]. In the last case, no diperoxide was formed and the major product was benzophenone. The ozonide is presumably formed from reaction of the carbonyl oxide and the aldehyde, which reaction competes successfully with diperoxide



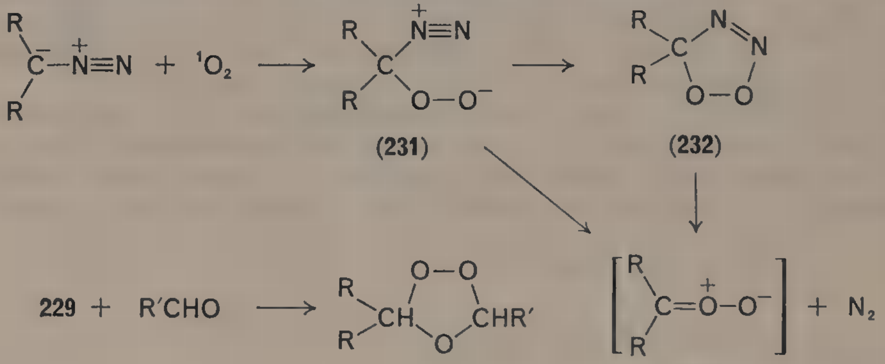
formation. Results to date indicate that ozonide formation is limited to diazo compounds containing two aryl substituents.

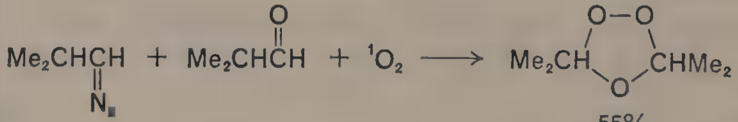
Some saturated hydrocarbons are oxidized at room temperature when carbenes are generated in them in the presence of oxygen[329]. The reaction seems to involve photolysis to give a triplet carbene which reacts with oxygen to give a diradical of the type **228**. The carbonyl oxide diradical then abstracts hydrogen from the alkane to give an alkyl radical and $R_2\dot{C}{-}O{-}OH$; the alkyl radical may react with **228**, RCOOH or oxygen to give eventually alcohols and carbonyl compounds by steps similar to those involved in other autooxidations of hydrocarbons.

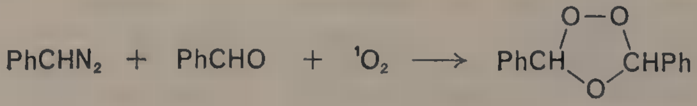
TABLE 34. The oxidation products obtained from the photodecomposition of various diazo compounds in cyclohexane saturated with oxygen

Diazo compound	Irradiation time (min)	Cyclohexanol (%)	Cyclohexanone (%)
	300	29	19 (55)[a]
None	300	1	1
Ph_2CN_2	88	21	13 (81)[a]
$N_2C(COOEt)_2$	300	1	1
	300	1	1

[a] Yield of ketone from diazo compound by gas chromatography.

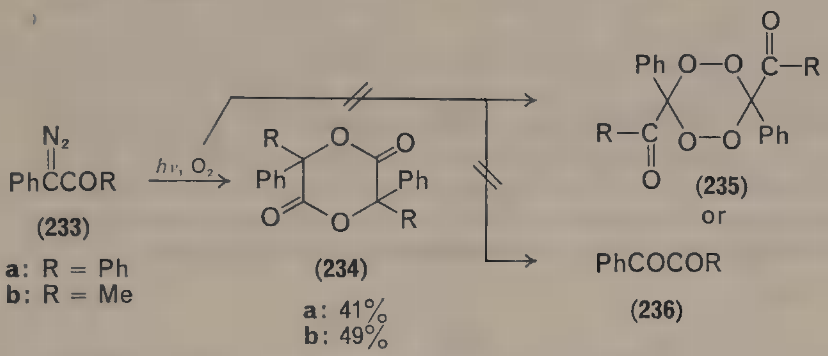

(231) (232) (229)


55%

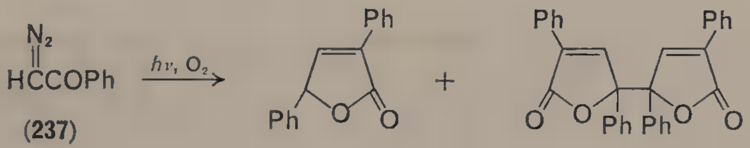

52%

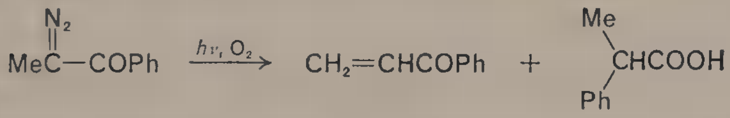
Triplet carbenes react with oxygen more readily than singlet carbenes, apparently yielding a triplet carbene–oxygen adduct. This method has been extended to cases where diazo compounds can be converted to ozonides by allowing them to react with singlet oxygen in the presence of an aldehyde[330]. This reaction is observed with both aryl and alkyl diazo compounds. A possible mechanism involves attack by the electrophilic singlet oxygen at an electron-rich centre of the diazo compound. The resulting intermediate **231** may decompose directly to give nitrogen and the zwitterion **229** or it may cyclize first to the heterocycle **232**.

The photochemical reaction of diazo ketones **233** with molecular oxygen in aromatic solvents gave tetraphenylglycolide (**234a**) and 3,6-dimethyl-3,6-diphenylglycolide (**234b**), respectively, instead of the peroxide (**235**) or diketone (**236**)[331].



By contrast, diazo ketones (**237**) afforded products resulting from 1,2-hydrogen shift and 1,3-dipolar addition of the keto-carbene intermediate.





b. *Reaction with alcohols.* When diazomethane and *t*-butanol mixtures were photolysed, the major products were *t*-butyl methyl ether and 2-methylbutan-2-ol[332]. From the amounts formed, the O—H bond of *t*-butanol is 10·9 times as reactive as a C—H bond. Competitive reactions with roughly equimolar mixtures of alcohols gave the following relative reactivities of O—H bonds toward attack by methylene:

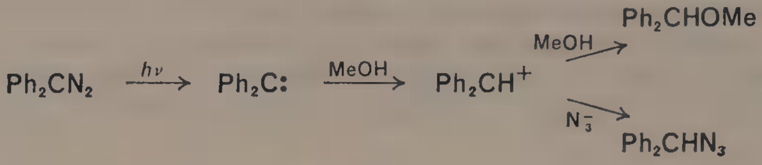
$$\mathrm{ROH+CH_2N_2} \xrightarrow{h\nu} \mathrm{ROCH_3+C{-}H\ insertion\ products}$$

Reactivities of RO—H bonds for :CH₂:

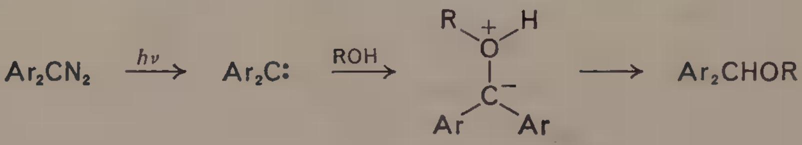
MeO—H	EtO—H	*i*-PrO—H	*t*-BuO—H
2·01	1·95	1·37	1·00

This is the order of decreasing acidity of the alcohols as well as the order of increasing steric hindrance. Photolysis of diphenyldiazomethane in methanol afforded benzhydryl methyl ether in 70% yield[333]. The quantum yields of the photolyses in methanol and in aprotic solvents were identical within experimental error.[334]

Photolysis of diphenyldiazomethane in a methanolic solution of lithium azide produced benzhydryl methyl ether and benzhydryl azide in virtually the same ratio as that obtained in the solvolysis of benzhydryl chloride. These results suggested a diphenylcarbonium ion intermediate, arising by protonation of diphenylcarbene:

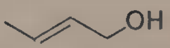
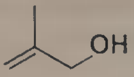
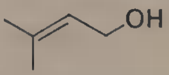
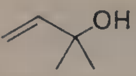


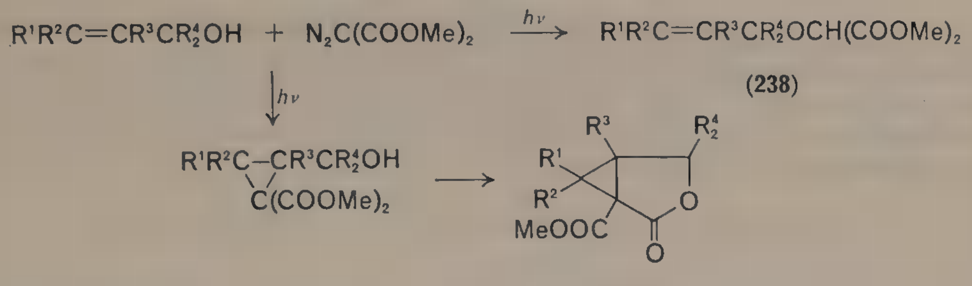
From studies of isotope effects it has been deduced that diphenylcarbene reacts with the oxygen atom of ROH, giving an ylide, subsequent rearrangement of which gives Ph_2CHOR. The kinetics were rather complex[335, 336]. With *i*-propanol, hydrogen abstraction to give diphenylmethane and acetone competed with formation of benzhydryl *i*-propyl ether. If hydrogen abstraction and autooxidation are attributed to triplet carbene, the kinetics require the reversible interconversion of the singlet and triplet states, indicating a delicate balance of mechanisms.



The reaction of allyl alcohol with biscarbomethoxycarbene produced by direct photolysis of dimethyl diazomalonate afforded two principal products, that of O—H insertion (**238**) and bicyclo[3.1.0]lactone (**239**). The product **239** is presumably formed by lactonization with elimination of methanol from the initially formed cyclopropylcarbinol arising by addition of the carbene to the double bond[337, 338].

TABLE 35. Photolysis of dimethyl diazomalonate in allylic alcohols

Alcohol	Direct (%) (238)	Direct (%) (239)	Sensitized (%) (239)
	24·5	31·9	38·7
	14·9	33·2	19·7
	34·1	21·9	39·4
	11·5	69·2	7·2
	21·2	11·8	50·1

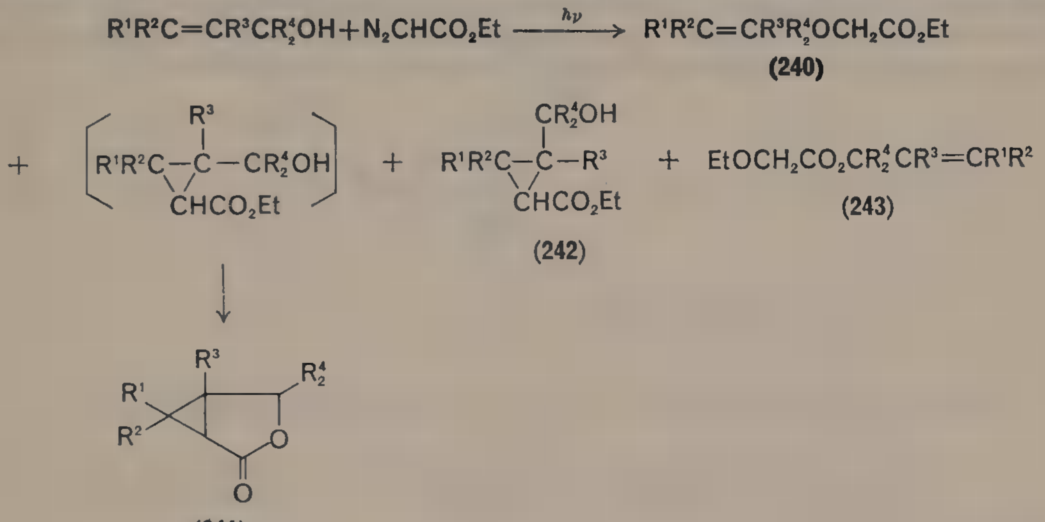


$$R^1R^2C{=}CR^3CR^4_2OH + N_2C(COOMe)_2 \xrightarrow{h\nu} R^1R^2C{=}CR^3CR^4_2OCH(COOMe)_2$$

(238)

(239)

Photolysis of ethyl diazoacetate in allylic alcohols gave similar products, **240** and **241**, together with *trans*-cyclopropylcarbinol (**242**) and Wolff rearrangement product (**243**). *trans*-Cyclopropylcarbinol cannot be converted to bicyclo[3.1.0]-lactone. The most marked difference between direct and sensitized photolysis is in the relative ratio of the products of insertion and addition. The benzophenone-sensitized photolysis of dimethyl diazomalonate gave bicyclo[3.1.0]lactone, but no O—H insertion product. Similarly, the sensitized photodecomposition of ethyl diazoacetate in allylic alcohols gave mainly the carbon–carbon double-bond addition products.



$$R^1R^2C{=}CR^3CR^4_2OH + N_2CHCO_2Et \xrightarrow{h\nu} R^1R^2C{=}CR^3R^4_2OCH_2CO_2Et$$

(240)

(242)

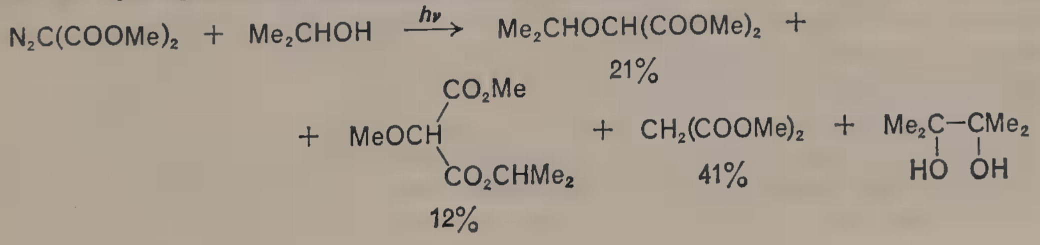
$$+ EtOCH_2CO_2CR^4_2CR^3{=}CR^1R^2$$

(243)

(241)

The most probable mechanism of the O—H insertion involves an electrophilic singlet carbene attack on the oxygen atom of the alcohol to give an oxygen ylide followed by the proton migration from oxygen to carbon. Distribution of the products depends on the structure of the allylic alcohols and seems to be controlled mainly by steric factors.

The photolysis of dimethyl diazomalonate in alcohols produced substantial amounts of dimethyl malonate, and the efficiency of hydrogen abstraction varies with the hydrogen donor properties of the alcohol[339].



$$N_2C(COOMe)_2 + Me_2CHOH \xrightarrow{h\nu} Me_2CHOCH(COOMe)_2 + MeOCH(CO_2Me)(CO_2CHMe_2) + CH_2(COOMe)_2 + Me_2C(OH){-}C(OH)Me_2$$

The formation of pinacol in *i*-propanol fits a scheme in which the triplet abstracts hydrogen to give a radical pair followed by another hydrogen abstraction and radical recombination. Both the photosensitized and benzoyl-peroxide-induced decomposition of dimethyl diazomalonate in ethanol and in *i*-propanol gave dimethyl malonate in 74–80% yields.

$$N_2C(COOMe)_2 + RR'CHOH + Ph_2CO \xrightarrow{h\nu} CH_2(COOMe)_2$$

c. *Reaction with ethers.* The major reaction of methylene with ethers is nearly random insertion into the various C—H bonds. Two minor reactions are displacement, leading to methyl ethers, and apparent insertion into the C—O bond. The displacement reaction with methyl alkyl ethers results in the formation of dimethyl ether and an olefin[239]. It is not suppressed by the presence of oxygen nor does it occur when the methylene is produced by mercury photosensitization. The reaction is therefore envisaged as resulting from the initial attack of singlet methylene on the oxygen atom to give an ylide intermediate, followed by β-elimination.

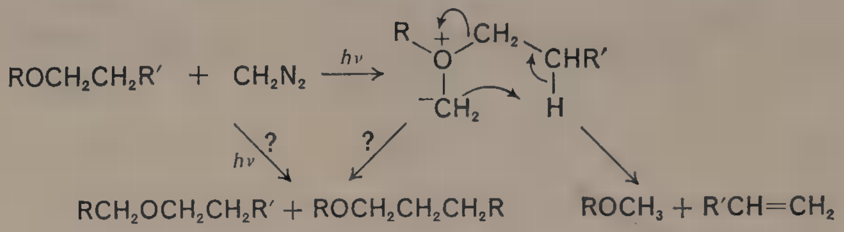
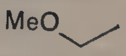
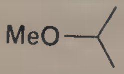
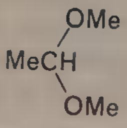
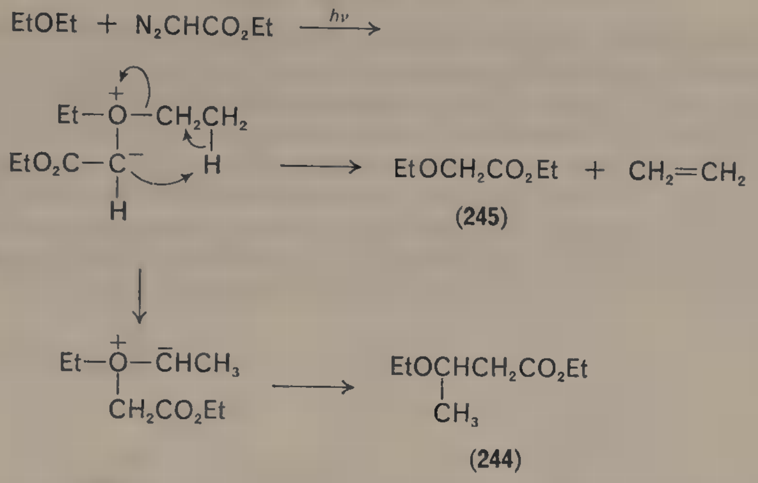
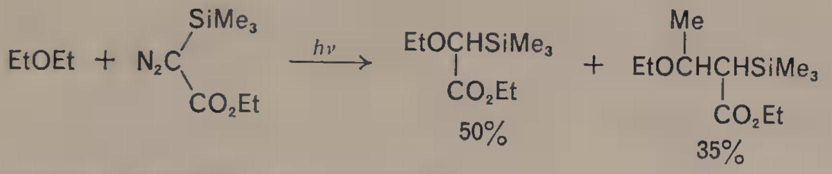


TABLE 36. The relative amounts of displacement and C—O insertion of methylene with ethers

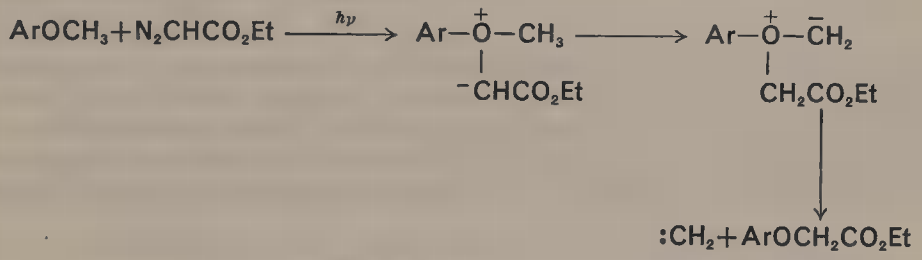
Ethers	Phase	Displacement (%)	C—O Insertion (%)
	Gas	4·0	0
	Liquid	0	0
	Gas	3·2	0
	Liquid	0	0
	Gas	10·0	2
	Liquid	5·6	0
 $MeCH(OMe)_2$	Gas	3·9	4·6
	Liquid	1·6	11·3

Photolysis of ethyl diazoacetate in diethyl ether led to **244** and **245** as the principal products[340]. The product **244** in the observation of CIDNP emission can be rationalized in terms of oxygen ylide intermediate which then undergoes Stevens rearrangements via a homolysis–recombination mechanism[341]. Formation of a different ylide intermediate followed by Hoffman type β-elimination of ethylene by a non-radical path is a reasonable explanation for the formation of **245**. Many substituted anisols and silyl-substituted methyl ethers gave rise to methyl elimination products when treated with ethyl diazoacetate and diphenyldiazomethane. These reactions may also be rationalized by an oxygen ylide intermediate from which,





after prototropy methylene, is split off[342]:

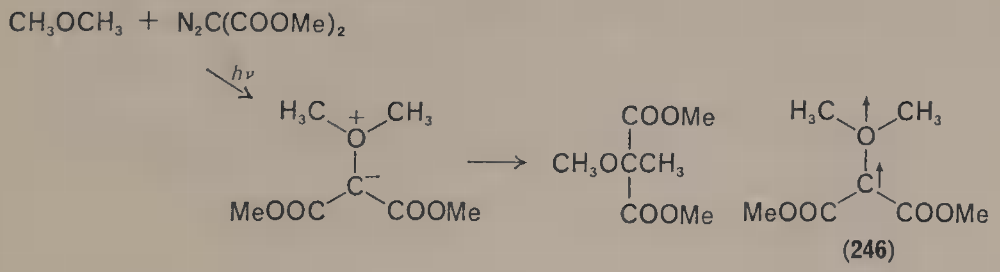


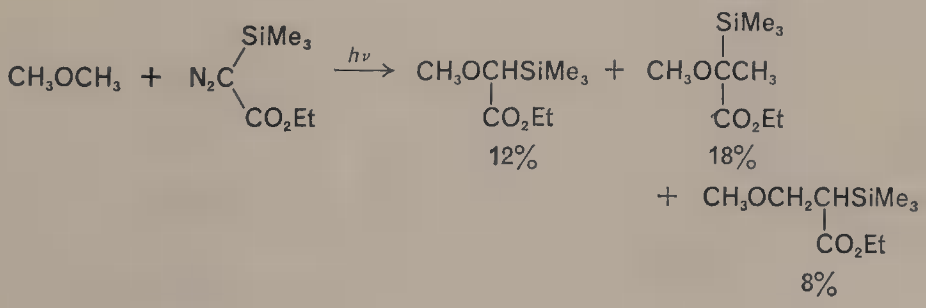
$$Me_3SiCH_2OCH_3 + N_2CHCO_2Et \xrightarrow{h\nu} Me_3SiCH_2OCH_2CO_2Et + MeOCH_2CO_2Et$$

$+$C—H insertion products

$$PhOCH_3 + PhRCN_2 \xrightarrow{h\nu} PhOCHRPh + PhRC{=}N{-}N{=}CRPh$$

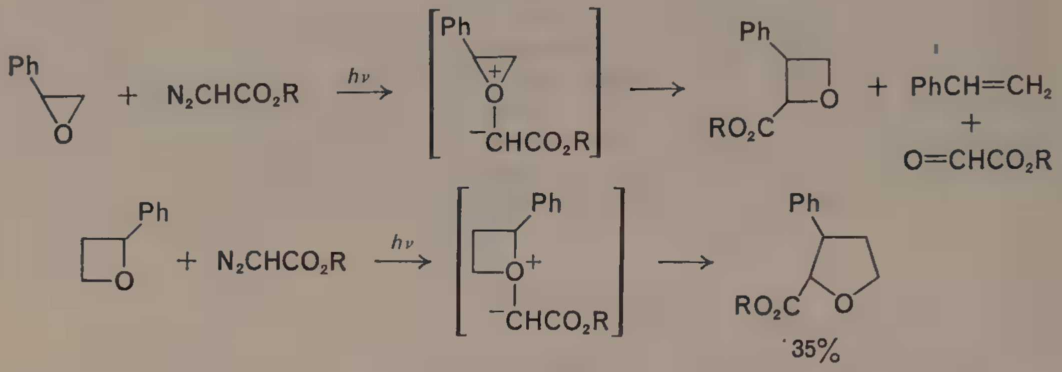
(R = H, Ph)





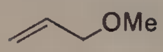
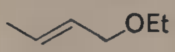
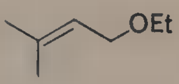
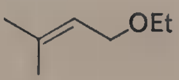
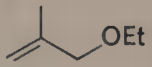
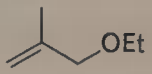
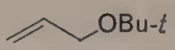
Insertion into the C—O bond is the predominant reaction of ethyl trimethylsilyldiazoacetate[291] and dimethyl diazomalonate[188] with dimethyl ether. The insertion reaction probably involves the formation of an oxygen ylide intermediate. However, the sensitized reaction produces no such products. Apparently complexes of the type **246** either are not formed or do not rearrange to products.

Similarly, C—O bond insertion was observed in the reaction with carboethoxycarbene with cyclic ethers. The reaction of ethyl diazoacetate with 2-phenyloxirane gave an oxetane, styrene and glyoxalate[343]. 2-Phenyloxetane produced a mixture of *cis*- and *trans*-2-ethoxycarbonyl-3-phenyltetrahydrofurans[344].



Addition of biscarbomethoxycarbene to the C=C double bond of allyl ethers was accompanied by apparent O–allyl bond insertion products which can be considered to form through the intermediate oxygen ylides by allylic rearrangement[317]. The bulky *t*-butyl group on the oxygen atom seems to interfere with the formation of the ylide. The corresponding reaction with ethyl trimethylsilyldiazoacetate[291] results in

TABLE 37. Yield of products from the photolysis of dimethyl diazomalonate in allyl ethers

Allyl ethers	Mode of decomposition	Insertion (%)	Addition (%)
	hν	31	20
	hν	37	17
	hν	15	38
	hν	16	25
	hν + Ph_2CO	trace	52
	hν	15	38
	hν + Ph_2CO	trace	62
	hν	0	39

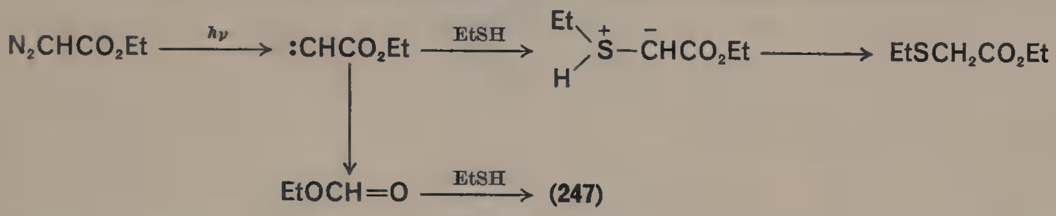
the formation of a C—O insertion product via [2,3]-sigmatropic rearrangement of the oxonium ylide and of addition products. However, no C—O insertion product was observed when diphenyl diazomethane was photolysed in allyl ether.

4. Reaction with sulphur compounds

Insertion of carbenes into the S—H bond of thiols has been achieved by the photodecomposition of ethyl diazoacetate[345] and of bis(phenylsulphonyl)-diazomethane[346]. Probably, singlet carbethoxycarbene reacts with the sulphur

$$\mathrm{N_2CHCO_2Et + EtSH \xrightarrow{h\nu} \underset{53\%}{EtSCH_2CO_2Et} + \underset{\substack{\mathbf{(247)}\\ 6\%}}{EtOCH_2COSEt}}$$

atom to give a sulphur ylide intermediate, followed by proton migration as with alcohols. The product **247** involves the Wolff rearrangement of the carbene to a



ketene. The corresponding benzophenone-sensitized irradiation of ethyl diazoacetate in ethyl mercaptan gives products in similar yields. The radical mechanism is probably involved in the S—H insertion even in direct photolysis as follows:

$$\mathrm{N_2CHCO_2Et \xrightarrow{h\nu} {:}CHCO_2Et \xrightarrow{EtSH} EtS{\bullet} + {\bullet}CH_2CO_2Et}$$

$$\mathrm{EtS{\bullet} + N_2CHCO_2Et \longrightarrow N_2 + EtS\dot{C}HCO_2Et}$$

$$\mathrm{EtS\dot{C}HCO_2Et + EtSH \longrightarrow EtS{\bullet} + EtSCH_2CO_2Et}$$

The same radical reaction of ethyl diazoacetate can be achieved thermally by employing azoisobutyronitrile (AIBN) as a radical initiator. Radical-induced decomposition of diazo compounds was also proposed by Horner and coworkers[347, 348]. The formation of the S—H insertion product was rapid in the presence of, and very slow in the absence of, the radical initiator. No other product was found except a trace of diethyl disulphide:

$$\mathrm{EtSH + N_2CHCO_2Et + AIBN \xrightarrow{60\,^{\circ}C} \underset{97\%}{EtSCH_2CO_2Et} + (EtS)_2}$$

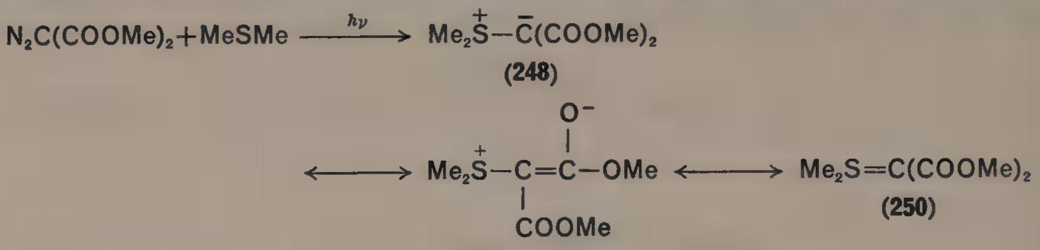
Since no rearrangement product was detected in the aromatic thiol (Table 38), the carbene may not be involved in these reactions, and the insertion into the sulphur–hydrogen bond might occur only by radical chain reactions.

Dialkyl sulphides afforded stable sulphur ylides by adding carbenes with strongly electron-withdrawing substituents. Biscarbomethoxycarbene, generated photochemically from dimethyl diazomalonate, reacts with alkyl and aryl sulphides and sulphoxides to form stable sulphonium and sulphoxonium biscarbomethoxymethylides[349, 350]. The ability of sulphur to stabilize an adjacent negative charge remains an interesting phenomenon.

Table 38. Photodecomposition of ethyl diazoacetate in thiols

Thiol	Mode of decomposition	S—H insertion (%)	Rearrangement (%)
EtSH	*hν*	53	6
EtSH	*hν*+Ph_2CO	70	6
i-PrSH	*hν*	31	5
t-BuSH	*hν*	35	6
PhSH	*hν*	74	0
PhSH	*hν*+Ph_2CO	90	0
p-MeOPhSH	*hν*	58	0

Comparison of the sulphur ylides to nitrogen ylides indicates that factors beyond electrostatic stabilization must be involved. The simplest explanation involves delocalization of electron density into low-lying d orbitals of sulphur[351]. It has been pointed out that a combination of only s and p type orbitals can also accommodate

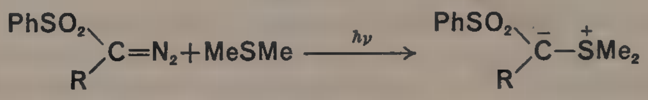


$$N_2C(COOMe)_2+MeSMe \xrightarrow{h\nu} Me_2\overset{+}{S}-\overset{-}{C}(COOMe)_2$$

(248)

$$\longleftrightarrow Me_2\overset{+}{S}-\underset{\displaystyle COOMe}{\underset{|}{C}}=\overset{\displaystyle O^-}{\overset{|}{C}}-OMe \longleftrightarrow Me_2S{=}C(COOMe)_2$$

(249) **(250)**

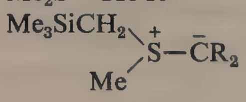


R = PhCO, MeCO or $PhSO_2$

such a valence shell expansion[352] (ylene structure **250**). A large shift (~110–170 cm^{-1}) to lower energy in the carbonyl stretching frequency in the infrared spectrum of the biscarbomethoxymethylides compared to the analogous sulphonium salts also demonstrates extensive delocalization of charge by such

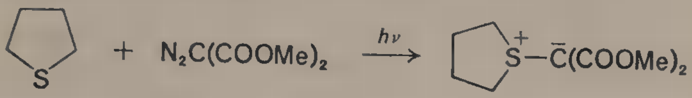
Table 39. Formation of sulphonium ylides from bis(carbonyl)diazo compounds and sulphides[349, 350]

(R = COOMe, R^1 = COOEt, R^2 = COMe, R^3 = $\overset{\overset{\displaystyle O}{\|}}{P}Ph_2$)

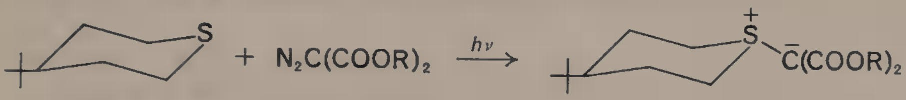
Sulphides	Ylides	Melting point (°C)	i.r. (C=O)	Yield (%)
Me_2S	$Me_2\overset{+}{S}-\overset{-}{C}R_2$	169–170	1625, 1675	88
Et_2S	$Et_2\overset{+}{S}-\overset{-}{C}R_2$	150	1625, 1655	57
Ph_2S	$Ph_2\overset{+}{S}-\overset{-}{C}R_2$	127–128	1650, 1675	12
Me_2S	$Me_2\overset{+}{S}-\overset{-}{C}R^1_2$	134–135	1625, 1655	87
Me_2S	$Me_2\overset{+}{S}-\overset{-}{C}R^2_2$	166–167	1570, 1600	52
Me_2S [353]	$Me_2\overset{+}{S}-\overset{-}{C}R^2R^3$		1572	
Me_3SiCH_2SMe [291]		132–134		

carbanion stabilizing groups. An increase in the ylide carbon–carbonyl carbon π-bond order accompanies the decrease in the π-bond order of the carbonyl group (betaine structure **249**).

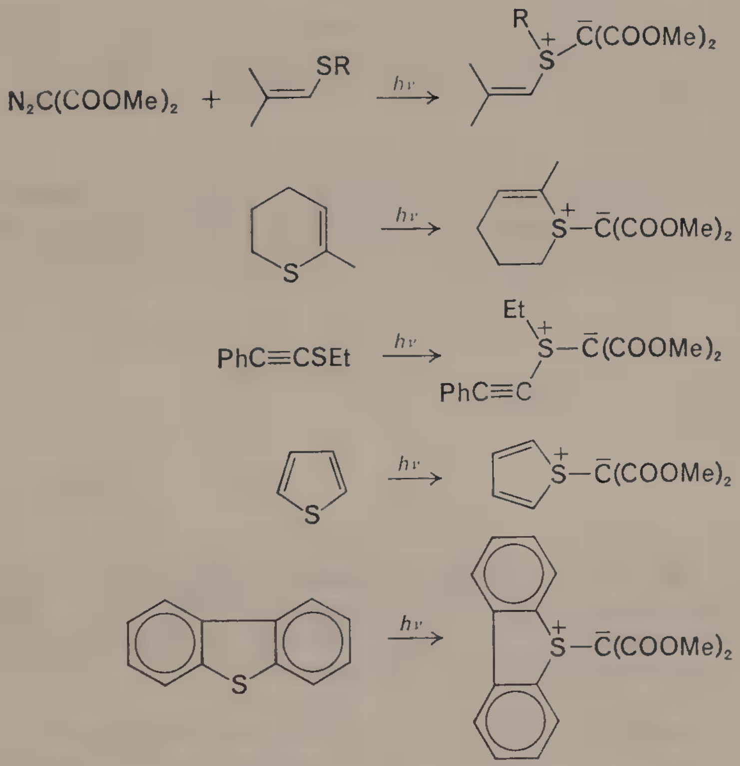
In the reaction of dimethyl diazomalonate with saturated cyclic sulphides, the corresponding sulphonium ylides were also obtained as stable colourless solids. Irradiation of dimethyl diazomalonate in pentamethylene sulphide gave 41% of sulphonium ylide. Thiethane did not give sulphonium ylides because of its photopolymerization[354]:



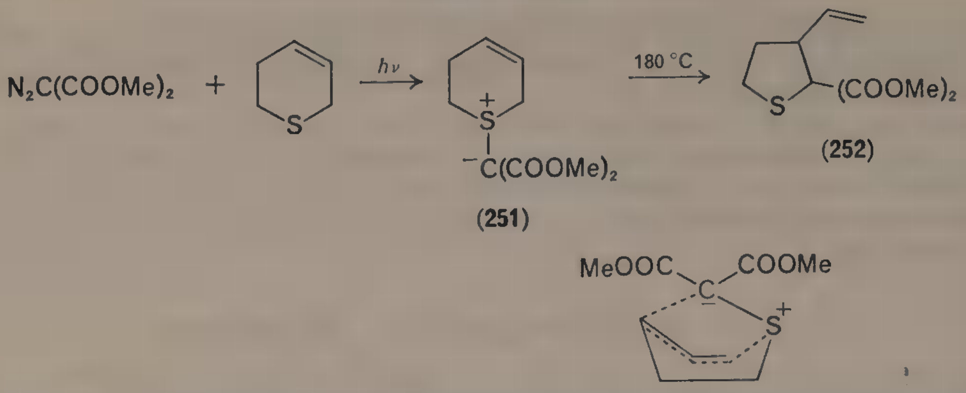
High stereoselectivity is observed with 4-*t*-butyltetrahydrothiopyran[355]:



Even vinylic[356] and acetylenic sulphides[354], thiophene and benzothiophene[354], in which the lone pair of sulphur is highly delocalized, may trap the carbene produced in the photolysis of dimethyl diazomalonate. These ylides are quite stable at room temperature:



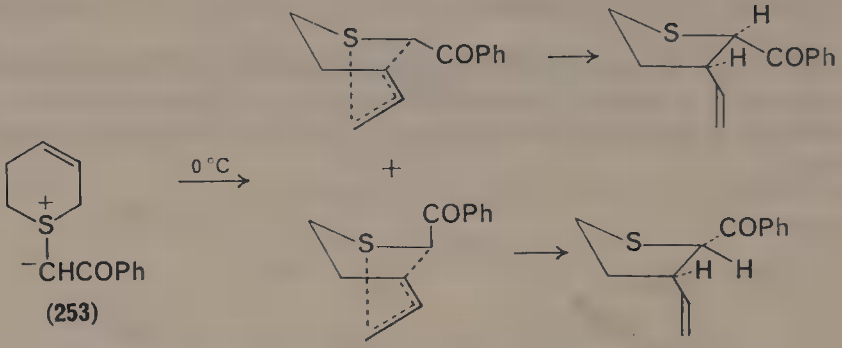
The photolysis of dimethyl diazomalonate in Δ^3-dihydrothiopyran[317] gave the sulphonium bis(carbomethoxy)methylide (**251**), which rearranged to **252** in 83% yield on heating at 180 °C for 30 min. The ylide **251** could be isolated and rearranges only at higher temperatures, while ylides derived from open-chain allylic sulphides gave rearranged products at room temperature. This low susceptibility of the ylide (**251**) toward rearrangement is probably due to the transition state of the concerted allylic rearrangement requiring the unfavoured boat form of the dihydropyran ring bearing the COOMe group *endo* to the sulphur atom.



(251)

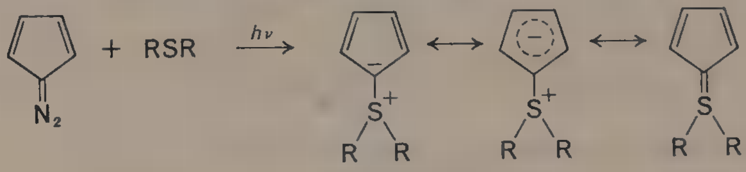
(252)

A clear preference for the *exo* orientation was also seen in the rearrangement of **253** [358].



(253)

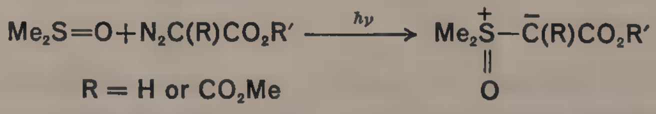
Photolysis of diazocyclopentadiene in alkyl sulphides also gives stable cyclopentadienylides in high yields[359]. Dimethylsulphonium cyclopentadienylide is considered to be the resonance hybrid of the ylide structures **254**, **255** and the



(254) (255) (256)

Ylide structure Ylene structure

ylene structure **256**, with the ylide structures predominating[360]. Stabilized oxosulphonium ylides, unavailable by the direct condensation of sulphoxides and α-halocarbonyl compounds[361], are suited for the carbene approach[350, 362]. Both thermal methods and photolysis have been employed.

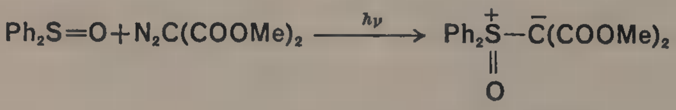


$$Me_2S{=}O + N_2C(R)CO_2R' \xrightarrow{h\nu} Me_2\underset{\underset{O}{\|}}{\overset{+}{S}}-\overset{-}{C}(R)CO_2R'$$

R = H or CO$_2$Me

R′ = Me, Et

30–60%



$$Ph_2S{=}O + N_2C(COOMe)_2 \xrightarrow{h\nu} Ph_2\underset{\underset{O}{\|}}{\overset{+}{S}}-\overset{-}{C}(COOMe)_2$$

12%

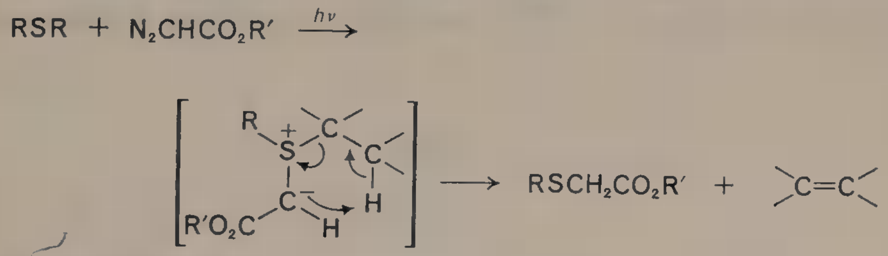
The relative reactivity of the sulphur atom of dimethyl sulphide toward carbene was estimated from the product distribution in the photolysis of dimethyl diazomalonate in mixture of cyclohexene and dimethyl sulphide[349]. It was suggested that the biscarbomethoxycarbene reacts with dimethyl sulphide about 6 times faster than with the double bond of cyclohexene. Similar high reactivity of sulphur toward carbenes was also observed in the photolysis of equimolar mixtures of dimethyl sulphide and other nucleophiles.

TABLE 40. Yields of products obtained from dimethyl diazomalonate and dimethyl sulphide in the presence of an equimolar amount of a second substrate

Second substrate	Yield of ylide (%)	Yield of adducts (%)
Cyclohexene	61	15[a]
2-Methyl-2-butene	49	8·5[b]
cis-4-Methyl-2-pentene	60	5[b]
Cyclopentadiene	44	—
Methanol	78	10[c]
Diethyl ether	73	12[d]

[a] Mixture of 7,7′-dicarbomethoxynorcarane and 2-cyclohexenylmalonate in the ratio of 2·1 : 1.
[b] Olefin adduct only.
[c] O—H insertion product.
[d] Ethylene elimination and C—H insertion products.

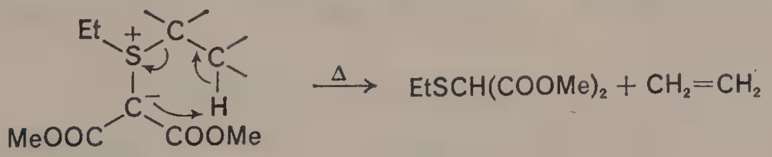
Ethyl diazoacetate and aryl diazomethanes did not yield stable sulphonium ylides, but afforded decomposition products of the latter[363, 364]:



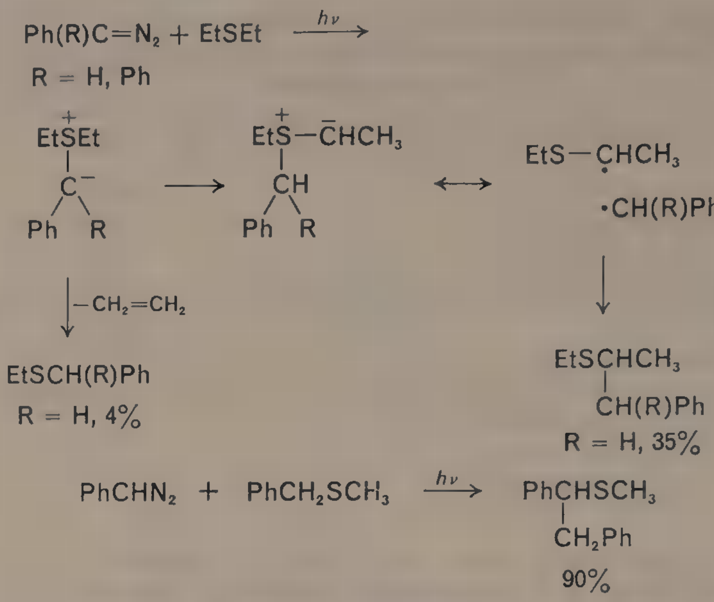
R = Et, *i*-Pr, or *t*-Bu

The reactions of alkyl sulphides bearing a β-hydrogen atom with ethyl diazoacetate yielded, by β-elimination, alkyl thioacetates formed by thermal intramolecular olefin elimination from the intermediate sulphonium ylides via a five-member cyclic transition state.

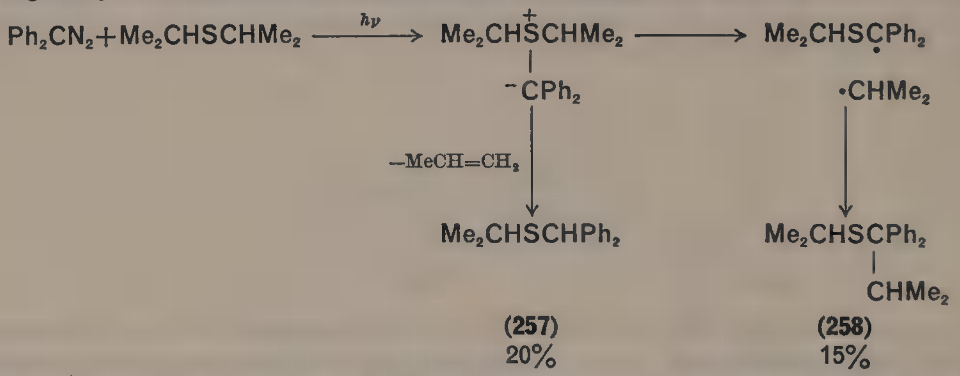
Additional results concerning the behaviour of sulphonium ylides are available. Thermal decomposition of biscarbomethoxymethylides gave dimethyl alkylthiomalonate in quantitative yield[365]. This supports the proposed ylide mechanism in the reactions of carbethoxycarbene with hetero atoms bearing β-hydrogens.



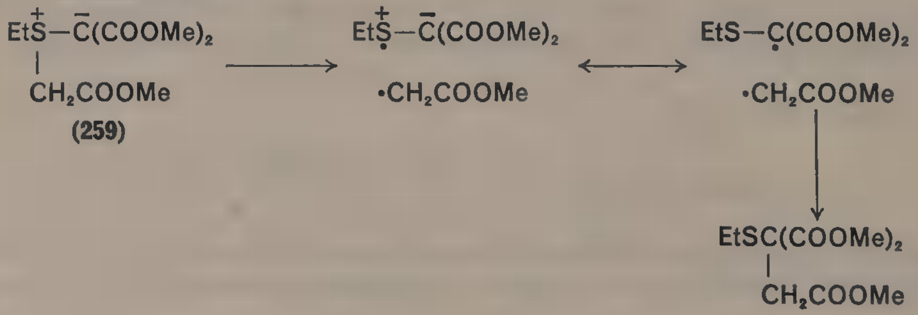
Photolysis of phenyl- and diphenyl-diazomethanes in diethyl and benzyl methyl sulphides gave mainly α-C—H insertion, with some β-elimination products, but phenyldiazomethane with *i*-propyl and *t*-butyl sulphides gave the β-elimination products[364]. The C—H insertion has been suggested to proceed via sulphur ylides followed by benzyl or benzhydryl migration from sulphur to carbon.



Some C—S insertion of carbene was also observed. The photolysis of diphenyldiazomethane in diisopropyl sulphide gave *i*-propyl benzhydryl sulphide (**257**) and *i*-propyl(*i*-propylthio)diphenylmethane (**258**) in 20 and 15% yields, respectively. The sulphur ylide could, by thermal Stevens rearrangement, yield **258**.

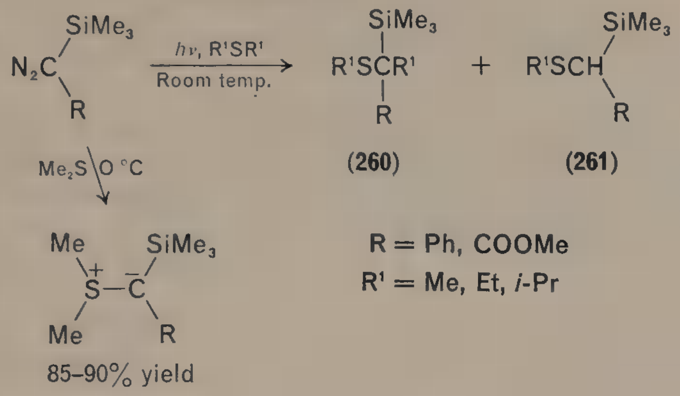


Such 1,2-shifts are forbidden in a concerted reaction mechanism. In fact, the accumulated evidence points to a diradical pathway[366]. A CIDNP enhancement of the n.m.r. signal of the methylene group is observed if the reaction is carried out in an n.m.r. spectrometer[354].



Hence, C—S insertion of carbenes is considered to involve homolytic cleavage of the sulphonium ylide yielding a radical pair, which collapses to the product. Intervention of radical pair intermediates has been suggested in the reaction of sulphonium salts with bases[366–368].

Stevens rearrangement was also observed in the photolysis of trimethylsilyldiazoacetate and trimethylsilyl(phenyl)diazomethane in dimethyl, diethyl and di-*i*-propyl sulphides at room temperature[369].



(260) (261)

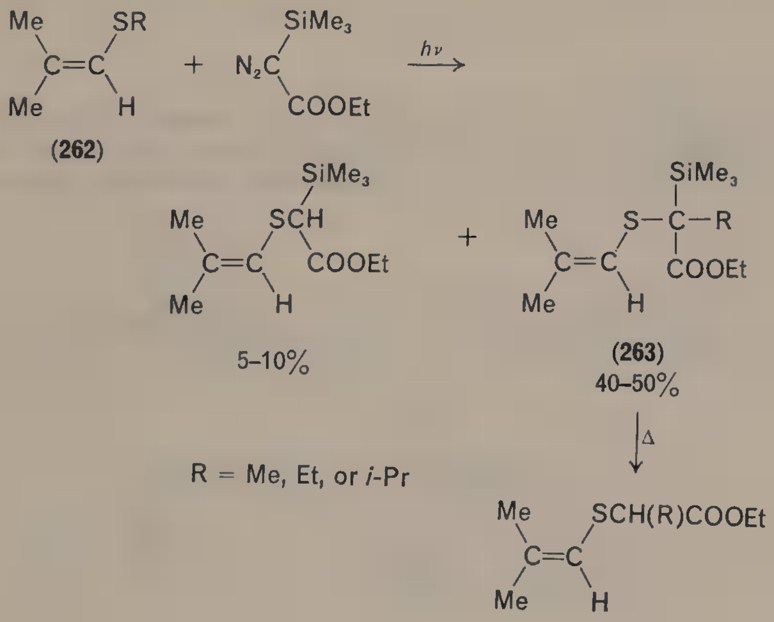
85–90% yield

R = Ph, COOMe

R' = Me, Et, *i*-Pr

TABLE 41. Photolysis of ethyl trimethylsilyldiazoacetate and trimethylphenyldiazomethane in alkyl sulphides at room temperature

R	R¹	260 (%)	261 (%)
COOEt	Me	37	0
COOEt	Et	43	6
COOEt	*i*-Pr	31	25
Ph	Me	30	4
Ph	Et	15	25
Ph	*t*-Bu	0	27



(262)

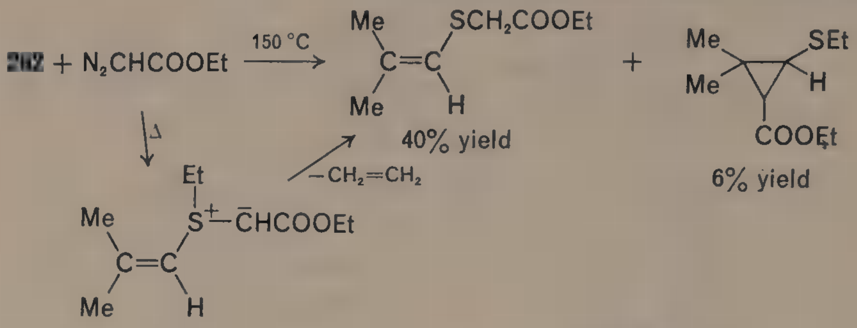
5–10%

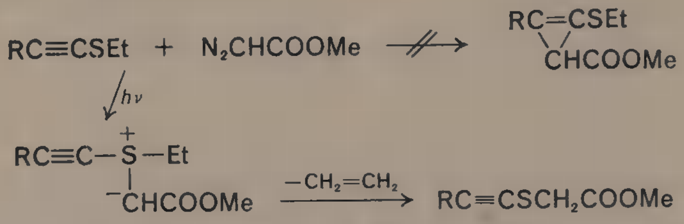
(263)
40–50%

R = Me, Et, or *i*-Pr

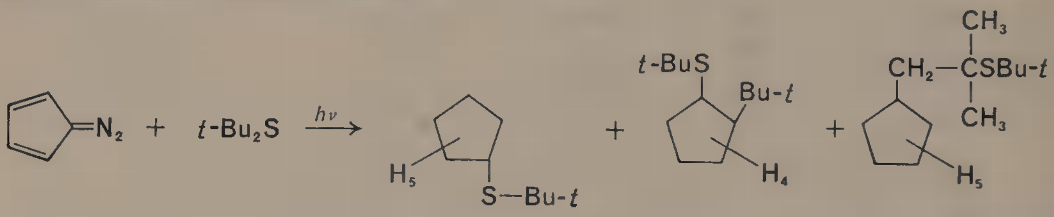
The α-C—H and β-elimination reactions were found to yield minor products. A sulphonium ylide was also isolated when the reaction was carried out below 0 °C. However, this ylide does not rearrange to the C—S insertion product **260**.

The corresponding reaction with the vinyl sulphide (**261**) affords **262** and **263**; product **263** results formally via carbene insertion into the C—S bond of **261**. No addition product was observed[370]. Thermal decomposition of ethyl diazoacetate in

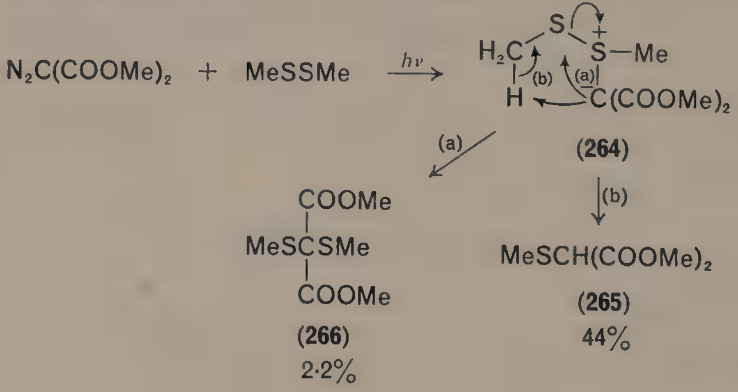




vinyl sulphides and acetylenic sulphides gave mainly β-elimination products. No C—S insertion product has been observed[356, 357]. In the photolysis of diazocyclopentadiene in di-*t*-butyl sulphide, C—S insertion, β-elimination and the C—H insertion products were obtained[359].



In the photolytic reactions of diazo carbonyl compounds with dialkyl disulphides, the products arising from thiocarbonyl elimination have been observed. Thus, the reaction of dimethyl diazomalonate with dimethyl disulphide afforded dimethyl

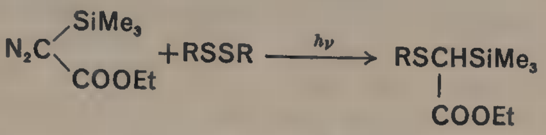


(**264**)

(**266**)
2·2%

(**265**)
44%

methylthiomalonate (**265**) and dimethyl dimethylthiomalonate (**266**) via an ylide intermediate (**264**)[354, 364].

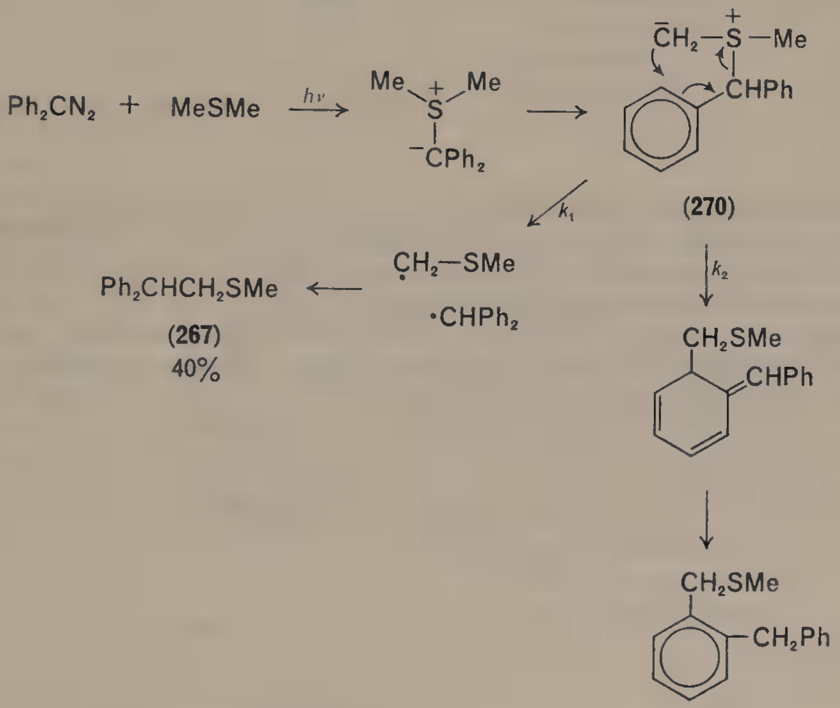


$$N_2C(SiMe_3)(COOEt) + RSSR \xrightarrow{h\nu} RSCH(SiMe_3)(COOEt)$$

R = Me, 49%; R = Et, 95%

$$N_2CPh_2 + MeSSMe \xrightarrow{h\nu} \underset{49\%}{MeSCHPh_2}$$

Photolysis of diphenyl and phenyldiazomethanes in dimethyl sulphide led to **267**, **268** and **269**. Product **267** can be rationalized in terms of Stevens rearrangement of the intermediate sulphur ylide; products **268** and **269** do not conform to this scheme, but rather to [2,3]sigmatropic rearrangement of sulphur ylide[364] (Sommelet–Hauser rearrangement).

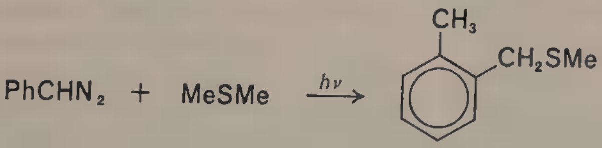


(**270**)

(**267**) 40%

(**268**) 10%

The ratio of Sommelet–Hauser to Stevens rearrangement varied when the photolysis of diphenyldiazomethane in dimethyl sulphide was carried out in different



(**269**) 20%

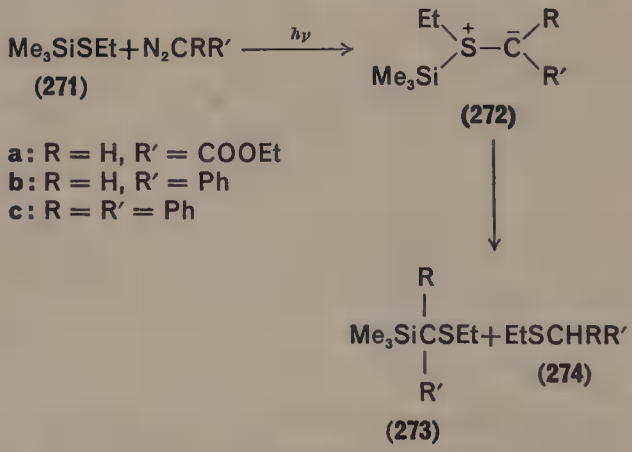
types of solvents. The striking result is the formation of a normal Sommelet–Hauser type product (orbital symmetry-allowed [2,3]sigmatropic process) in polar solvent conditions, whereas in non-polar conditions only a Stevens type product (orbital symmetry forbidden process) is formed. Possibly, in the ylide **270**, the methylene carbanion attacks the benzene ring followed by proton migration—hence, the necessity for a more polar medium. In non-polar solvents this requirement is not met, so that homolytic cleavage competes successfully with carbanion attack ($k_1 > k_2$) and the product is derived from the net orbital symmetry forbidden 1,2-shift.

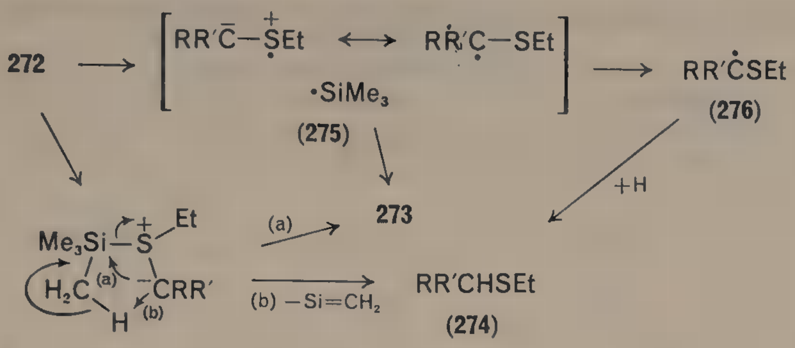
TABLE 42. Solvent effects on the reaction of diphenyldiazomethane with dimethyl sulphide[a]

Solvents	Product ratio, **268**/**267**
Cyclohexane	0·2
Benzene	0·3
Acetone	3·2
Mesityl oxide	3·5

[a] Mole ratio of sulphide to solvent is 0·3.

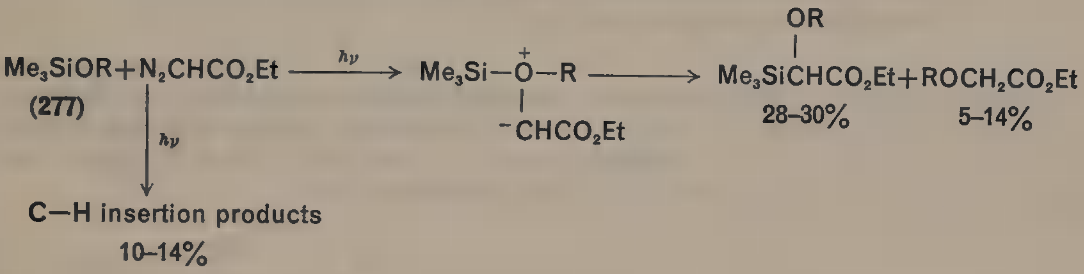
1,2-Alkyl shifts of the trialkylsilyl group have also been reported in the reaction of diazo compounds with silyl sulphides and silyl ethers[371]. Carbethoxycarbene produced in the photolysis of diazoacetate reacts with ethylthio(trimethyl)silane (**271**) to yield ethyl trimethylsilyl(ethylthio)acetate (**273**) in 38% yield and ethyl ethylthioacetate (**274**) in 29% yield. The photolysis of diphenyl and phenyldiazomethanes in ethylthio(trimethyl)silane afforded products similar to **273** and **274**. The formation of **273** may involve the sulphonium ylide (**272**) followed by 1,2-migration of the silyl group involving a geminate radical-pair intermediate **275**, which collapses to **273**. The radical **276** through hydrogen abstraction, yields **274**. While it may account for the products, the geminate ion-pair mechanism has never been established for 1,2-migration of the silyl group. A concerted 1,2-migration of the trimethylsilyl group might be involved since silicon may expand its valence shell, and the decomposition of the sulphonium ylide via a concerted, five-member, cyclic transition state could give **274** and Si=C, the fate of which is unknown[372, 373].





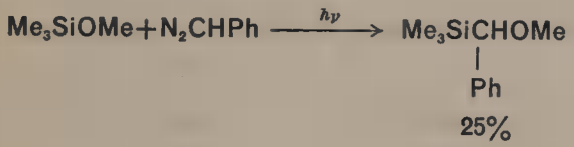
(275) (276) (274)

1,2-Migration of a silyl group from the oxonium site to a carbon may also take place in the reaction between carbenes and alkoxytrimethylsilanes (277).



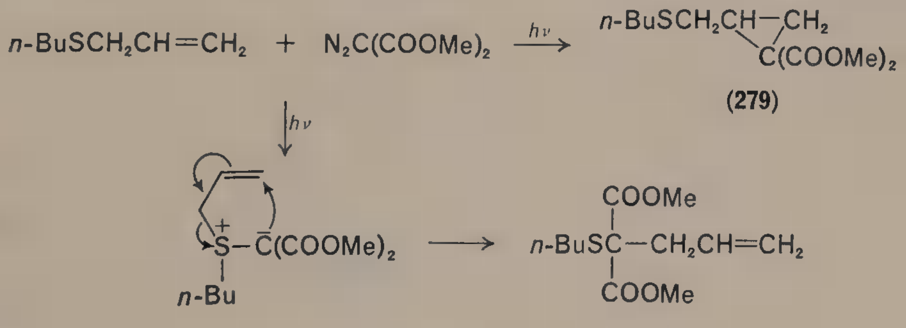
$$\underset{(277)}{Me_3SiOR}+N_2CHCO_2Et \xrightarrow{h\nu} Me_3Si-\overset{+}{O}(-R)-{}^{-}CHCO_2Et \longrightarrow \underset{28\text{–}30\%}{Me_3SiCH(OR)CO_2Et}+\underset{5\text{–}14\%}{ROCH_2CO_2Et}$$

$$Me_3SiOR+N_2CHCO_2Et \xrightarrow{h\nu} \underset{10\text{–}14\%}{\text{C—H insertion products}}$$



$$Me_3SiOMe+N_2CHPh \xrightarrow{h\nu} \underset{25\%}{Me_3SiCH(Ph)OMe}$$

Since the carbene attacks a sulphur atom more rapidly than the carbon–carbon double bond, the reaction with allylic sulphides may also proceed by attack on the sulphur atom. The ylide may rearrange with complete allylic inversion as demanded by 2,3-sigmatropic symmetry control. Thus, the photolysis of dimethyl diazomalonate in *n*-butyl allyl sulphide gave **278** as the major and **279** as the minor product:

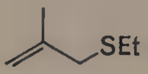
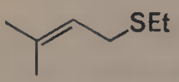


(279)

(278)

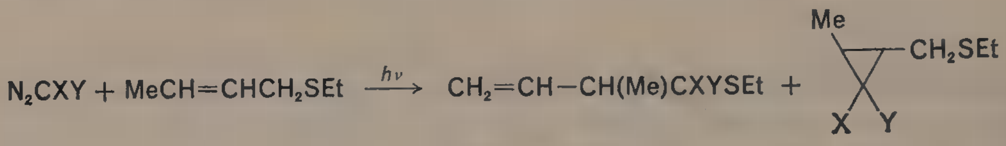
In the benzophenone-sensitized photolysis, addition products were favoured indicating that electrophilic singlet carbene is capable of accepting the electron from sulphur more easily than the triplet. Copper salt or copper powder catalysis, on the other hand, yielded exclusively the products of the 2,3-sigmatropic process[374].

TABLE 43. Product yields in the photolysis of dimethyl diazomalonate in allylic sulphides

Sulphide	C—S insertion (%)	Cyclopropane (%)
	51 (18)[a]	10 (37)[a]
	46 (7)	12 (29)
	53 (31)	7 (19)
	43 (19)	12 (27)

[a] Benzophenone photosensitized reaction.

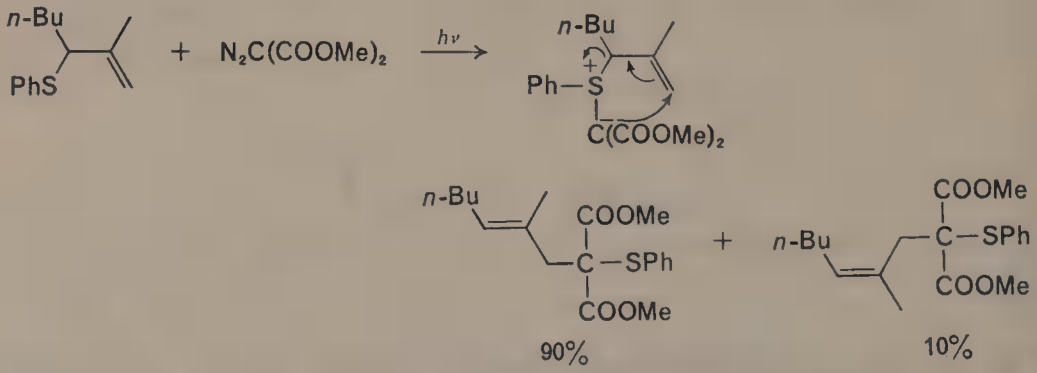
In the reaction of allylic sulphides with ethyl diazoacetate, a greater lack of specificity was observed[363]. In the photolysis of phenyl and diphenyldiazomethanes, on the other hand, the C—S insertion product is observed in 20–30% yields, but only a trace of cyclopropane or none at all was obtained[364]:



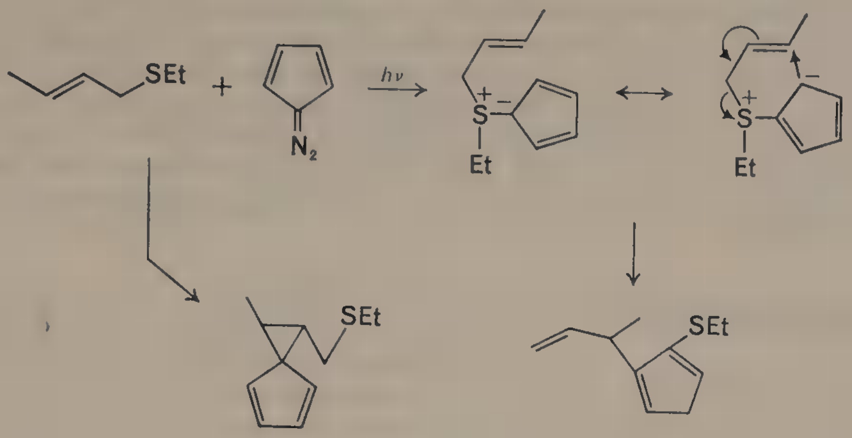
$$N_2CXY + MeCH{=}CHCH_2SEt \xrightarrow{h\nu} CH_2{=}CH{-}CH(Me)CXYSEt +$$

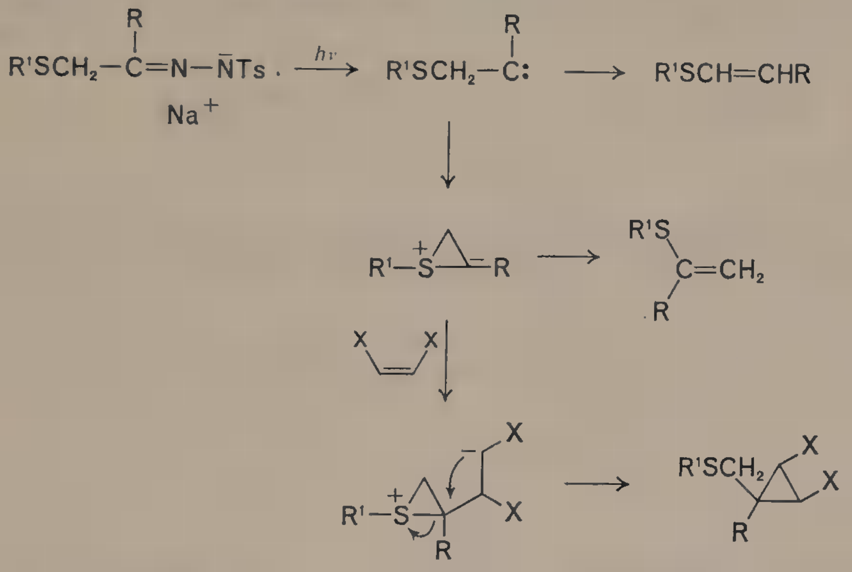
X = H, Y = CO_2Et	19–23%	6–8%
X = H, Y = Ph	31%	4%
X = Y = Ph	36%	0
X = $SiMe_3$, Y = CO_2Et	60%	12%

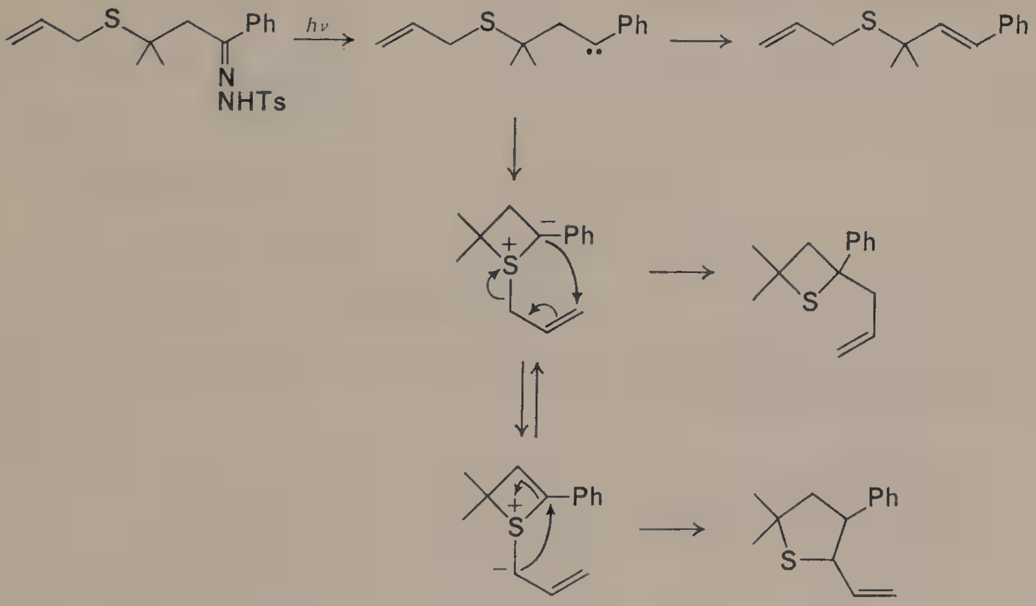
Introduction of a bulky group at $C_{(3)}$ leads to preferential formation of the *trans* isomer at the newly created double bond. Of the two orientations at $C_{(3)}$, the larger $C_{(3)}$ substituent should preferentially occupy the pseudo-equatorial orientation[375]:



Cyclopentadienylidene gave, with allylic sulphides, insertion into the C—S bond as well as addition. The former could arise from an intermediate sulphonium ylide followed by 3,3-sigmatropic rearrangement[376]:



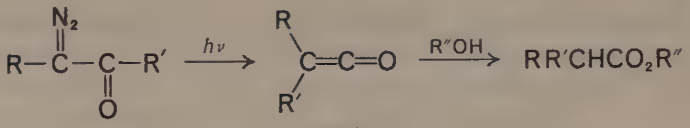




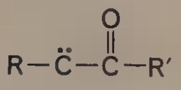
Intramolecular carbene reaction on the sulphur atom was also found. α-Allyl and α-arylthioalkylcarbenes generated by a modification of the Bamford–Stevens method gave labile episulphonium ylides, which then rearranged to vinyl sulphides[377, 378]. The episulphonium ylides could be trapped by diethyl maleate or dimethyl fumarate. An α-allylthioalkylcarbene generated by the photolysis of allylthioacetophenone tosylhydrazone afforded α-allylthiostyrene, which gave a smooth thio-Claisen rearrangement. 3-Thiabicyclo[3.1.0]hexane was obtained when allylthioacetophenone tosylhydrazone was decomposed photochemically in the presence of bases.

J. Wolff Rearrangement

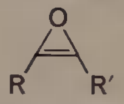
The Wolff rearrangement of α-diazocarbonyl compounds has received much mechanistic attention. Thus, photolysis of α-diazo ketones in protic solvents yields carboxylic acid derivatives. Ketenes (**280**) have been proposed as reaction intermediates[80, 81, 85]. In aprotic media ketenes are often obtainable in preparative quantities. Many studies have attempted to determine whether loss of nitrogen precedes migration to give an intermediate ketocarbene (**281**) and/or oxirene (**282**).



(**280**)



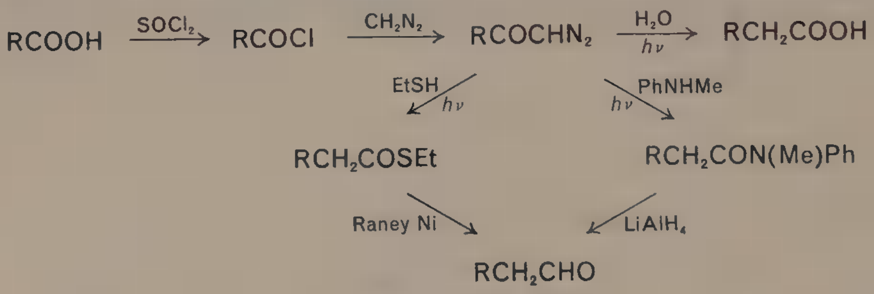
(**281**)



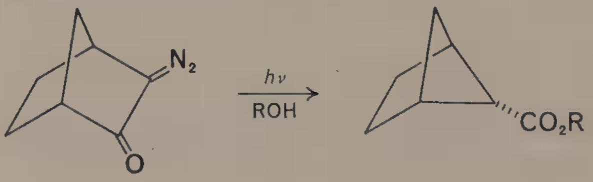
(**282**)

I. Synthetic utility

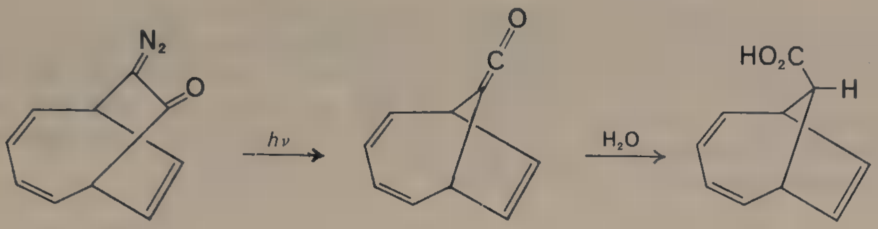
The reaction has considerable synthetic use, e.g. for chain lengthening[379]:



In cyclic systems ring contraction occurs and the reaction is useful in synthesis of strained small-ring compounds:

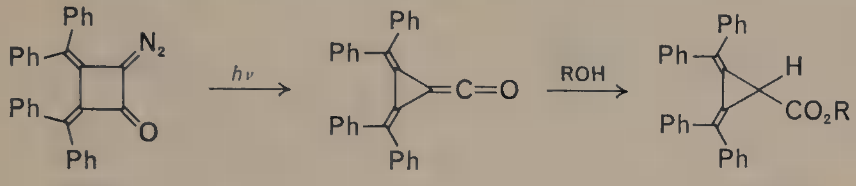


(Reference 380)

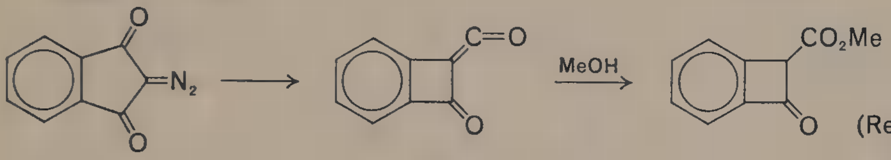


(Reference 381)

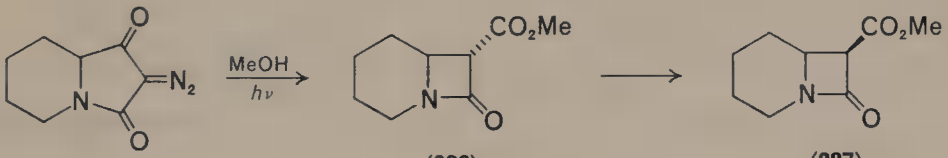
When **283** in benzene solution was irradiated at room temperature, in the presence of an alcohol, the product (**284**) was obtained via the Wolff rearrangement[382]. The photolysis of **285** gave in 65% yield a 2 : 5 mixture of β-lactam (**286**) and its epimerization product (**287**). The reaction yields some compounds whose production by other methods is either impossible or very difficult. For instance, the photolysis of **288** is a convenient method of obtaining 6-aminoindene (**289**)[385]. Horner and



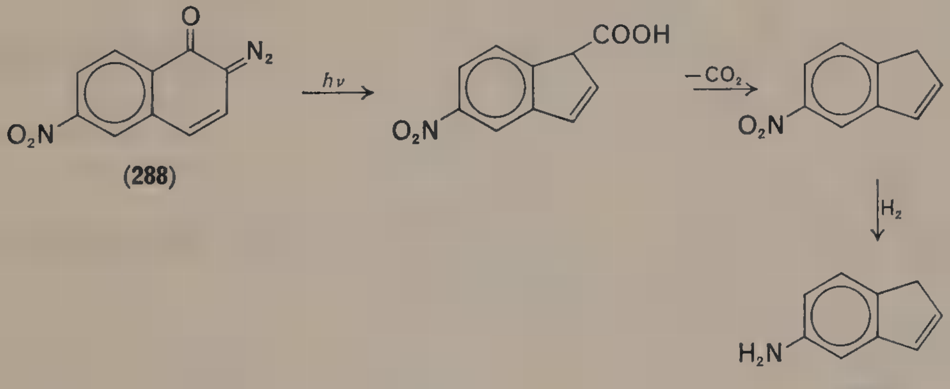
(**283**) (**284**)



(Reference 383)

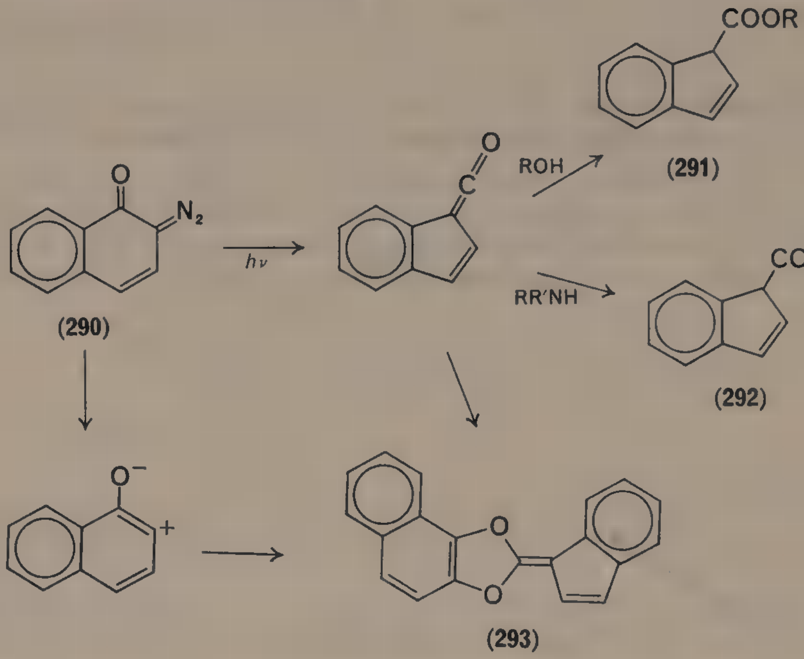


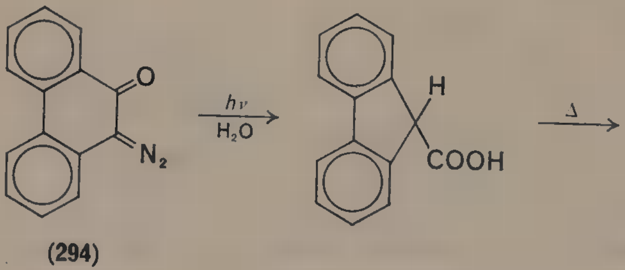
(**285**) (**286**) (**287**)



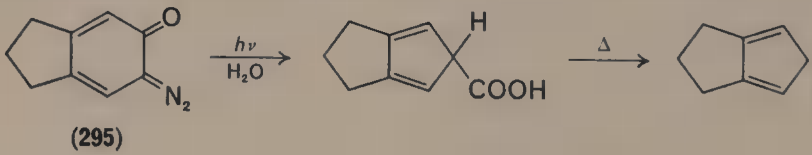
(**288**) (**289**)

coworkers irradiated the σ-quinonoid diazoketone (**290**) in alcohol or in the presence of aromatic amines, and separated derivatives of the corresponding ketene in the form of esters or anilides of indenecarboxylic acid[386]. In boiling xylene, the product was an adduct of the ketene identified as **293**. Diazoketones **294**–**296** undergo smooth Wolff rearrangement, but only 2% ring contraction occurs with **296**, presumably owing to an increase of *c.* 50 kcal mol^{-1} in strain energy.

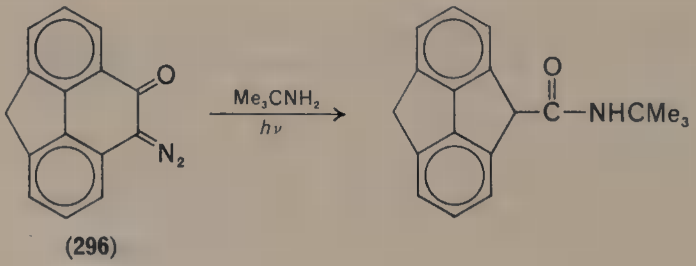




(References 387, 388)

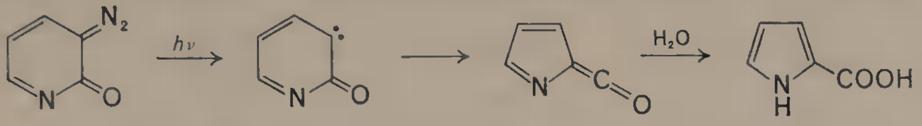


(References 389, 390)



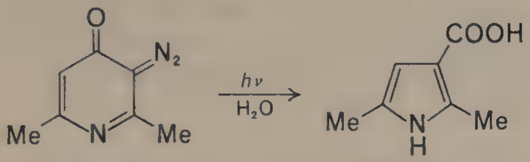
(References 388, 391)

Similarly pyridine and quinoline derivatives yield pyrrole- and indole-carboxylic acids[389, 392]. Photolysis of **298**, through ring contraction, gives 2,5-dimethylpyrrole-3-carboxylic acid (**299**) when the reaction is carried out at low temperatures.

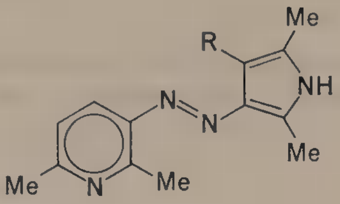


(**297**)

Without cooling, **298** reacts with **299** to give the azo dye **300a** which readily loses carbon dioxide leaving the azo compound **300b** [392].



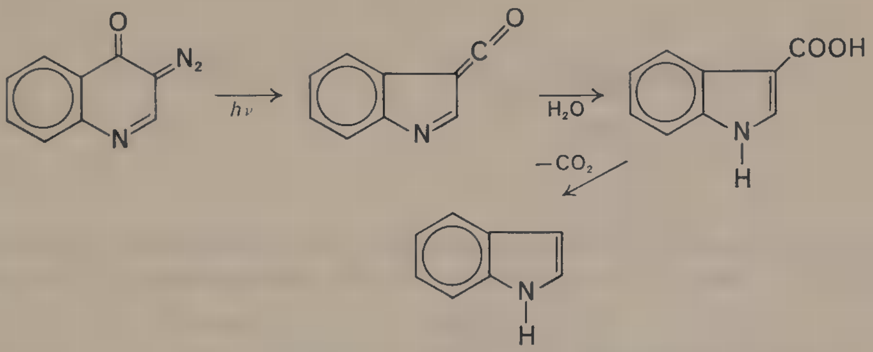
(**298**) (**299**)



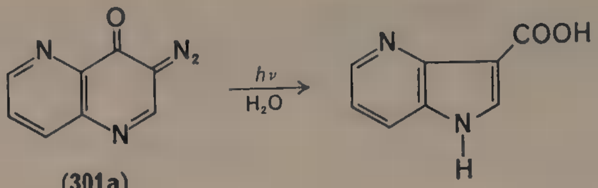
(**300**)

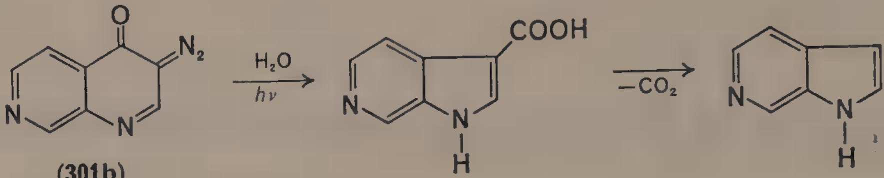
a: R = COOH
b: R = H

Quinoline derivatives decompose similarly on irradiation:

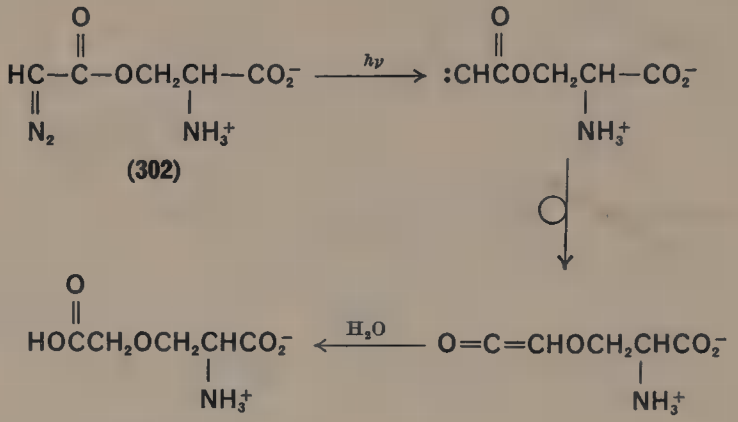


This reaction can be used to obtain the corresponding indoles including the unsubstituted indole, the 5-chloro- and 5,6-dimethoxyindoles and their carboxylic acids[392]. The photolysis of the diazo compound **301a** gives 4-azaindole-3-carboxylic acid which is characterized by a high stability and is incapable of decarboxylating. Its isomer, the 6-azaindole-3-carboxylic acid from (**301b**), is very easily decarboxylated, yielding 6-azaindole[393]. Wolff rearrangement of α-diazoesters to alkoxyketenes, and products obtained from these were reported in a study of the photolysis of diazoacetyl enzymes[394–396]. A diazoester is attached at the active site of the enzyme and subsequently reacts with neighbouring amino acid residues. In particular, photolysis of diazoacetyl chymotrypsin presumably generates a carbene that reacts by a rearrangement analogous to that of diazo ketones, either by insertion into water or by insertion into amino acid residues. Histidine and tyrosine residues have so far been identified as sites of attack.


(301a)


(301b)

The rearrangement encountered in these investigations was also illustrated with azaserine[396], which reacted in part as follows:

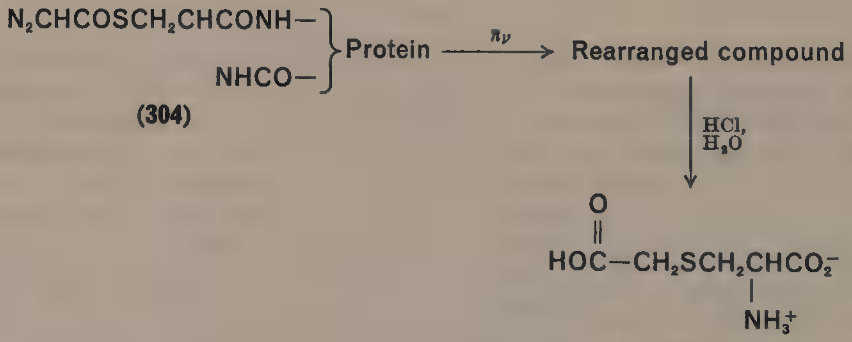

$$\underset{\underset{N_2}{\|}}{HC}-\overset{\overset{O}{\|}}{C}-OCH_2\underset{\underset{NH_3^+}{|}}{CH}-CO_2^- \xrightarrow{h\nu} :CH\overset{\overset{O}{\|}}{C}OCH_2\underset{\underset{NH_3^+}{|}}{CH}-CO_2^-$$

(302)

$$HO\overset{\overset{O}{\|}}{C}CH_2OCH_2\underset{\underset{NH_3^+}{|}}{C}HCO_2^- \xleftarrow{H_2O} O{=}C{=}CHOCH_2\underset{\underset{NH_3^+}{|}}{C}HCO_2^-$$

(303)

The product of photolysis of a diazothiolester protein derivative (**304**) in water, after hydrolysis, gave **305** as derived by Wolff rearrangement of the thialkoxy group[397]:


$$\left.\begin{array}{r}N_2CHCOSCH_2CHCONH-\\ NHCO-\end{array}\right\}\text{Protein} \xrightarrow{h\nu} \text{Rearranged compound}$$

(304)

$$\xrightarrow{HCl,\ H_2O} HO\overset{\overset{O}{\|}}{C}-CH_2SCH_2\underset{\underset{NH_3^+}{|}}{C}HCO_2^-$$

(305)

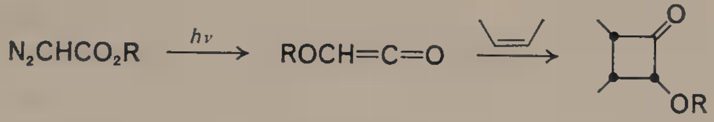
Ethyl diazoacetate (**306**), phenyl diazoacetate (**307**) and *N*-methyl diazoacetamide (**308**) also give products from Wolff rearrangement when photolysed in protic solvents. The major competing reaction is insertion into the O—H bond of the solvent.

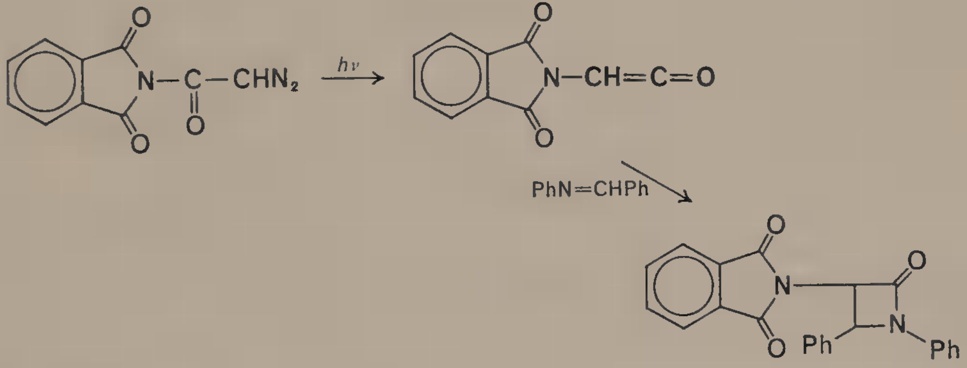
$$N_2CHCO_2R \xrightarrow[h\nu]{MeOH} ROCH_2CO_2Me + MeOCH_2CO_2R$$

(306)	R = Et	20–25%	75–80%
(307)	R = Ph	45–60%	40–55%

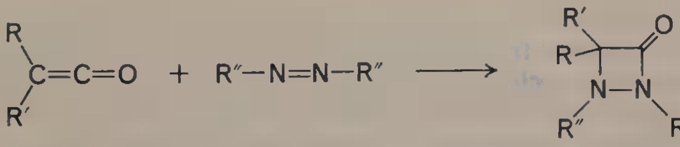
$$\begin{tikzcd} N_2CHCONHMe \arrow[r, "h\nu"] & :CHCONHMe \arrow[r, "H_2O"] \arrow[dd] & HOCH_2CONHMe \\ \textbf{(308)} & & 70\% \\ & O{=}C{=}CHNHMe \arrow[r, "H_2O"] & HO_2CCH_2NHMe \\ & & 30\% \end{tikzcd}$$

The ketenes formed in the Wolff rearrangement have been frequently subjected *in situ* to cycloaddition with C=C, C=N and N=N double bonds[398, 399]:





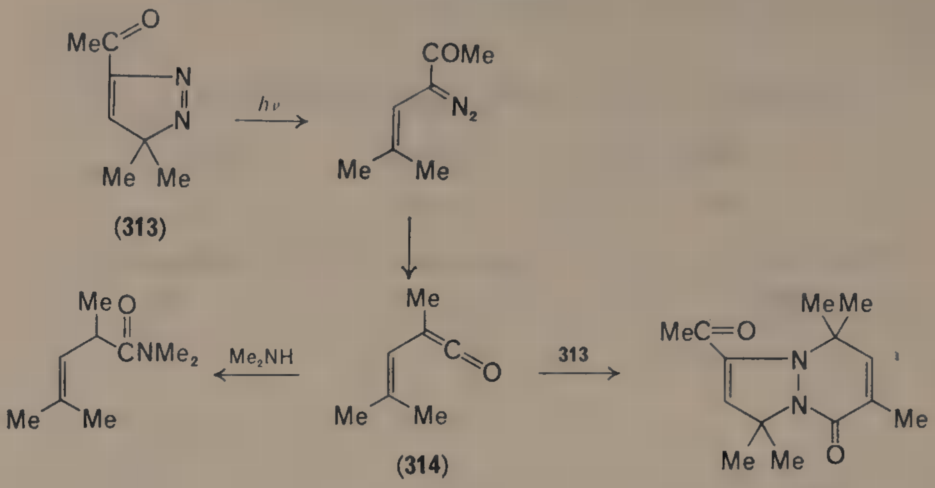
Horner obtained **309** from azibenzil and azobenzene, **310** from benzoyl diazomethane and azobenzene, **311** from diphenylketene and azodibenzoyl, and **312** from azibenzil and α,α′-azotoluene[400, 401]. There is no doubt that the α-diazocarbonyl compounds used are first converted to the corresponding ketenes which then react with the azo compounds to form the corresponding derivatives of 1,2-diazetidine.



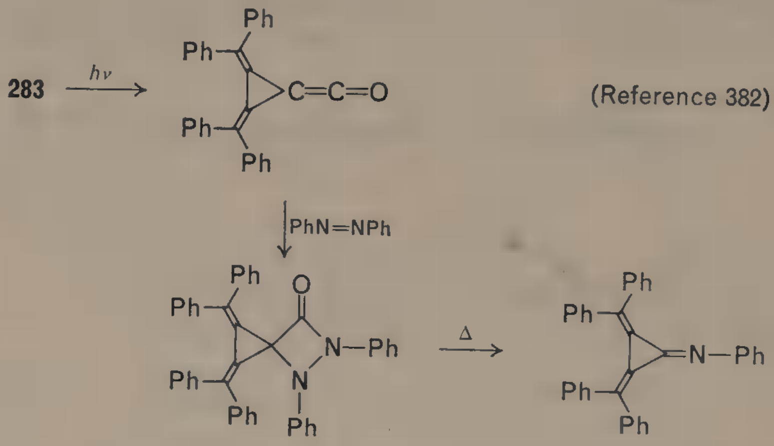
(309) R = R′ = R″ = Ph
(310) R = H, R′ = R″ = Ph

(311) R = R′ = Ph, R″ = COPh
(312) R = R′ = Ph, R″ = CH_2Ph

Photolysis of 5-acetyl-3,3-dimethyl-3*H*-pyrazole (**313**) gives rise to a ketene intermediate **314**, which reacts with **313** to produce the adduct **315**[402]. The ketene

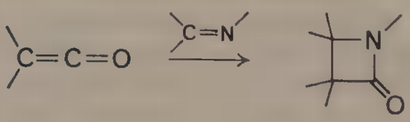


(313) (314) (315)



(Reference 382)

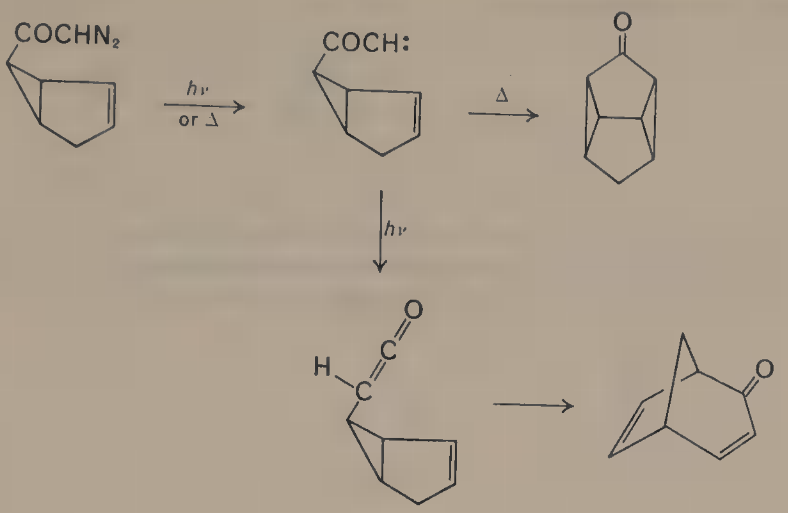
obtained from the photolysis of **283** reacts with azobenzene to give spiro compounds[382]. Ketenes formed by photolysis of diazoketones can also add to azomethines to give β-lactams[403]:

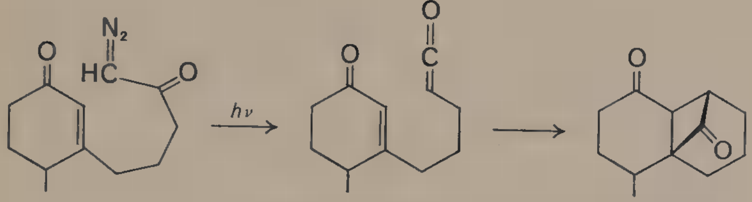


The scope of this cycloaddition is limited above all by reaction of the starting compound itself or its primary fragments (carbenes) prior to rearrangement. With diazoketones intramolecular cycloadditions occur preferentially at the ketene stage in the photochemical reaction[404a], but at the carbene stage in the catalytic process[404b].

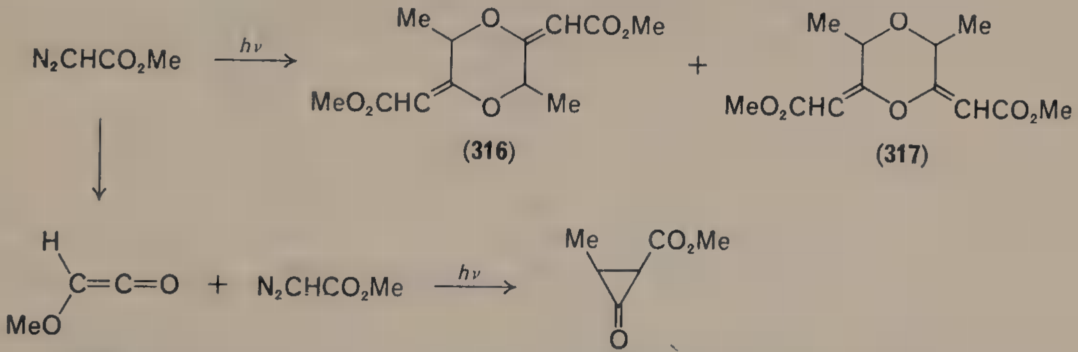
Methyl diazoacetate upon photolysis in benzene affords two tetrameric isomers **316** and **317** (overall yield 55%)[406], which apparently arise from dimerization of the cyclopropane (**319**) formed by addition of methoxyketene (**318**) to carbomethoxycarbene.

Irradiation of α,β-epoxydiazomethylketones (**320**) in benzene afforded compounds to which the butenolide structure **322** was attributed[407].





(Reference 405)

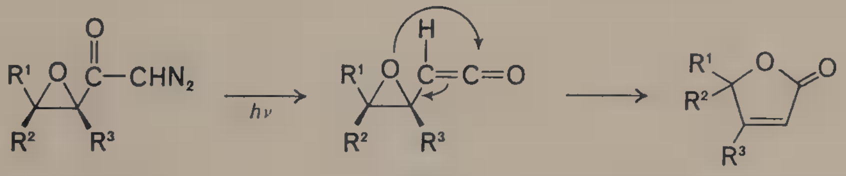


(316)

(317)

(318)

(319)



(320)

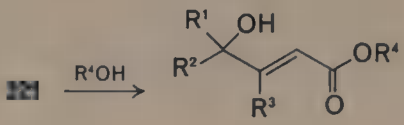
(321)

(322)

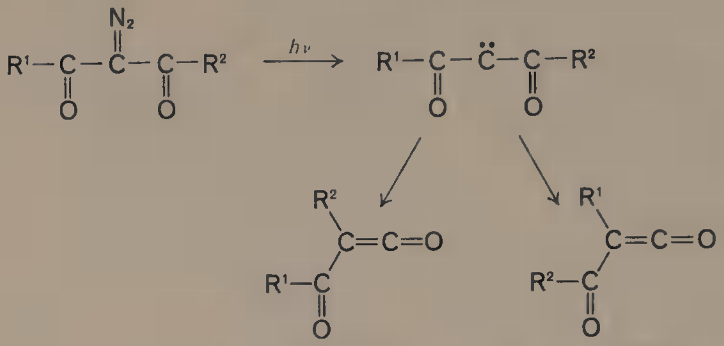
a: R^1 = R^2 = Ph, R^3 = H
b: R^1 = R^2 = H, R^3 = Ph

c: R^1 = H, R^2 = R^3 = Ph
d: R^1 = R^2 = Me, R^3 = H

The same reaction in the presence of an excess of methanol or ethanol yielded γ-hydroxy-α,β-unsaturated esters[407].



On rearrangement of unsymmetrically-substituted 2-diazo-1,3-dicarbonyl compounds, both R^1 and R^2 may migrate in the diacylcarbene providing an indication of the relative migration tendencies of various groups[408–410].

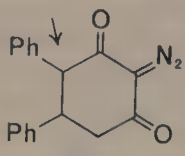


(323) (324)

TABLE 44. The relative migration tendencies of various groups

		Product ratios		Total yield (%)
R^1	R^2	323	324	323+324
Et	Me	51	49	84
Ph	H	100	0	90
Ph	Me	96	4	64
OEt	Me	100	0	78
OMe	Ph	100	0	88

Cyclic 2-diazo-1,3-dicarbonyl compounds can also be included in these investigations. The arrows in structures **325**[411], **326**[412] and **327**[413] indicate the centres of selective migratory aptitude.



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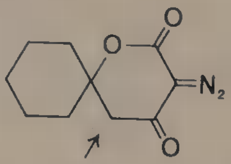

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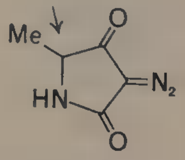
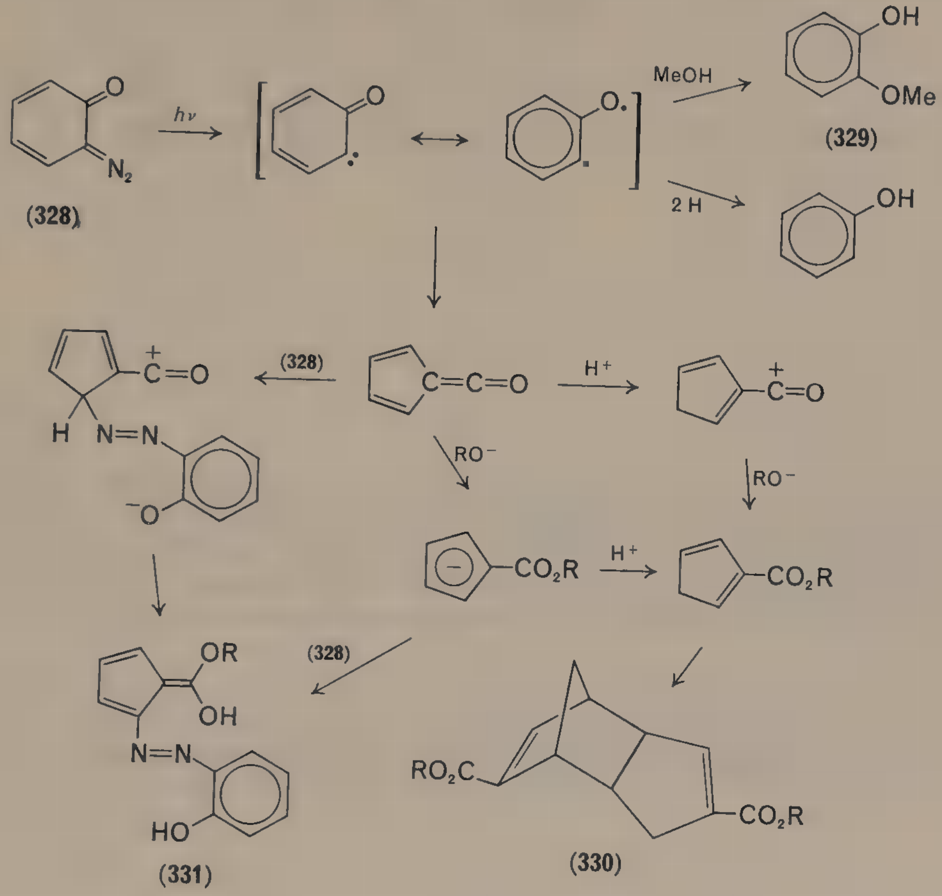


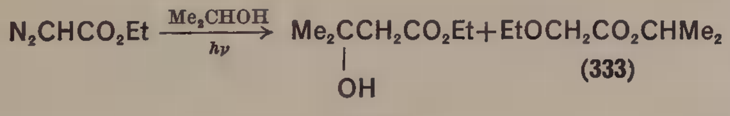
(327)

The photolytic decomposition of 6-diazo-2,4-cyclohexadien-1-one in methanol affords a guaiacol (**329**), phenol, a dimer (**330**) of methyl cyclopentadienecarboxylate and a reddish pigment **331** [414].



2. The mechanism of Wolff rearrangement

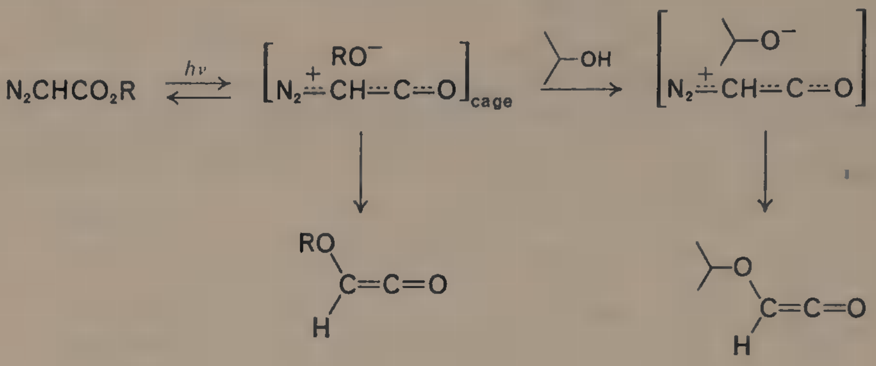
To date, the most thorough study of the Wolff rearrangement of diazo esters has been conducted by Strausz and coworkers[415–419]. From the photolysis of ethyl diazoacetate in *i*-propanol they obtained **332** (9%), **333** (29%), **334** (25%) and **335** (12%). The ethoxy ether **333** results from ethoxy migration to form ethoxy ketene which is trapped by *i*-propanol. The hydroxy ester stems from C—H insertion into



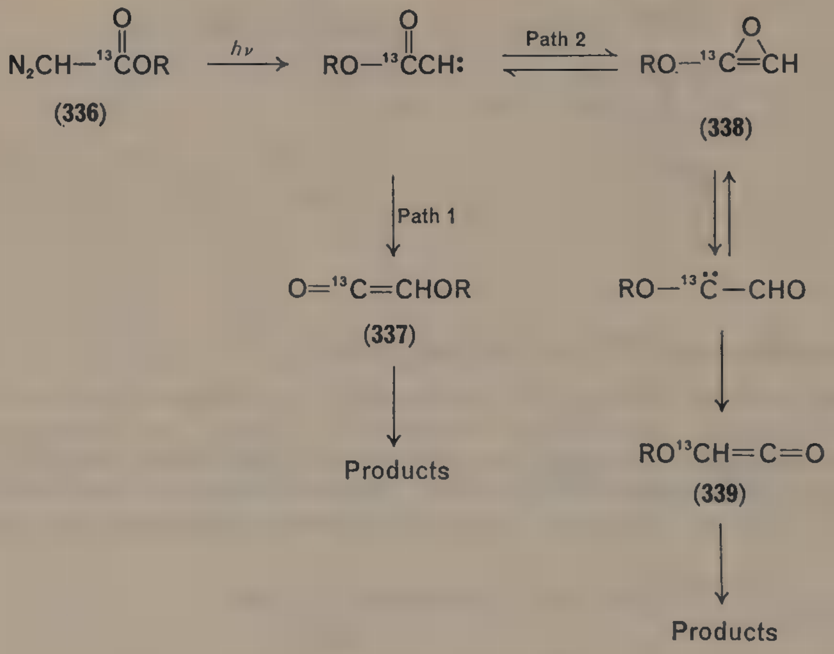
$$N_2CHCO_2Et \xrightarrow[h\nu]{Me_2CHOH} \underset{\substack{|\\ OH \\ \textbf{(332)}}}{Me_2CCH_2CO_2Et} + \underset{\textbf{(333)}}{EtOCH_2CO_2CHMe_2}$$

$$+\underset{\textbf{(334)}}{Me_2CHOCH_2CO_2Et} + \underset{\textbf{(335)}}{Me_2CHOCH_2CO_2CHMe_2}$$

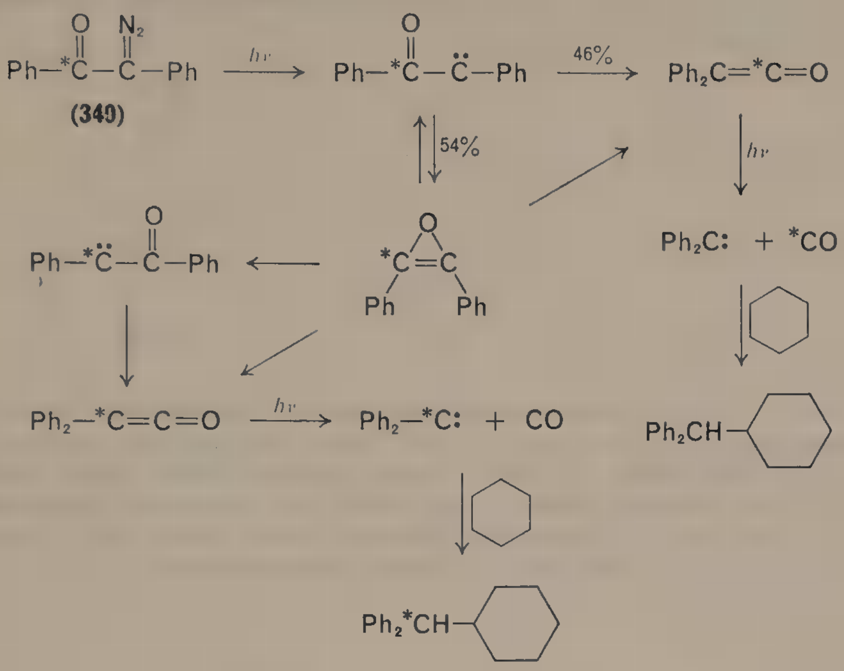
the solvent; the ether **334** arises from O—H insertion and may also be a product of transesterification. Control studies indicated that the formation of **335** is a photo-induced process which does not involve carbenes. Instead, a mechanism involving light-induced heterolysis of the diazo ester was suggested:



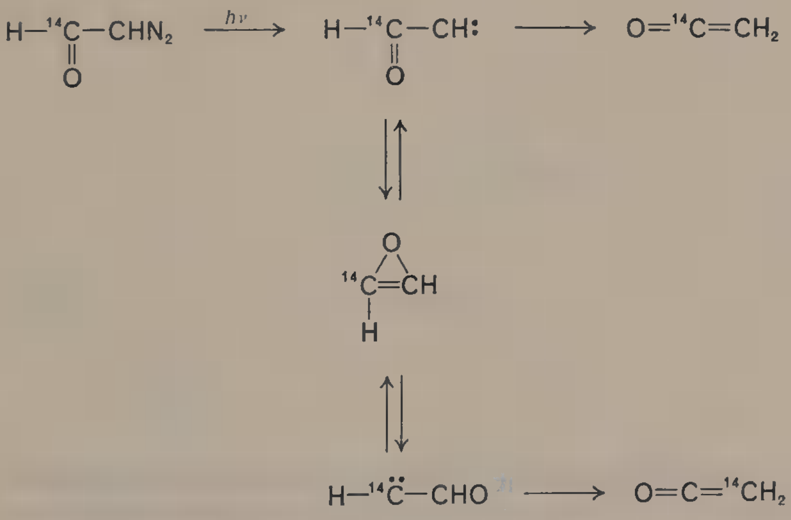
The mechanism of the Wolff rearrangement of α-diazo ketones and esters in the gas phase has been studied by ^{13}C-labelling of diazo derivatives **336**. The results are attributed to the formation of two different ketenes **337** and **339**, involving also an oxirene intermediate **338**. Franzen applied the ^{14}C-labelling technique for the photolysis of azibenzil (**340**). He concluded that oxirene was not an intermediate[420].



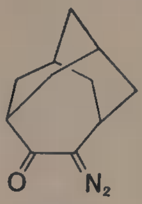
However, more recently, Strausz and coworkers found in the photolysis of ^{13}C-labelled azibenzil in cyclopentane that the isotopic composition of CO indicated scrambling of the oxygen atom to an extent corresponding to 54% oxirene participation in the reaction[418]:


(340)

By the same technique, 28–32% oxirene participation (path 2) was indicated in the gas-phase photolytic decomposition of methyl and ethyl diazoacetate (**336**). Molecular orbital calculations suggest that ketene is more stable than the isomeric oxirene or formyl carbene by *c.* 70 kcal mol^{-1} [421].



An experiment with ^{14}C-labelled α-diazohomoadamantanone (**341**) yielded only the acid **342**. No radioactivity could be found in the carbon dioxide upon oxidative decarbonylation, and hence the oxirene **343** did not intervene in any way in this reaction[422]. The photolysis of 2-diazo-1-^{13}C-naphthalen-1(2*H*)-one (**344**) yields indene-1-carboxylic acid containing all the label in the carboxy group[423]. This result shows that no isomerization of the oxocarbene **345** to **347** takes place. Compound **348** may be formed directly via Wolff rearrangement of **344** by concerted N_2 expulsion and ring contraction.



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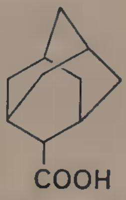
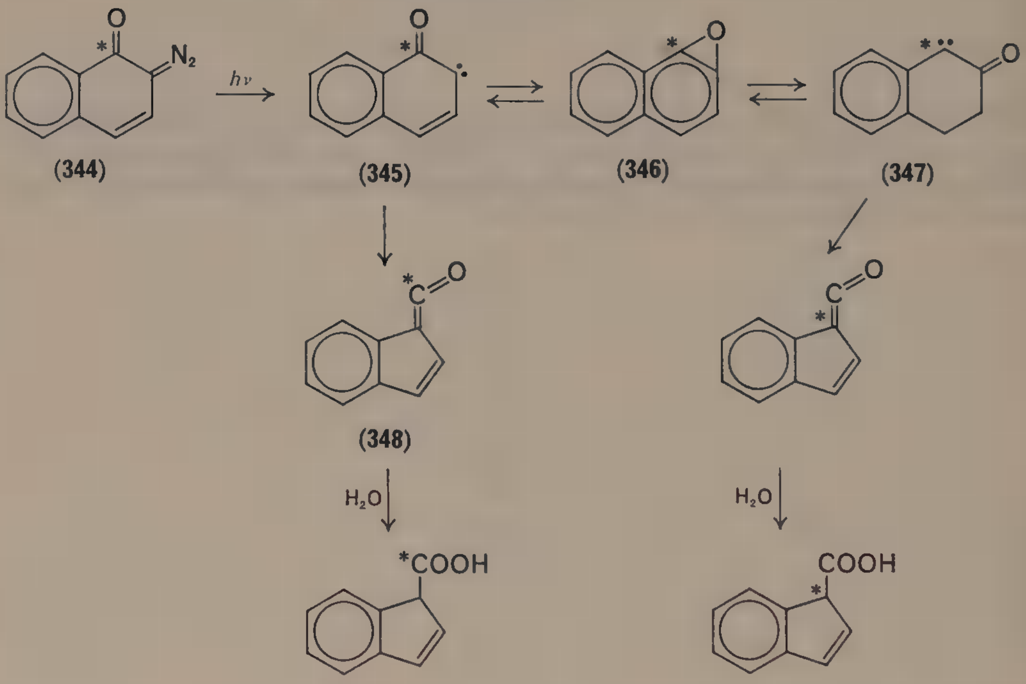


(342)

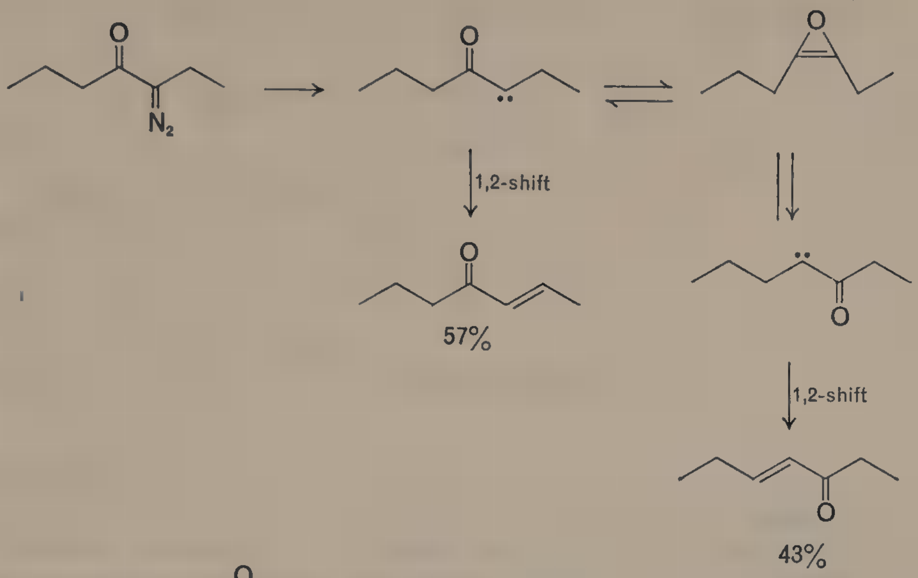
(343)

A test for the transient formation of oxirenes was based on the observation that when a methylene group is adjacent to the diazo function, decomposition to the oxocarbene is followed by a 1,2-shift to the carbene carbon atom, resulting in formation of an α,β-unsaturated ketone. Thus, for unsymmetrically substituted diazoketones, different α,β-unsaturated ketones would form if the oxocarbene initially produced equilibrated with an oxirene intermediate[424].

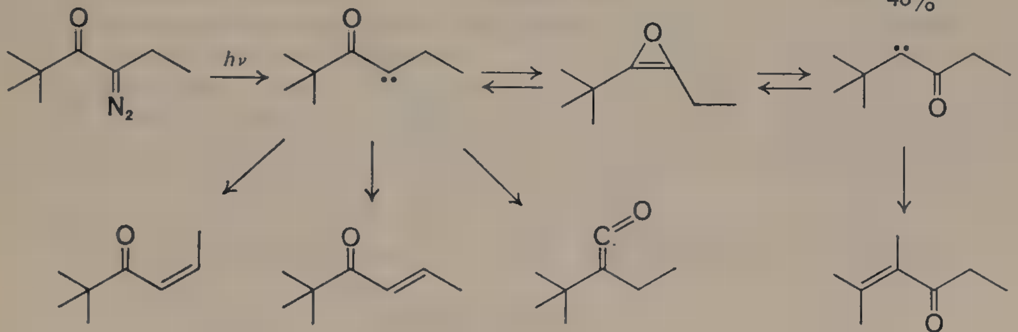


Proof of oxirene formation that is completely independent of the Wolff rearrangement was obtained with unsymmetrical α-diazo dialkyl ketones[425] and some aryl substituted α-diazo ketones[426]. The trapping reaction yielding **349** strongly suggests that oxirenes are true intermediates, and not transition states[427].

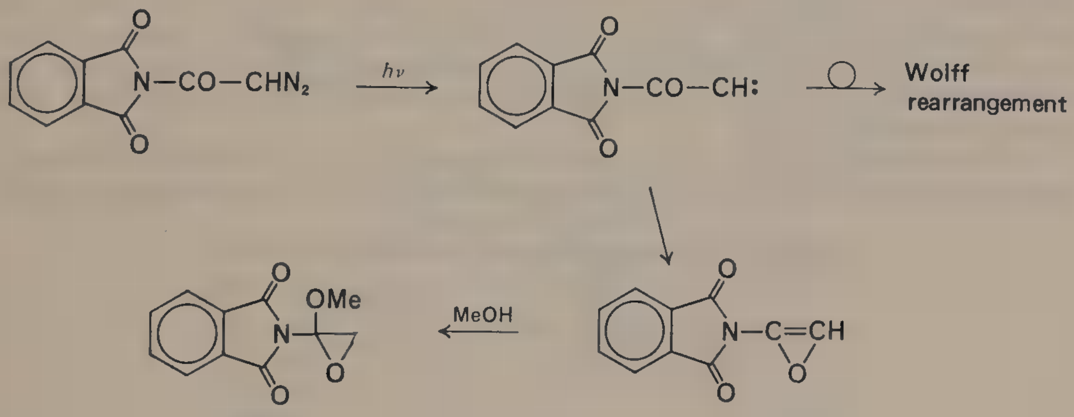
Photolysis of dimethyl diazomalonate in the presence of methanol-d_4 affords **350** and **351** in the ratio 9 : 4. The absence of **352** suggests that no oxirene intermediate is involved, and the Wolff rearrangement to **351** proceeds with methoxy



1,2-shift
57%
1,2-shift
43%



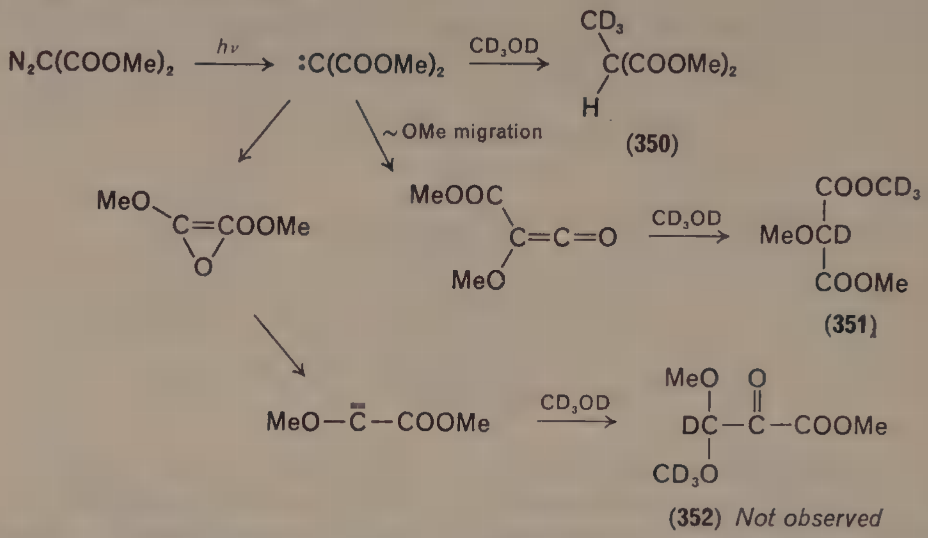
hν



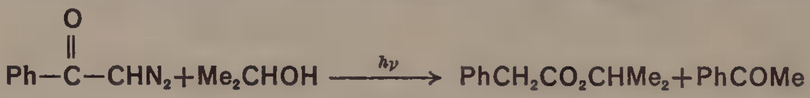
N—CO—CHN₂
hν
N—CO—CH:
Wolff rearrangement
N—C=CH
MeOH
OMe

(349)

group migration, as indicated below[428]:



Photolysis of the diazoketone in the presence of sufficient benzophenone, so that the latter absorbed >95% of the light, yielded only traces of the enones obtained by direct excitation. Thus, it can be assumed that triplet species do not rearrange via oxirene intermediates. There seems to be general agreement that singlets must be involved. Padwa and Layton[429] report that photosensitized decomposition of diazoacetophenone in *i*-propanol results in a decrease in yield of Wolff rearrangement product and an increase in reduced product as compared to direct photolysis:



$$\mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CHN_2 + Me_2CHOH \xrightarrow{h\nu} \underset{(A)}{PhCH_2CO_2CHMe_2} + \underset{(B)}{PhCOMe}}$$

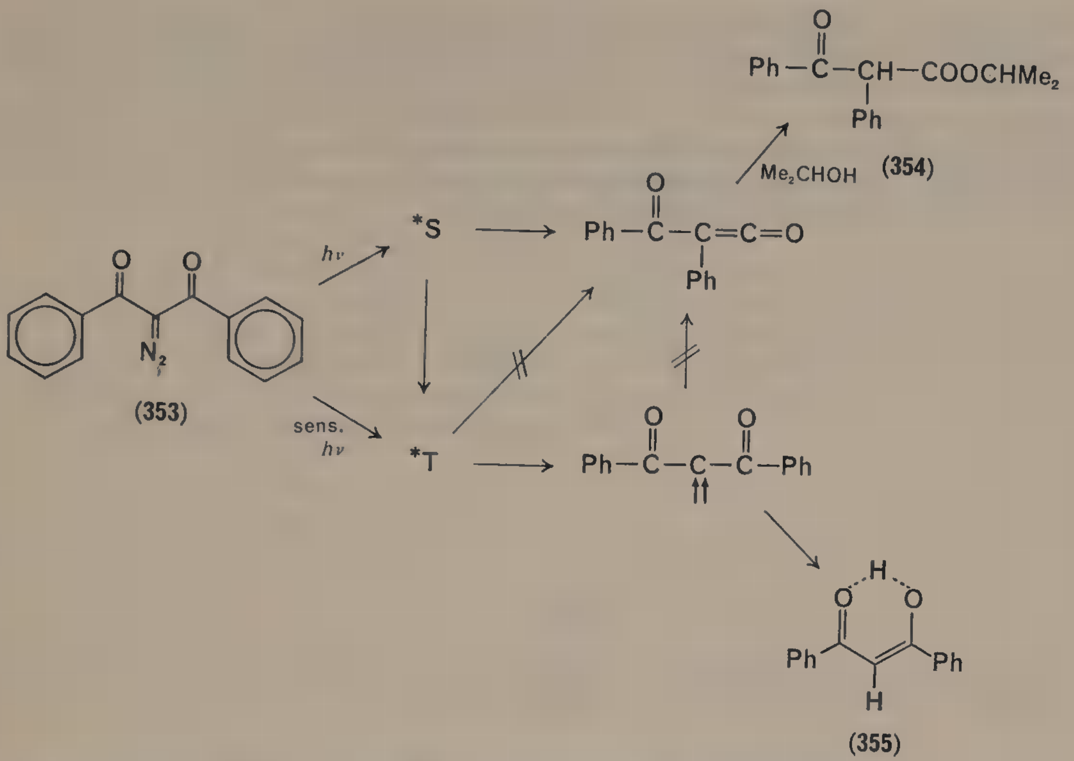
A/B		
	Direct $h\nu$	2·5
	Sensitized $h\nu$	0·003

Diazodibenzoylmethane (**353**) undergoes two primary photochemical processes leading to **354** and to dibenzoylmethane (**355**)[430]. The formation of **354** is related to the lowest excited singlet state of **353** and the formation of **355** is related to the lowest triplet state of **353**. The quantum yields of both processes, Φ_{354} and Φ_{355}, are strongly wavelength dependent. It is unambiguously demonstrated that the population of two excited states depends on the energy of the excited light, thus causing a wavelength effect.

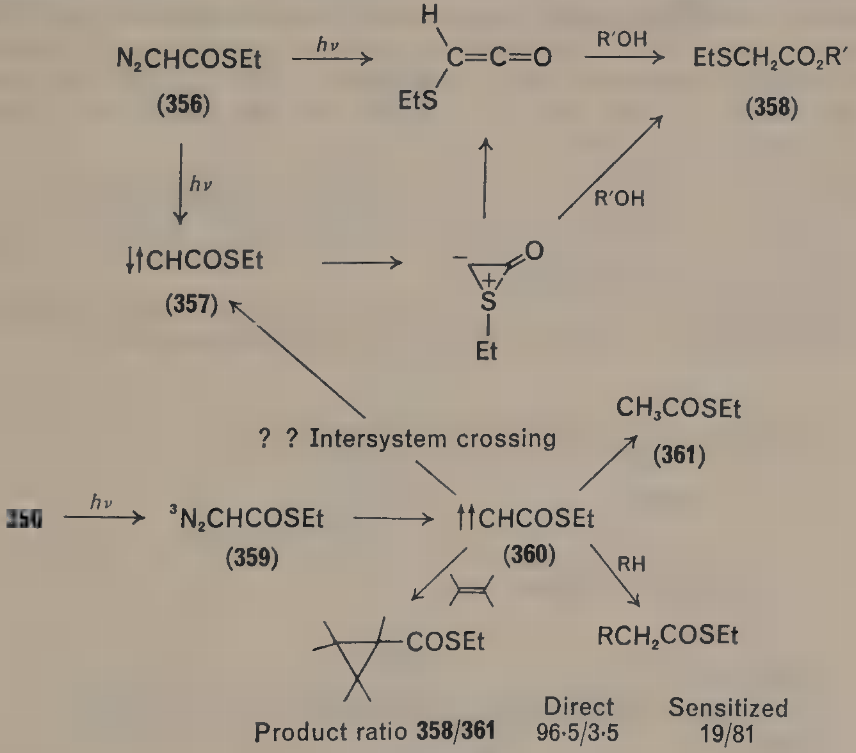
Photosensitized decomposition differs from photolytic decomposition of diazothiolacetate in that rearrangement is suppressed and products derived from radical-

TABLE 45. Wavelength effect on the photolysis of 353

Wavelength of irradiation (nm, 297 K)	Ratio 355	354
366	1	0·80
313	1	0·31
254	1	0·17
Pyrex (77 K)	1	20
Sensitized (Michler ketone)	19	1

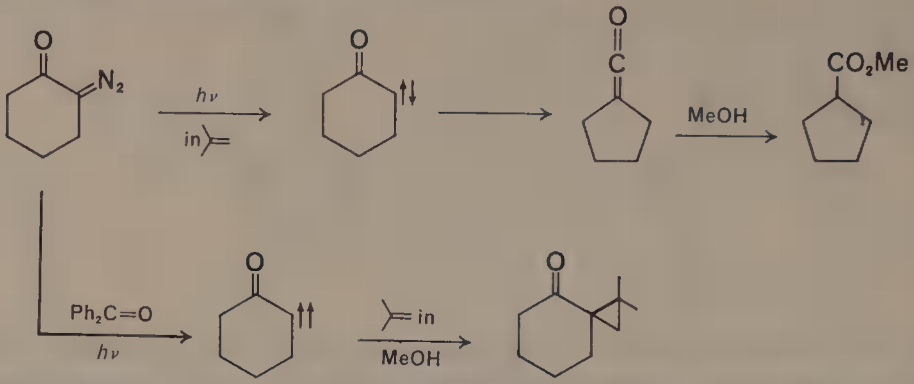


like abstraction and insertion are obtained[431]. Photosensitized decomposition of diazothiolacetate (**356**) is a triplet process and the various reactions of triplet ethyl α-diazothiolacetate (**359**) and/or triplet carbene (**360**) are summarized in Scheme 9.

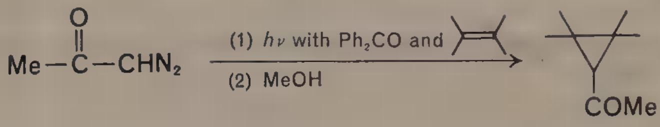


SCHEME 9

It is apparent that there can be only minor intersystem crossing in the photosensitized decomposition of **356**. Nevertheless, Wolff rearrangement products (**358**) are formed in photosensitized decomposition of **356**. Jones and Ando showed[432] that aliphatic diazoketones such as diazocyclohexanone underwent Wolff rearrangement on unsensitized irradiation. The corresponding carbene could not be trapped with olefins. Photosensitized decomposition gave an intermediate that did give Wolff rearrangement and was trapped by olefins:



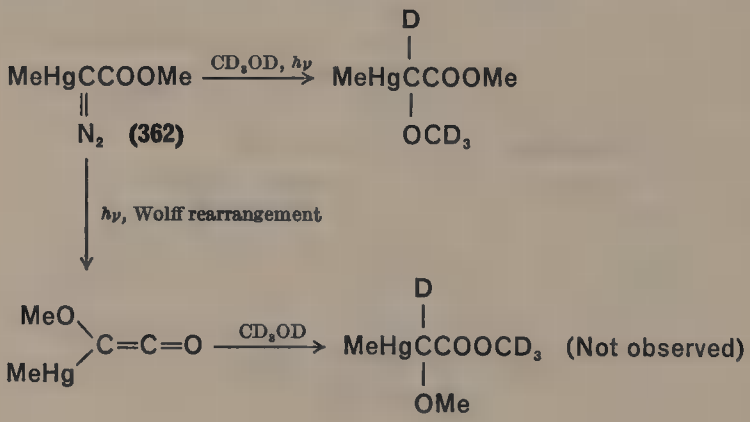
The sensitized decomposition of diazoacetone in olefins yields similar adducts while none could be found in the unsensitized reactions:



It is tempting to describe these changes in the most simple terms, that is, singlet carbenes are involved in the unsensitized and triplet in the sensitized decompositions. The singlet finds an accessible pair of electrons in the adjacent carbon–carbon single bond and reacts with these at a faster rate than with the more distant π-electrons of the external olefin.

Carbenes that are formed by photolysis of diazo compound **362** are rapidly deactivated to their ground states, probably because of an internal 'heavy atom effect'. This modifies their chemistry and provides a useful probe for determining the spin multiplicity of the ground state[433–435].

Use of methanol-d_4 shows that it is the methyl group of the ether which comes from the alcohol, and no product of Wolff rearrangement is evident:



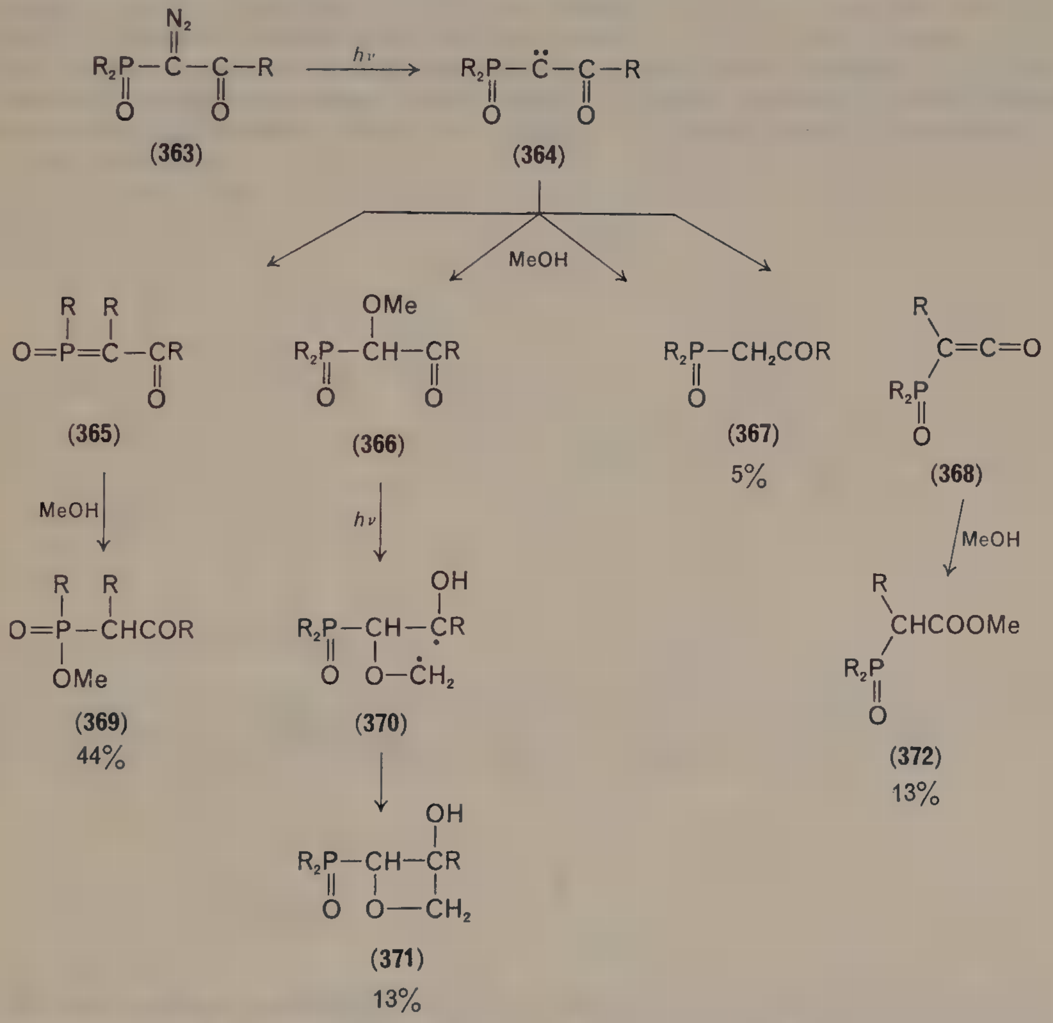
$$\underset{\underset{N_2}{\|}}{MeHgCCOOMe}\ \textbf{(362)} \xrightarrow{CD_3OD,\ h\nu} MeHg\overset{D}{\underset{OCD_3}{C}}COOMe$$

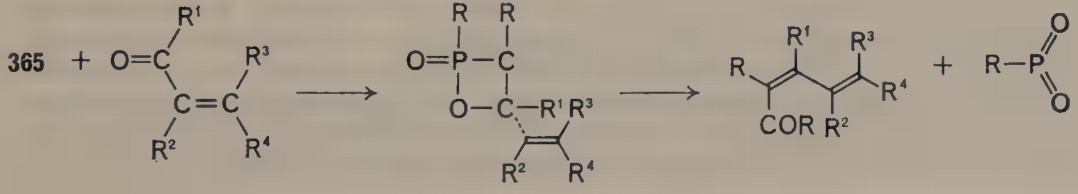
$$\textbf{362} \xrightarrow{h\nu,\ \text{Wolff rearrangement}} (MeO)(MeHg)C{=}C{=}O \xrightarrow{CD_3OD} MeHg\overset{D}{\underset{OMe}{C}}COOCD_3 \quad \text{(Not observed)}$$

Since photolysis of mercury-free diazoacetates in alcohol gives rise to products of oxygen–hydrogen insertion, carbon–hydrogen insertion, Wolff rearrangement and 'exchange' reactions, the presence of a mercury atom adjacent to the carbene site enhances the selectivity of the intermediate[436].

Irradiation of **363** in methanol leads to competition between the phosphorylcarbene and methylene phosphorane oxide rearrangement: **364–365–369**, and the equally possible classical Wolff rearrangement **364–368–372**, the methyl esters **369** and **372** are formed in the ratio of approximately 4 : 1.

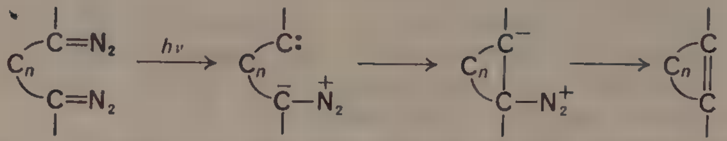
It is possible, however, to reverse this ratio by introducing a *p*-dimethylamino group into the benzoyl group of **363**. Furthermore, **364** reacts with methanol by O—H insertion although the phosphorane oxide **366** cannot be isolated; it undergoes intramolecular photochemical reduction of the carbonyl group to form the diradical **370**, which then cyclizes to the oxetane **371**. Intermediate **365** afforded dienes on reaction with conjugated ketones[437].





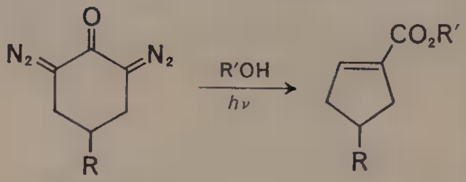
K. Bisdiazo Compounds

Bisdiazo compounds are potential intermediates for the synthesis of strained cyclic olefins:



Vicinal bisdiazo compounds yield acetylenes[438–440]. This route has led to the successful synthesis of a cycloheptyne and of cyclohexyne[439, 440].

In 1959, Kirmse reported the ring contraction of 2,6-bis(diazo)cyclohexanone and interpreted the result on the basis of a Wolff rearrangement[441]. Later studies gave similar results[442–444]. However, a recent alternative explanation is that in the proposed carbene intermediate obtained from **373** the interaction of a carbanion with a carbene centre should compete favourably with σ-bond migration. While **374** may yield the ketene **375**, the exceedingly low activation energy associated with nitrogen elimination from aliphatic diazonium salts suggests that formation of the cyclopropenone could compete with σ-bond cleavage[445]. A methanolic solution of



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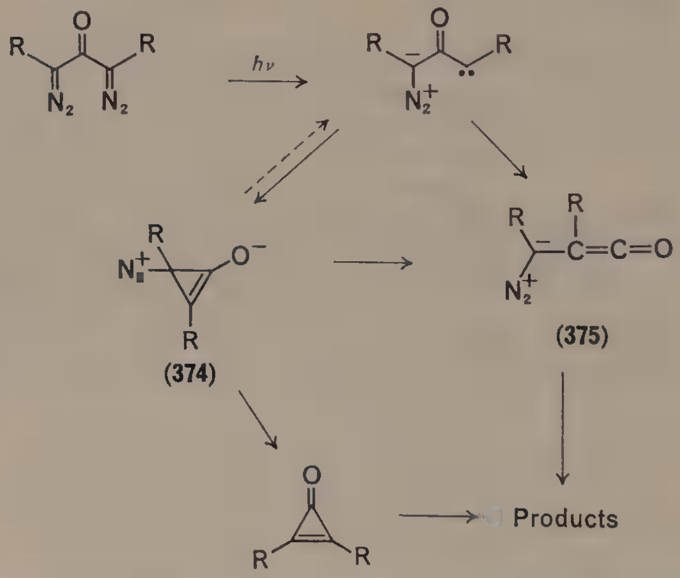
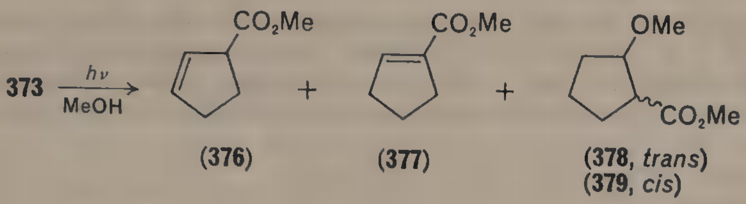
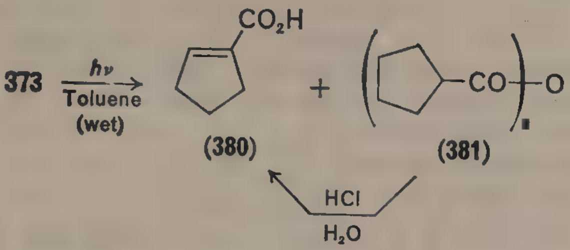


373 was irradiated at −40 °C to yield methyl cyclopentene-3-carboxylate (**376**, 15%), methyl cyclopentene-1-carboxylate (**377**, 61%), methyl *trans*-2-methoxycyclopentane carboxylate (**378**, 5%) and methyl *cis*-2-methoxycyclopentanecarboxylate (**379**, 10%). Irradiation of (**373**) in toluene or furan at −40 °C or benzene at 10 °C containing a trace of water gave the ring-contracted cyclopentene-1-carboxylic acid (**380**) and the corresponding anhydride (**381**) in a combined 65% yield. Irradiation of 1,3-bisdiazo-1,3-diphenyl-2-propanone (**382**) at −40 °C in a

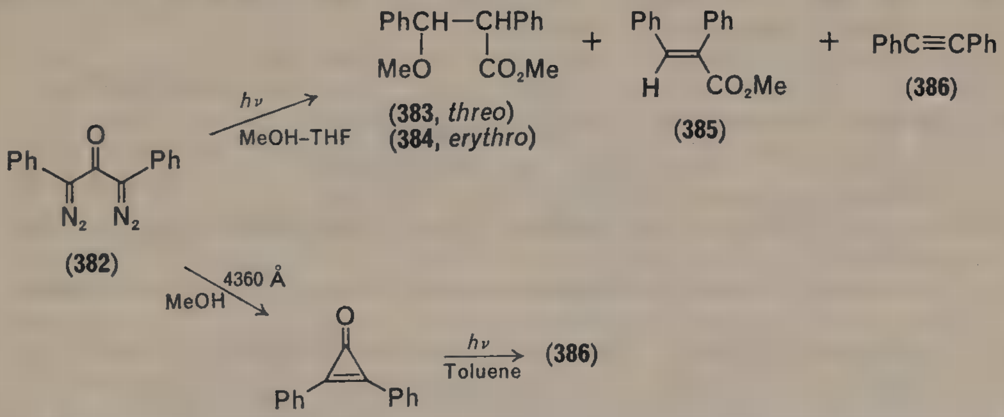


(376) (377) (378, *trans*) (379, *cis*)



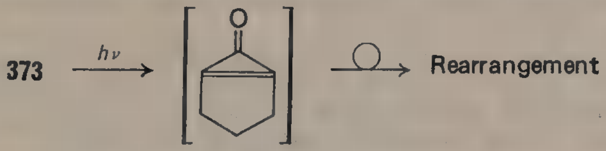
(380) (381)

4 : 1 methanol–tetrahydrofuran (v/v) solution gave methyl *threo*-2,3-diphenyl-3-methoxypropionate (**383**, 41%), methyl *erythro*-2,3-diphenyl-3-methoxypropionate (**384**, 13%), methyl *trans*-2-phenylcinnamate (**385**, 5%) and diphenylacetylene (24%). Irradiation of **382** under conditions at which diphenylcyclopropenone was photostable, indeed resulted in the isolation of the latter. Photolysis of **387** at −40 °C in an inert solvent such as toluene resulted in a 65% yield of the acetylene (**386**) as the only characterized product.



(383, *threo*) (384, *erythro*) (385) (386) (382)

In the photolytic decompositions, cyclopropenones are established as the major primary products, at least in the acyclic cases. This also provides support for the intermediacy of the cyclopropenenone **388** in the photolysis of **373**.



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CHAPTER 10

The electrochemistry of the diazo and diazonium groups

ALBERT J. FRY
Wesleyan University, Middletown, Connecticut, USA

I. INTRODUCTION

This review includes a discussion of the electrochemical oxidation and reduction of diazo compounds (**1**) and diazonium salts (**2**), where R can be any of a wide variety of alkyl or aryl substituents, or, with **1**, hydrogen. Diazo compounds have been both oxidized and reduced electrochemically; on the other hand, the positive charge in **2** inhibits anodic electron removal, and hence diazonium salts have only been reduced electrochemically.

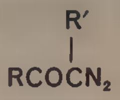
R_2CN_2 **(1)** $RN_2^+X^-$ **(2)**

Many mechanistic features of the reactions to be discussed herein are similar to those observed in the electrochemistry of a number of other simple functional groups. The reader may wish to explore such analogies by referring to one or more reference works on organic electrochemistry, of which there are several texts[1–3] and review articles[4–7] explicitly written for the organic chemist unfamiliar with this area. The review by Fry and Reed[7] reviews elementary considerations involved in interpreting the electrochemical behaviour of systems containing multiple bonds, and much of what is said there could be applied in the present context. Most of the references cited above also elaborate upon the principles and techniques employed in organic electrochemistry, and hence the present article will presuppose a working knowledge of the appropriate concepts. The emphasis herein is, at any rate, heavily upon the chemical reactions undergone by **1** and **2** at electrodes, rather than upon electrochemical details.

II. THE DIAZO GROUP

A. Reduction

Most studies of the electrochemical reduction of diazo compounds have been carried out with diazocarbonyl compounds (3). Since they constitute the mechanistically best-understood class of diazo compounds, their electrochemical behaviour will be discussed in some detail. It is probably true that many of the same considerations can be applied to an understanding of the electrochemistry of simple alkyl and aryl diazo compounds, but there are probably differences, as we shall see.



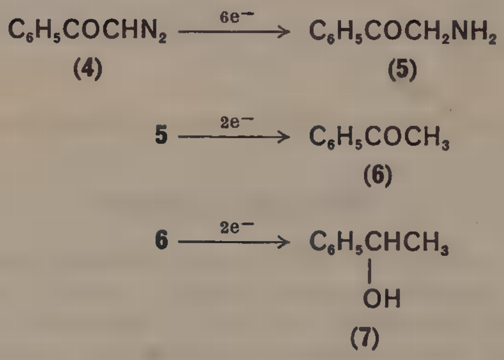
$$\overset{R'}{\overset{|}{RCOCN_2}}$$

(3)

$C_6H_5COCHN_2$

(4)

The electrochemical reduction of diazocarbonyl compounds is nicely understood by reference to diazoacetophenone (**4**) [8]. This compound exhibits three polarographic waves in aqueous buffer at pH 6. The heights of the three polarographic waves correspond to uptake of six, two and two electrons, respectively, suggesting stepwise reduction of **4** to α-aminoacetophenone (**5**), then acetophenone (**6**) and finally α-phenylethanol (**7**) (Scheme 1).



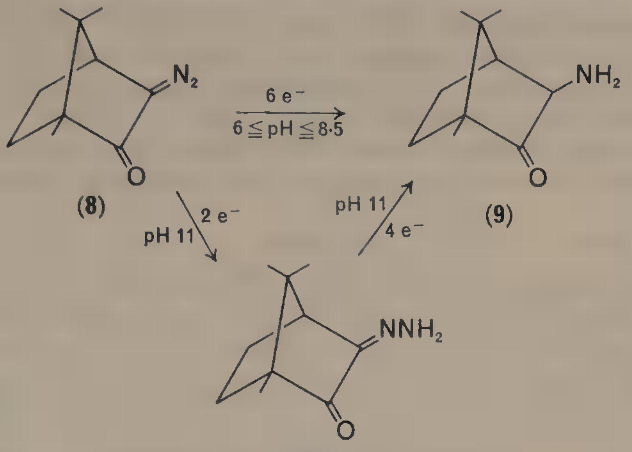
$$\underset{(4)}{C_6H_5COCHN_2} \xrightarrow{6e^-} \underset{(5)}{C_6H_5COCH_2NH_2}$$

$$5 \xrightarrow{2e^-} \underset{(6)}{C_6H_5COCH_3}$$

$$6 \xrightarrow{2e^-} \underset{(7)}{C_6H_5\underset{OH}{\underset{|}{C}}HCH_3}$$

SCHEME 1

Controlled-potential coulometry confirmed the numbers of electrons consumed in each step as six, two and two, respectively[8], and the suggestion that the second and third waves in the polarogram of **4** correspond to reduction of intermediates **5** and **6** was supported by the observation that **5** does exhibit two polarographic waves corresponding to the last two of **4**, and that **6** exhibits a single wave at the potential of the third wave of **4** (or second wave of **5**)[8]. The reduction of **4** to **5** is clearly particularly complex in nature, involving as it does overall addition of six electrons and six protons. Although one could imagine a large number of sequences in which these electron and proton transfers could take place, other investigations have thrown considerable light upon this conversion. For example, diazocamphor (**8**) also exhibits a six-electron wave over the pH range 6–8·5, and the aminoketone (**9**) (stereochemistry uncertain) is the product of preparative electrolysis[9]. In alkali, however, the six-electron wave of **8** splits into two waves, a two-electron wave followed by a four-electron wave (Scheme 2) [9]. Controlled-potential electrolyses at the potentials of the first and second waves of **8** in alkali afford hydrazone **10** and aminoketone **9**, respectively. Presumably **10** is also an intermediate in the reduction of **8** in the pH range 6–8·5. The conversion of **8** to



(10)

SCHEME 2

10, like many other organic electrode processes, especially reductions of multiple bonds[7], probably involves an alternating sequence of electron and proton transfers (Scheme 3), i.e. a so-called ECE process. One might imagine an alternate sequence

$$\underset{(1)}{R_2CN_2} \xrightarrow{e^-} R_2\dot{C}{-}N{=}\bar{N} \underset{(11)}{\longleftrightarrow} R_2\bar{C}{-}N{=}N\cdot$$

$$11 \xrightarrow{H^+} \underset{(12)}{R_2\dot{C}{-}N{=}NH}$$

$$12 \xrightarrow{e^-} R_2\bar{C}{-}N{=}NH \xrightarrow{H^+} \underset{(13)}{R_2C{=}NNH_2}$$

SCHEME 3

to 12 involving initial proton transfer (equation 1). A number of lines of evidence favour Scheme 3, however: (a) diazo camphor is unstable in acid (pH < 6)[9]; (b) the radical anion (11) has been observed by e.s.r. spectroscopy in the reduction of

$$1 \xrightarrow{H^+} R_2\overset{+}{C}{-}N{=}NH \xrightarrow{e^-} 12 \qquad (1)$$

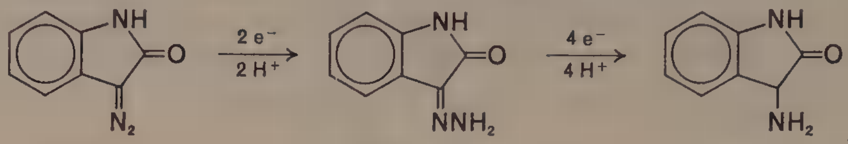
diazoacetophenone (although under quite different experimental conditions)[10]; and (c) diazoacetophenone (4) is reduced to acetophenone (6) in a *two*-electron process at pH 5[11], demonstrating that protonation of 1 leads to a different reduction pathway involving protonation on carbon (equation 2).

$$1 \xrightarrow{H^+} R_2CHN_2^+ \xrightarrow[-N_2]{e^-} R_2CH\cdot \xrightarrow{e^-} R_2CH^- \xrightarrow{H^+} R_2CH_2 \qquad (2)$$

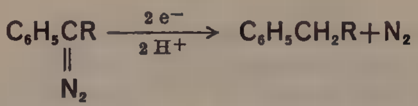
The conversion of hydrazone 10 to amine 9 involves no new chemistry; it is known that hydrazones[12, 13], including those α- to a carbonyl group[14], are reduced electrochemically in a four-electron step, and that this involves initial cleavage of the N—N bond, followed by reduction of the resulting imine. Thus the overall six-electron reduction of diazo compounds 1 may now be seen to involve a sequence of three two-electron reductions (equation 3). Each of the latter in turn presumably is itself an ECE process, analogous to the conversion of 1 to 13.

$$1 \xrightarrow[2\,H^+]{2\,e^-} 13 \xrightarrow[2\,H^+]{2\,e^-} R_2C{=}NH \xrightarrow[2\,H^+]{2\,e^-} R_2CHNH_2 \qquad (3)$$

The electrochemical behaviour of 3-diazooxindole (**14**) is very similar to that of **8**. In base (pH > 8·5), a two-electron reduction to hydrazone **15** is observed, followed by a four-electron reduction to amine **16** at more negative potentials[15] (equation 4). Of course, at lower pH a single six-electron step is observed. Ethyl diazophenylacetate (**17**) is reduced cleanly to ethyl phenylacetate in aqueous dioxane at pH 7 (*cf.* the conversion of **4** to [illegible] in acid, already discussed) (equation 5)[16]. More



(14) **(15)** **(16)** (4)



$$C_6H_5C(=N_2)R \xrightarrow[2\,H^+]{2\,e^-} C_6H_5CH_2R + N_2 \qquad (5)$$

[**17**: R = CO_2Et; **18**: R = $P(O)(OEt)_2$]

surprisingly, the diazophosphonate **18** is reduced in similar fashion in 90% yield even in alkaline media, in contrast with the behaviour of **4**, **8** or **14** under such conditions[16]. The reasons for this difference are not clear.

In the only study carried out to date under aprotic conditions, Elofson and coworkers explored the electrochemical behaviour of several diazo compounds in sulfolane[17]. Like **17**, ethyl diazoacetate suffered clean reduction to ethyl acetate and nitrogen. Diazomethane was not reducible electrochemically. Reduction of diazodiphenylmethane (**19**) was more complex: diphenylmethane (**24**, 20%) and benzhydrylamine (**23**, 20%) were the major products, but azodiphenylmethane (**22**, yield unspecified) could also be identified as a product by the use of mass spectrometry. Formation of **22**–**24** was rationalized by the reactions shown in Scheme 4. It would appear that successive electron and proton transfers to **21** should

$$\underset{\mathbf{(19)}}{(C_6H_5)_2CN_2} \xrightarrow{e^-} (C_6H_5)_2\dot{C}N_2^{-} \xrightarrow{H^+} \underset{\mathbf{(20)}}{(C_6H_5)_2\dot{C}HN_2}$$

$$\mathbf{20} \longrightarrow \underset{\mathbf{(21)}}{(C_6H_5)_2CH\cdot} + N_2$$

$$\mathbf{20} + \mathbf{21} \longrightarrow \underset{\mathbf{(22)}}{(C_6H_5)_2CHN{=}NCH(C_6H_5)_2}$$

$$[illegible] \xrightarrow{\text{reduction}} \underset{\mathbf{(23)}}{(C_6H_5)_2CHNH_2}$$

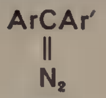
$$\mathbf{21} \xrightarrow{\text{H-abstraction}} \underset{\mathbf{(24)}}{(C_6H_5)_2CH_2}$$

SCHEME 4

be at least as likely as hydrogen abstraction as a route to **24**, and that **23** might be formed by electrochemical reduction of **20**, not **22**, but the scheme seems essentially sound. Judging from these results, the electrochemistry of diazo compounds in aprotic media differs considerably from that in protic media. Further experimentation to clarify these differences would appear to be in order.

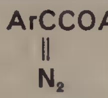
B. Oxidation

Anodic oxidation of a variety of diazo compounds, e.g. **25**–**27**, in acetonitrile has been shown to proceed by initial formation of a short-lived intermediate,



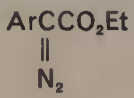
$\mathrm{ArC(=N_2)Ar'}$

(25)



$\mathrm{ArC(=N_2)COAr'}$

(26)



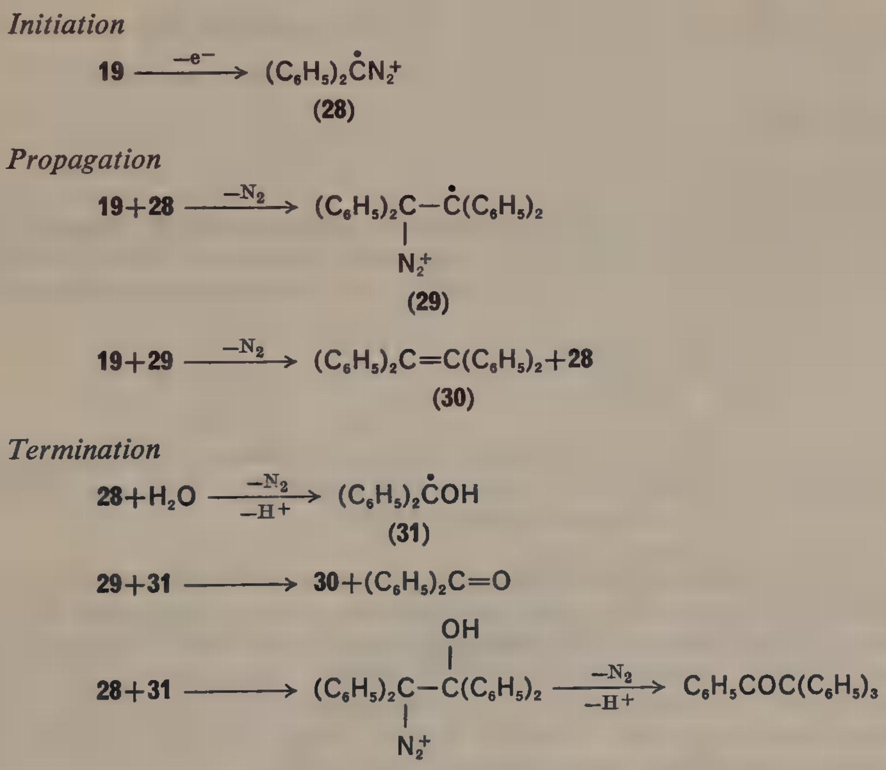
$\mathrm{ArC(=N_2)CO_2Et}$

(27)

presumably the corresponding radical cation[18–20]. The oxidation potentials of each class of compounds were found to be linearly correlated with Hammett σ^+ and σ [18, 20]. Furthermore, the rates of reaction of members of a given class of diazo compound with benzoic acid were found to be linearly correlated with their oxidation potentials[18, 20]. For example, the rates of reaction of substituted diazodiphenylmethanes (**25**) with benzoic acid were found to obey the following relationship (equation 6)[18]:

$$\log k_{\mathrm{R}} = -6{\cdot}13E_{\frac{1}{2},\mathrm{R}} + 5{\cdot}59 \qquad (6)$$

where k_{R} and $E_{\frac{1}{2},\mathrm{R}}$ are the rate of reaction and oxidation potential, respectively of a given diazo compound. Similar correlations were observed for other classes of diazo compounds, e.g. **26** and **27**. The success of such correlations was ascribed to the fact that both processes occur at the diazo group, the position of highest electron density.



Initiation

$$\mathbf{19} \xrightarrow{-e^-} (\mathrm{C_6H_5})_2\dot{\mathrm{C}}\mathrm{N_2^+} \quad \mathbf{(28)}$$

Propagation

$$\mathbf{19}+\mathbf{28} \xrightarrow{-\mathrm{N_2}} (\mathrm{C_6H_5})_2\underset{\mathrm{N_2^+}}{\mathrm{C}}-\dot{\mathrm{C}}(\mathrm{C_6H_5})_2 \quad \mathbf{(29)}$$

$$\mathbf{19}+\mathbf{29} \xrightarrow{-\mathrm{N_2}} \underbrace{(\mathrm{C_6H_5})_2\mathrm{C}=\mathrm{C}(\mathrm{C_6H_5})_2}_{\mathbf{(30)}}+\mathbf{28}$$

Termination

$$\mathbf{28}+\mathrm{H_2O} \xrightarrow[-\mathrm{H^+}]{-\mathrm{N_2}} (\mathrm{C_6H_5})_2\dot{\mathrm{C}}\mathrm{OH} \quad \mathbf{(31)}$$

$$\mathbf{29}+\mathbf{31} \longrightarrow \mathbf{30}+(\mathrm{C_6H_5})_2\mathrm{C}=\mathrm{O}$$

$$\mathbf{28}+\mathbf{31} \longrightarrow (\mathrm{C_6H_5})_2\underset{\mathrm{N_2^+}}{\mathrm{C}}-\overset{\mathrm{OH}}{\mathrm{C}}(\mathrm{C_6H_5})_2 \xrightarrow[-\mathrm{H^+}]{-\mathrm{N_2}} \mathrm{C_6H_5COC(C_6H_5)_3}$$

Scheme 5

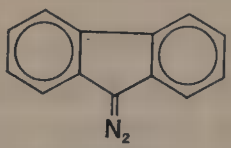
The radical cations from oxidation of diazo compounds decompose in complex fashion. From diazodiphenylmethane (**19**), for example, tetraphenylethylene (**30**) is the major product (80% yield) but benzophenone, benzpinacolone and benzhydrol[19] are also formed. An important mechanistic clue was provided by coulometric experiments, which demonstrate that the anodic process involves a chain reaction: at an initial concentration of **19** of 0·05 M, 25 molecules of **19** react for every electron passed; when the initial concentration of **19** is 0·004 M, only seven molecules of **19** react per electron. The products were rationalized as in Scheme 5 [19, 21].

Oxidation of **19** in the presence of *n*-propylamine, on the other hand, consumed two electrons per molecule of **19** and afforded benzophenone *n*-propyl imine (**32**)

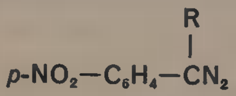
$$(C_6H_5)_2C{=}NC_3H_7$$

(32)

as the product[19]. This reaction may have synthetic utility as a route to imines (Schiff bases). Other diazo compounds which were found to undergo electrochemical oxidation to afford the corresponding olefin include the following (yields of olefin in parentheses)[21]:



45%

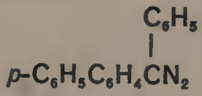


$$p\text{-}NO_2{-}C_6H_4{-}\overset{R}{\overset{|}{C}}N_2$$

(R = H, 70%)

(R = CH_3, 30%)

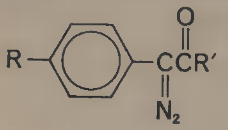
(R = C_6H_5, 60%)



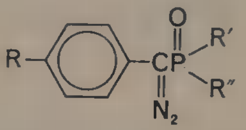
$$p\text{-}C_6H_5C_6H_4\overset{C_6H_5}{\overset{|}{C}}N_2$$

(major product)

A different anodic pathway appears to intervene when the diazo group is alpha to a carbonyl group[22] (**33**) or one of its phosphorus analogues[16] (**34**). With such compounds a complex set of products is formed, some of which apparently arise by



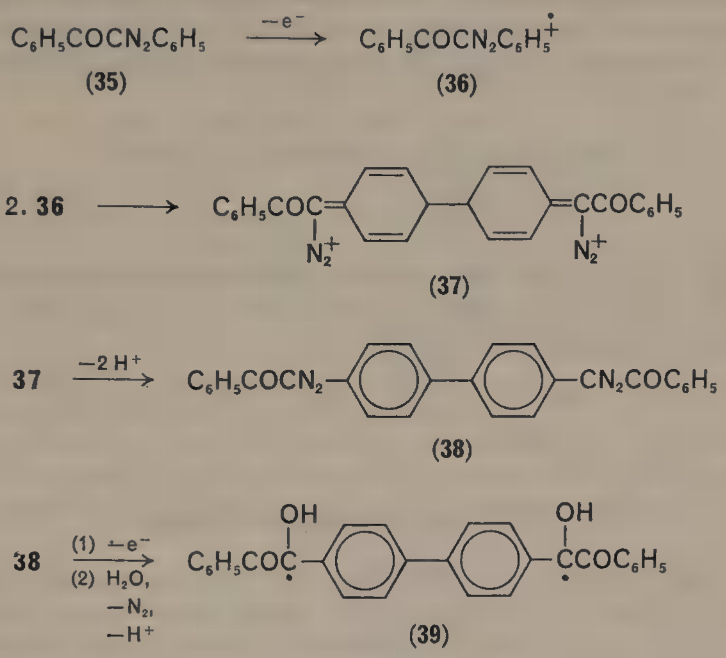
(33)



(34)

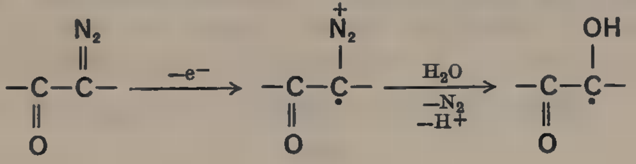
R′ = aryl or OR, R″ = OR

coupling of two molecules of substrate at the *para* position. This was established by permanganate oxidation of the neutral fraction from the electrochemical reaction, after removal of acidic materials. For example, anodic oxidation of benzoylphenyldiazomethane (**35**) in acetonitrile containing lithium perchlorate and sodium bicarbonate afforded benzoic acid (27%), benzilic acid (trace), benzil (9%), benzoin (? %), benzaldehyde (? %) and a neutral fraction which afforded diphenic acid (17%) and benzoic acid (35%) upon treatment with permanganate[22]. The coupling was rationalized as illustrated in Scheme 6. All of the observed products can be rationalized in terms of intermediates **36** and **39** (which could also be written as a quinoid structure), though other mechanisms could be imagined. (It should be noted, incidentally, that there are many precedents for *para* coupling of anodically generated radical cations[23].) The difference between the anodic behaviour of aryldiazo compounds, e.g. **19**, and species such as **35**, appears to lie in the site at which the corresponding radical cations couple: coupling of two **28** species occurs at the diazo carbons, while with **36** coupling is between two *para* sites. Apparently the electron-withdrawing carbonyl and phosphoryl groups in **33** and **34**, respectively, inhibit coupling at the diazo carbon.



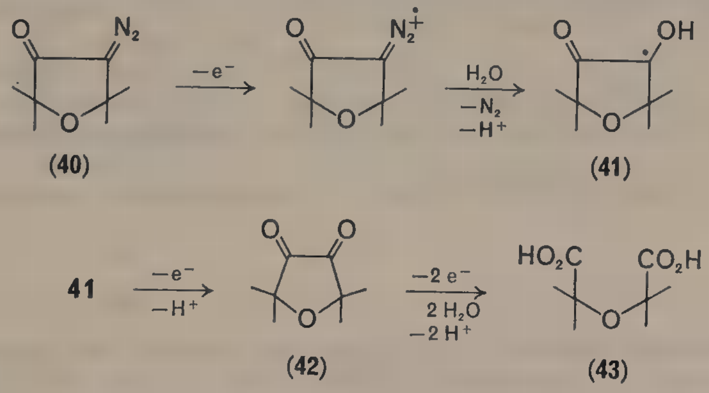
SCHEME 6

The anodic conversion of the diazo group to an n-hydroxycarbonyl radical[22] (equation 7) (*cf.* the conversion of **38** to **39**) can not only explain the formation of



$$\underset{\underset{\textstyle O}{\|}}{-C}-\overset{\overset{\textstyle N_2}{\|}}{C}- \xrightarrow{-e^-} \underset{\underset{\textstyle O}{\|}}{-C}-\overset{\overset{\textstyle \overset{+}{N_2}}{|}}{\underset{\bullet}{C}}- \xrightarrow[-H^+]{H_2O,\ -N_2} \underset{\underset{\textstyle O}{\|}}{-C}-\overset{\overset{\textstyle OH}{|}}{\underset{\bullet}{C}}- \qquad (7)$$

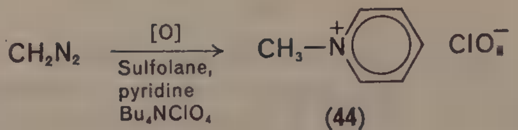
benzoin and benzil from oxidation of **34**, but also explains the anodic conversion of diazoketone **40** to the dicarboxylic acid **43** (along with a trace of diketone **42**)[24].



SCHEME 7

40 appears to be the only aliphatic diazoketone whose anodic electrochemistry has been examined. The generality of the conversion exemplified by **40** → **43**, and its possible synthetic utility as a means of carbon–carbon bond cleavage alpha to the carbonyl group of aliphatic ketones (via the corresponding diazoketones) remain to be established.

Elofson and coworkers obtained *N*-methylpyridinium perchlorate (**44**) by electrochemical oxidation of diazomethane in sulfolane in the presence of pyridine (equation 8)[17]. These workers suggested a mechanism involving successive generation



(**44**) (8)

of diazomethane radical cation (**45**), methylene radical cation (**46**) and finally methyl cation (equation 9). It is more likely that the product **44** derives from nucleophilic attack upon **45** (or possibly **46**) by pyridine.

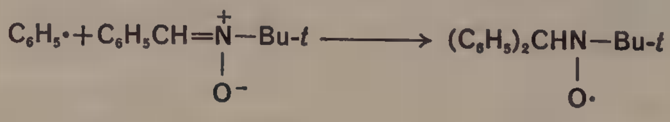
$$\underset{}{CH_2N_2} \xrightarrow{-e^-} \underset{(\mathbf{45})}{CH_2N_2^{\dot{+}}} \xrightarrow{-N_2} \underset{(\mathbf{46})}{CH_2^{\dot{+}}} \xrightarrow{H\cdot} CH_3^+ \xrightarrow{Pyr} \mathbf{44} \qquad (9)$$

III. THE DIAZONIUM GROUP

Electrochemical reduction of arenediazonium salts in aqueous media exhibits some confusing features. Two polarographic waves are observed, the height of the first being controlled by adsorption. Microcoulometry at the dropping mercury electrode shows that the two waves correspond to uptake of one and four (overall) electrons, respectively. The products of preparative electrolysis at a mercury pool are either aryl mercury compounds or phenylhydrazines; which is formed depends not only on the electrode potential, but also the rate of stirring[26]. In aprotic media, on the other hand, arenediazonium salts are electrochemically better behaved. A one-electron wave is observed in aprotic media, e.g. sulfolane or acetonitrile, corresponding to the electrode process described by equation (10)[17, 27]. There is a

$$ArN_2^+ + e^- \longrightarrow \underset{(\mathbf{47})}{ArN^{+}\cdot} \longrightarrow Ar\cdot + N_2 \qquad (10)$$

good linear correlation[27] between the polarographic half-wave potentials of substituted benzenediazonium ions and Hammett σ substituent constants (σ^+ for *para* substituents capable of donating electrons by resonance). Free phenyl radicals formed by decomposition of intermediate **47** have been identified in several ways: (a) electrolysis in the presence of α-phenyl-*N*-*t*-butyl nitrone, a well-known radical trap, affords radical **48** (equation 11) which can be readily detected by e.s.r. spectroscopy[28], and (b) isomer ratios, total rate ratios and partial rate factors for arylation

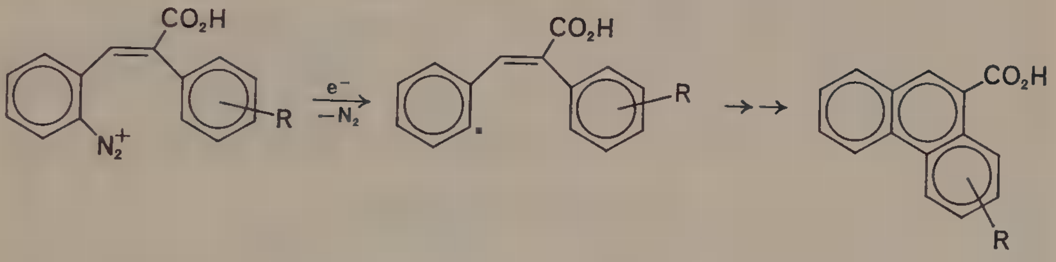


$$C_6H_5\cdot + C_6H_5CH{=}\underset{O^-}{\overset{+}{N}}-Bu\text{-}t \longrightarrow (C_6H_5)_2CH\underset{O\cdot}{N}-Bu\text{-}t \qquad (11)$$

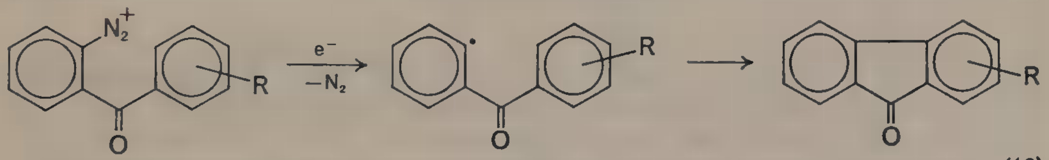
(**48**)

by electrochemically-generated phenyl radicals coincide with those for phenyl radicals generated by thermolysis of benzoyl peroxide or *N*-nitrosoacetanilide, indicating that there is no electrophilic component to the arylation (from decomposition of the parent diazonium ion) and that the phenyl radical reactivity is not influenced by the electrode surface[29]. Yields of phenylated products are somewhat lower than with benzoyl peroxide or *N*-nitrosoacetanilide, but the only radical generated is the phenyl radical, unlike other routes. (Thus, benzoyl peroxide thermolysis affords products derived from both phenyl and benzoyloxy radicals[30].) Other advantages of the electrochemical reduction of arene diazonium ions as a preparative route to aryl free radicals include the facts that aryl radicals may in principle be generated over a wide temperature range, and that diazonium ions are among the most easily reducible organic functional groups, so that a wide variety of substituents may be accommodated in the aromatic ring. Elofson, Gadallah and Schulz found not only that benzenediazonium tetrafluoroborate is converted to phenylpyridines in 81% yield (α : β : γ = 56 : 27 : 17) upon electrolysis in pyridine as solvent, but that metallic mercury alone can effect reduction of the diazonium ion (87% yield of phenylpyridines)[31]. In fact, phenylation of pyridine could be effected (though more slowly) by simply allowing the diazonium tetrafluoroborate to react directly with pyridine (92% yield of phenylpyridines). It was also found possible to phenylate pyridine *N*-oxide with electrochemically generated phenyl radicals. Yields of phenylpyridine *N*-oxides were better (35%, α : β : γ = 89 : 1 : 10) than with conventional methods of phenyl radical generation[31].

Elofson and Gadallah have shown that it is possible to effect electrochemical cyclization of the appropriate diazonium α-phenylcinnamic acids in nearly quantitative yield[32] (equation 12). They also found it possible to effect electrochemical cyclization of diazotized 2-aminobenzophenones (**49**) to fluorenones (**51**) (equation 13). Surprisingly, the same process was found to occur thermally, and it was suggested that this occurs by intramolecular reduction of the diazonium group by the other ring (an intramolecular charge-transfer process). Depending on the experimental conditions, greater or lesser amounts of benzophenones (**52**) and diarylmercury



(12)



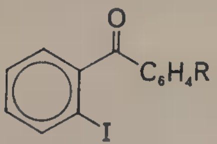
(49) (50) (51) (13)

$C_6H_5COC_6H_4R$

(**52**)

$(C_6H_5COC_6H_4)_2$—Hg

(**53**)



(**54**)

compounds (**53**) accompanied products from decomposition of **49**. Yields of **52** were highest in aprotic solvents, where hydrogen abstraction by radical **50** is easiest; conversely, yields of fluorenones were best in protic media, or in aprotic thermolyses of **49**, which therefore apparently do not involve radicals **50** as discrete intermediates. Finally, reduction of **49** by iodide ion in aprotic media afforded 2-iodobenzophenones (**54**) in good yield; electron transfer from iodide ion affords **50** and an iodine atom, which then couple in the solvent cage.

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CHAPTER 11

The influence of the diazo and diazonium groups

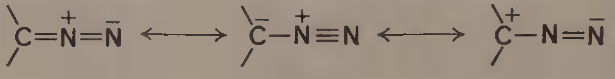
EDWARD S. LEWIS
Department of Chemistry, Rice University,
Houston, Texas, USA

I. INTRODUCTION

A major interest in organic chemistry is the effect of structural change on reactivity, especially the effect of change in structure of one part of a molecule on reactivity at some other part of the molecule. The influence of such a change in structure is rather conventionally divided into steric effects and electronic effects, although these are neither totally sufficient nor completely separable. An example of the insufficiency lies in the existence of secondary isotope effects, where the effect arises exclusively from a difference in mass of two substituents having identical electronic effects and sizes. An example of the inseparability of steric and electronic effects can be found in the efforts to understand the effect of *ortho* substituents on aromatic side chain reactivity, where, despite strong efforts, no reasonable and consistent electronic effects have been found by methods often capable of separating steric and electronic effects in other cases.

We can nevertheless begin to understand the electronic part of substituent effects by combining qualitative considerations of inductive effects from electronegativities and formal or real charges with resonance effects, alternatively estimated by various molecular orbital methods, of which the semi-empirical methods now appear to be the most quantitative. Similarly, steric effects can be related to Van der Waals' interactions by qualitative or quantitative methods.

On these bases, the diazo (I) and diazonium ion (II) groups would be expected to have very strong influences, because of the formal charges in the first, the real positive charge in the second, as well as the unsaturation which gives the possibility of extensive resonance interaction in both. The direction of the effect is somewhat equivocal in the diazo compounds, since even the sign of the charge nearest to the rest of the molecule is uncertain, depending on the relative weights of contributing structures **Ia** and **Ib**. Structure **Ic** is unimportant partly because it has the wrong geometry. In the diazonium ion the substituent effect is unequivocally that of electron withdrawal; it will be acid strengthening, it can be expected to have a positive Hammett σ or Taft σ_1.



(Ia) (Ib) (Ic)

$$C-\overset{+}{N}\equiv N$$

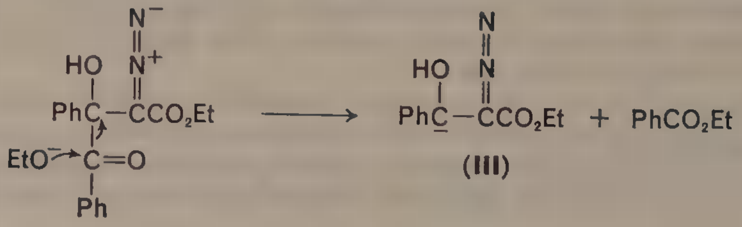
(II)

The experimental realization of these expectations is another problem. In order to determine the effect of the diazo or diazonium groups on a reaction elsewhere in the molecule, it is necessary to have such a reaction occur, leaving these nitrogen functions untouched. The extraordinary reactivity of these two functional groups makes all such studies difficult, for the majority of the reagents will attack these very reactive functional groups before reacting elsewhere in the molecule. The low thermal stability of diazo and diazonium compounds sometimes makes it uncertain whether or not the loss of nitrogen has occurred before, after or in concert with a reaction elsewhere. We therefore lack the wide range of information on substituent effects for the groups, and for the diazo groups there is virtually no quantitative information. However, there are some available data, mostly qualitative, and these will be presented. The effect of the diazo group will be discussed first, then that of the diazonium ion group. Three sources have been especially useful in this compilation; the valuable book of Zollinger[1], the review on diazo compounds in acid by More O'Ferrall[2], and a review by Regitz[3] which covers several reactions of diazo compounds without loss of this functional group.

II. INFLUENCE OF THE DIAZO GROUP

A. The Carbonyl Group as a Model

The first question we can attack on the relative importance of structures **Ia** and **Ib** is to ask whether a doubly bonded structure rather like a Schiff base or a ketone is a better representation than a carbanion. We shall see that the carbanion structure **Ib** is more descriptive of the behaviour than any carbonyl-like one. In fact, only one reaction turned up to suggest the carbonyl-like structure. The reaction (equation 1) was postulated[4] on the basis of the formation of $PhCHOHCN_2CO_2Et$ and ethyl



(III) (1)

benzoate from the attempted condensation in basic ethanol of benzil with ethyl diazoacetate. Here the diazo group may have stabilized the intermediate carbanion, III.

B. The Carbanion Model; Protonation

The analogy of diazo compounds to carbanions is relatively better supported. Diazo compounds react very generally with acids[2], usually however giving diazonium salts too unstable to allow the drawing of quantitative conclusions. Other electrophiles also attack diazo compounds, and these reactions also contribute to our information.

One reaction showing the protonation unequivocally but casting little light on the equilibrium constant is the reaction of trifluorodiazoethane with fluorosulfonic acid (equation 2). The conversion to the diazonium salt, which is stable at −60 °C

$$F_3CCHN_2 + HO_3SF \longrightarrow F_3CCH_2\overset{+}{N}_2 + {}^-O_3SF \qquad (2)$$

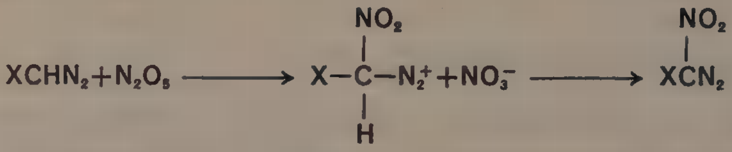
is quantitative[5]. Some other diazo compounds are acid stable to some extent, but it has not been established whether these correspond to stable diazonium salts or very weakly basic diazo compounds. They include diethyl diazomalonate, stable to methanolic H_2SO_4 [6], and $(RSO_2)_2CN_2$, which decompose at rate slow enough to measure in chlorosulphonic acid[7].

At a more familiar level ethyl diazoacetate hydrolysis rates correlate with H° up to the fastest rates measured[8]. This suggests that the equilibrium extent of protonation does not exceed a few percent in the most highly acidic media used. The rate of deprotonation of $\overset{+}{N}_2CH_2CO_2Et$ has not been measured, but the relative rates of proton and nitrogen loss come out of studies on the acid-catalysed exchange of tritium-labelled diazoacetic ester[9]. One can attempt to estimate the acidity of $\overset{+}{N}_2CH_2CO_2Et$, either by using a substituent constant derived from the aromatic series (discussed below), or by correcting the pK_a of $N{\equiv}C{-}CH_2CO_2Et$ for an electronegativity and electrostatic change. This leads, depending on how the various corrections are applied, to $pK_a = -7 \pm 5$, a not very useful or firmly based number, but at least consistent with the available data. Kreevoy[10] has estimated from kinetic considerations based on the decomposition of diazoacetate ion that for $\overset{+}{N}_2CH_2CO_2^-$, $pK_a \geqslant 0$.

The protonation of diazo compounds which do not have these base weakening and carbonium ion destabilizing substituents is even more uncertain insofar as the equilibrium constants are concerned. The details of protonation of diazo compounds and the subsequent reactions are discussed by More O'Ferrall[2]; in general, the expected stability of the carbonium ion determines whether or not the protonation is significantly reversible. Thus under ordinary circumstances only diazomethane shows exchange in acidic D_2O competing with nitrogen loss[11]. Clearly $R_2CHN_2^+$ and R_2CN_2 are interconvertible, but we have not been able to establish an equilibrium constant even in one case within orders of magnitude. In summary, the protonation does occur, though hardly with the facility that would be associated with carbanions.

C. The Carbanion Model; Electrophiles

Diazo compounds also react with other electrophiles. Condensations using base catalysis will be discussed later, but some react without any base catalysis. Ethyl diazoacetate, diazoacetonitrile, trifluorodiazoethane[12] and nitrodiazomethane[13] are nitrated by N_2O_5, presumably by way of the stable but strongly acidic diazonium salts (equation 3). Diazomethane is chlorinated[14] by *t*-butyl hypochlorite at −100 °C,



$$XCHN_2 + N_2O_5 \longrightarrow X{-}\overset{\displaystyle NO_2}{\underset{\displaystyle H}{C}}{-}N_2^+ + NO_3^- \longrightarrow X\overset{\displaystyle NO_2}{C}N_2 \qquad (3)$$

$X = CO_2Et, CN, CF_3, NO_2$

here the presumed chloromethanediazonium ion is protected from decomposition both by the low temperature and the very basic counter ion, *t*-BuO⁻.

A familiar electrophilic attack on diazomethane and other diazo alkanes is the reaction with acid chlorides[15] or anhydrides[16], yielding diazoketones (equation 4).

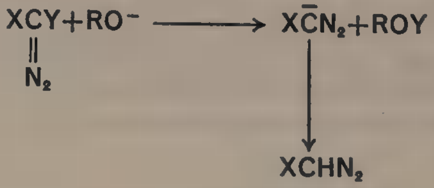
$$RCOCl + 2\ CH_2N_2 \longrightarrow RCOCHN_2 + CH_3Cl + N_2 \qquad (4)$$

The extra mole of diazomethane is believed to serve as a sink for the proton of the initial diazonium salt, $RCOCH_2N^+$, rather than as a base catalyst at an earlier stage.

The formation of polymethylene by the reaction of diazomethane with boron fluoride[17] is also evidence for electrophilic attack on the diazo centre, even though the immediate product is not observed. Similarly the reaction of diazo compounds in the absence of basic catalysts, with ketones or aldehydes, is an example of electrophilic attack, but with a non-isolable diazonium ion product[18].

D. Acidity of Diazo Compounds

Diazo compounds not only act as bases but they are also perceptibly, although not strongly, acidic. Diazomethane reacts with methyl lithium to give a lithium derivative[19]. Ionization is also possible with triphenylmethylsodium[20], which puts a lower limit on the acidity of diazomethane, since pK_a of triphenylmethane = 33 [21]. Ethyl diazoacetate has also been converted to the lithium salt[22], and ionization under relatively mild conditions is suggested by the facile hydrogen isotope exchange in base[9], compared to ethyl acetate which suffers hydrolysis much faster than exchange. Furthermore, ethyl diazoacetate and other acyldiazo compounds undergo aldol condensation with a variety of compounds with dilute ethanolic sodium hydroxide[4]. Diazosulphones even add to enamines[23], presumably via an initial proton transfer. The perceptible stability of the anions $N_2\bar{C}\overset{\overset{\displaystyle O}{\|}}{C}R$ is also indicated by reverse condensations observed in a number of cases, mostly of diacyldiazomethanes (equation 5). The mechanism is presumably that shown, and the diazo compound



$$X\underset{\underset{\displaystyle N_2}{\|}}{C}Y + RO^- \longrightarrow X\bar{C}N_2 + ROY,\quad X\bar{C}N_2 \longrightarrow XCHN_2 \qquad (5)$$

formed is often the one which would be expected to give the most stable anion. A number of examples are listed by Regitz[3], but except for showing that acyldiazomethane anions have a stability comparable or greater than that of ordinary enolate ions, quantitative conclusions are impossible.

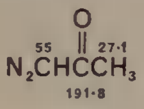
The chemical evidence is then that the diazo carbon is definitely nucleophilic, and is perceptibly, although not strongly, basic. It is also significantly more acidic than a comparable methyl group, although the magnitude of the enhancement of acidity is not known.

E. Remote Effects of the Diazo Group

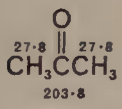
Before going on to physical evidence for the charge distribution about the diazo compounds, it is appropriate to comment briefly about reactivity more remote from the diazo group. An acid strengthening effect on the β carbon is suggested although not convincingly demonstrated by the cleavage mentioned earlier[4]. A few reactions at positions remote from the diazo group have been observed, but without rate measurements they are hard to interpret. Thus, potassium diazoacetate is prepared by saponification of the ethyl ester[24] by concentrated potassium hydroxide under conditions which would also be expected to saponify ethyl acetate, but relative rates are not known.

F. Effect of the Diazo Group on ^{13}C-n.m.r., Spectra

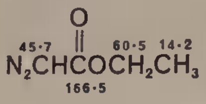
A possible approach to electronic effects in diazo compounds is the chemical shift in the n.m.r., for extensive electron withdrawal should reduce the nuclear shielding, and supply should increase it. There are few proton spectra for diazo compounds available, but a number of ^{13}C spectra of diazo compounds have been taken[25]. Several compounds, all diazo ketones or esters, are here presented, with chemical shifts (in p.p.m. downfield from TMS), together with some model compounds, taken from Breitmeyer and Voelter[26].


$N_2CH\overset{O}{\overset{\|}{C}}CH_3$

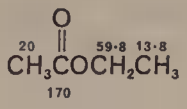
(IV)


$CH_3\overset{O}{\overset{\|}{C}}CH_3$

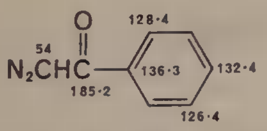
(V)


$N_2CH\overset{O}{\overset{\|}{C}}OCH_2CH_3$

(VI)


$CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_3$

(VII)



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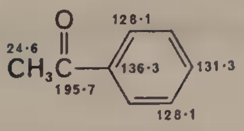

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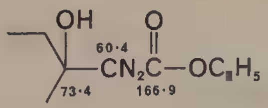


(X)

R_3COH
~ 69 ($R \neq H$)

These chemical shifts allow us to draw some conclusions, limited however by the small size of the sample. The important effects are on the diazo carbon, on the adjacent carbonyl carbon, and there is one example of a perceptible effect on the other carbon flanking the diazo group. More distant groups, as the ethyl group in **VI** and **VII**, or the phenyl group in **VIII** and **IX**, seem to be relatively uninfluenced (here differences of less than 2 p.p.m. are ignored, largely because the author is not competent to judge the sources of error in the various spectra). The carbonyl frequency is uniformly at higher field for the diazo compound than for the models. Since (in the one case of the tertiary alcohol, **X**, shown) the shift on the other side of the diazo group is in the other direction, this is probably not a consequence of an inductive effect of the diazo group; instead it probably represents a specific conjugation similar to that in α,β-unsaturated ketones, which also causes a higher field shift of the carbonyl frequency. Alternatively, the extra shielding could be a consequence of the formal negative charge on the diazo carbon (structure **Ib**).

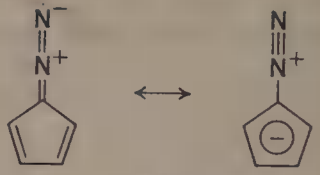
The chemical shift of the diazo carbon is especially interesting; any model with neutral carbon bonded with sp^2 hybridization to carbon, oxygen or nitrogen would predict chemical shift more than 100 p.p.m. from TMS. The observed shift of only 40–60 p.p.m. appears to require the addition of extra shielding, such as would be associated with a substantial negative charge associated with this carbon, for example through the important contribution of **Ib**.

In sum, the c.m.r. chemical shifts are in agreement qualitatively with the chemical evidence, namely that diazo compounds have a significant partial negative charge on carbon.

G. *Special Diazo Structures*

Certain diazo compounds have such important contributions of diazonium-like structures that they can really be thought of as members of one class as well as of the other. These include the diazo oxides, **XI**, which are the conjugate bases of *ortho*- or *para*-hydroxydiazonium ions, which we shall consider briefly in a later section. Another example is diazocyclopentadiene, **XII**, which appears to be virtually an aromatic molecule, and undergoes electrophilic substitution with facility[27].


(XI)


(XII)

III. THE DIAZONIUM ION GROUP

A. *Coverage*

The effect of the diazonium ion group will here be limited to discussion of aromatic diazonium salts. The relatively few aliphatic cases of any stability contribute little to our knowledge. There are also some inorganic 'diazonium salts' of the form L_nMN_2 or metal nitrogen complexes, which share little of the chemistry of the aromatic compounds; they will not be considered here.

Aromatic diazonium ions, ArN_2^+, have been extensively studied since their discovery more than a hundred years ago. Nevertheless, most of the chemistry involves either loss of N_2, and replacement by various groups (such as OH in the hydrolytic decomposition, halogen in the Sandmeyer reaction among many), or alteration of the N_2^+ group as in the reduction to phenylhydrazine or coupling to form ArN_2X (where X may be carbon, oxygen, nitrogen, sulphur, phosphorus, among others). With the one exception of partial reaction of tetrazotized aromatic diamines, discussed below in Section III.E, all these reactions are outside the scope of this chapter.

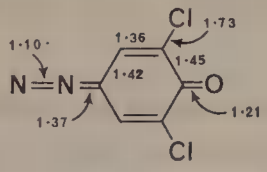
B. The Hammett Substituent Constants

Among the reactions suitable for discussing the effect of the diazonium ion group as a substituent are acidities and basicities of acids and bases containing the N_2^+ substituent, and the rates of various reactions, including electrophilic and nucleophilic substitution on the aromatic ring as long as the diazonium ion group remains attached after the reaction. The diazonium ion group was recognized as a powerfully electron-withdrawing substituent for as long as that phrase has had meaning, but the quantitative evaluation of the effect was not attempted until a number of acid strengths and reaction rates were measured with the goal of establishing the Hammett substituent constant σ [28]. Table 1 shows some of the results obtained for various cases. The absence of entries or estimates of one limit only reflects experimental problems, almost always due to side reactions which destroy the diazonium group. The nature of the various uncertainties is discussed in the original paper.

TABLE 1. Substituent constants for the diazonium ion group[28]

Group	Reaction	σ_m	σ_p	σ_p^-
$^+N_2C_6H_4OH$	Acid ionization	$<2{\cdot}1$		3·03
$^+N_2C_6H_4NH_3^+$	Acid ionization			3·43
$^+N_2C_6H_4CO_2H$	Acid ionization	1·76	1·91	
$^+N_2C_6H_4CH_2CO_2H$	Acid ionization		2·18	
$^+N_2C_6H_4COCH_3$	Bromination rate	$>0{\cdot}2$	$>1{\cdot}1$	

The large difference between σ and σ^- implies a large resonance interaction between the N_2^+ and the p-O^- (as shown in XI). This extra stabilization is confirmed by the low reactivity of these 'diazo oxides' in coupling reactions[29] (among others), as well as by the rather quinoid bond distances shown in XIII[30]. The distances shown are averages of chemically equivalent distances in two independent molecules.



(XIII)

The very large substituent effect is also evident from the acidity of o-carboxybenzenediazonium ion[28], which has a $pK_a = 1{\cdot}47$; it is almost ten times stronger than the *para* isomer, but of course no substituent constant should be assigned.

In spite of the fact that the results in the Table were determined more than 15 years ago, there has been very little revision. The value for $\sigma_m = 1{\cdot}76$, based on a single measurement, has been reported to be confirmed on the basis of studies of ionization equilibria of some diazodiazoles and other heterocycles[31]. A study of the ^{13}C-n.m.r. of diazonium salts is reported[32] to give chemical shifts simply related to σ and consistent with the old values.[28] A study[33] of the ^{35}Cl nuclear quadrupole resonance spectra of some chlorobenzenediazonium ions is reported to show substantial electron withdrawal by N_2^+, but in the order $o>m>p$. This order is stated to be consistent with the chemically determined substituent effects since the nqr chemical shifts are believed to be insensitive to resonance effects, but sensitive to inductive effects. A further confirmatory value of σ_p is presented in Section III.E.

The substituent effects in the Table can be subjectively weighted to give $\sigma_m = 1{\cdot}7$, $\sigma_p = 2$ and $\sigma_p^- = 3$, but it should be emphasized that they are only valid in aqueous solution, since charged and uncharged substituents will behave differently as the medium is changed. It is nevertheless clear that the N_2^+ group has a more powerful electron-withdrawing effect than any other single familiar group, and this is reasonable, for it combines the resonance effect of the isoelectronic cyano group ($\sigma_p = 0{\cdot}66$) with the pure charge effect of the trimethylammonium substituent ($\sigma_p = 0{\cdot}82$). It is perhaps the plausibility of the very large σ values for N_2^+ which has led to a general acceptance of these values, rather than conviction from an overwhelming mass of data.

C. Electrophilic Substitution on Diazonium Salts

Benzenediazonium ion has been nitrated with difficulty, and nitration occurs mostly in the *meta* position. This is consistent with Hammett's observation[34] that substituents with $\sigma_p > \sigma_m$ are *meta* directing. There are no direct data on the rates of electrophilic substitution on benzenediazonium ion, although the following, rather flawed, argument suggests that in one case it may be slower than the attack on nitrobenzene. When benzenediazonium ion is decomposed in nitrobenzene, *m*-nitrobiphenyl is an important product. When benzenediazonium fluoroborate is heated in trifluoroethanol and nitrobenzene[35], only 6% of the product is nitrobiphenyl, but most of the remainder is the expected fluorobenzene and phenyltrifluoroethyl ether. If this electrophilic arylation had been able to attack benzenediazonium ion as easily as nitrobenzene, then fluorobiphenyl or trifluoroethoxybiphenyl should have been observed. The absence of these products is not convincingly demonstrated, but again it is plausible and hence believable. The argument is somewhat strengthened because arylation with decomposing diazonium salts is believed to be very unselective, as would be expected for the postulated phenyl cation intermediate,† although a small discrimination among neutral organic solvents is observed[35].

The much more facile electrophilic attack on diazocyclopentadiene has been mentioned above.

D. Nucleophilic Substitution Activated by the Diazonium Group

In contrast to the rare and difficult electrophilic attacks on diazonium salts there are numerous examples of nucleophilic attack. Only those leaving the diazonium group intact, which still comprise a large body of data, are relevant here. The activation of nucleophilic aromatic substitution by an *o*- or *p*-N_2^+ group had been observed very early, especially by Hantzsch[42] and by Meldola[43]. Miller[44] identified the N_2^+ group as more strongly activating than any other substituent. Quantitative studies on the rates of attack of thiocyanate *ortho* and *para* to the diazonium ion group were undertaken[45]. The reaction is facile for halogen and the second-order rate constants are much faster in lower dielectric constant medium, as expected for this anion–cation reaction. The logarithm of the rate constants correlated well with

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† The actual intermediacy of the phenyl cation in the solvolysis of diazonium ions is somewhat controversial and is complicated but illuminated by the simultaneous occurrence of several reactions. The controversy centres around whether[35, 36] or not[37] nucleophiles are present in the rate-determining step, but there is no controversy over the description of all transition states as closely resembling the phenyl cation, and the consequent unselectivity of the reaction, which discriminates poorly between halide ions and water[36, 38], and allows attack on very poor nucleophiles such as chlorobenzene[39], fluoroborate ion[40] or molecular nitrogen[41].

the reciprocal of the dielectric constant for a range of aqueous *t*-butyl alcohol solvents, and also correlated well with the solubility of *p*-chlorobenzenediazonium fluoroborate in the same solvents. This strong and well-understood solvent dependence emphasizes the problem of a substituent constant for a charged group and makes a direct comparison of the activation by N_2^+ with that of one or more nitro groups generally futile.

In the mostly aqueous systems usually studied, the diazonium group is, however, very powerfully activating by comparison with any other group or combination of groups. In this qualitative vein, we note that in the reaction of thiocyanate ion with *p*-nitrobenzenediazonium ion in aqueous *t*-butyl alcohol, the replacement of nitro is more important than that of the diazonium group[45], behaviour which it would be unreasonable to attribute to the nitro group being a better leaving group. A similar but even more striking observation is that 2,4,6-trinitrobenzenediazonium ion and related substances suffer hydrolysis (at sufficiently high pH) with loss of nitrite by attack on carbon *ortho* to one diazonium ion group, rather than losing nitrogen by attack on the carbon activated by as many as three nitro groups[46].

It is necessary to be careful about the nature of the mechanism involved in these substitutions. Thus in apparent contradiction to the results with thiocyanate, at higher temperatures *p*-nitrobenzenediazonium ion reacts with aqueous bromide ion to give a mixture of *p*-nitrophenol and *p*-nitrobromobenzene. No isolated product was assignable to nitro group loss[47]. This behaviour is now believed[36] to be associated with the acidity-independent solvolysis rather than to an activated nucleophilic attack. The perceptible acceleration[47] by bromide ion is not much greater than that observed with other diazonium salts, and has been explained[36] using transition states strongly resembling the phenyl cation (see footnote above). Thus there is no unequivocal evidence of nucleophilic substitution of N_2^+ activated by a nitro group. Substitution of N_2^+ activated by a second N_2^+ group is, however, well established and is discussed below.

E. Chemistry of Bisdiazonium Salts

It was mentioned in Section III.A that the very rich chemistry of aromatic diazonium salts nearly always involved destruction of the N_2^+ group, and could not therefore give information about the influence or substituent effect of this group. This statement has two exceptions. The first of these is that the reciprocal relation between ρ and σ first pointed out by Hine[48] has been developed by Sager and Ritchie[49] to the point that the measurement of ρ for a reaction is related to the change (in substituent effect) of the reaction site. Thus the rather extensive study of substituent effects on diazonium salt equilibria has been rendered understandable by using a large positive σ for the diazonium ion group[50]. The second is that for any reaction of the diazonium group, for example the conversion of N_2^+ to Y (equation 6), one of the possible substituents X is a second diazonium group. This

$$XC_6H_4N_2^+ \longrightarrow XC_6H_4Y \qquad (6)$$

allows a host of reactions to be studied, subject only to the limitation that only one of the two diazonium groups must react. This limitation is not very restrictive: of the three most accessible tetrazonium salts, tetrazotized *p*-phenylenediamine allows in nearly all cases the isolation of the reaction of one group only; tetrazotized *m*-phenylenediamine is complex[51] in its behaviour and has not been extensively studied, and tetrazotized benzidine is, in the dye industry, regularly coupled at one end before the other[52], and would therefore be suitable for quantitative study, although it has not yet been done.

Tetrazotized *p*-phenylenediamine is subject to nucleophilic displacement of one diazonium ion group by Cl^-, Br^- and SCN^-[53]; second-order kinetics are followed and the products, *p*-chlorobenzenediazonium ion, etc., are quite stable under the reaction conditions. Iodide ion also reacts, but a very fast free-radical mechanism is involved, and we can only say that the *p*-N_2^+ group accelerates the mechanism to allow it to be seen and to overwhelm nucleophilic attack. Azide ion also attacks very rapidly, but the mechanism probably does not involve carbon attack[54]. The powerful activating effect of the *p*-N_2^+ group is clearly illustrated, and the fact that N_2^+ can be a leaving group in an activated nucleophilic substitution is also demonstrated.

The tetrazonium salt is also convertible to a monodiazotate.[55] Because this is believed to have the *anti* configuration, the equilibrium is not readily compared to the literature values [56, 57] for equilibrium diazotate formation which involve the *syn* isomers. However, the protonation equilibrium between the monodiazotate and its conjugate acid is directly comparable to measurements of this reaction with other *anti*-diazotates. One determination gives[58] for this equilibrium $\rho = 1{\cdot}17$, another gives[59] $\rho = 1{\cdot}45$, and combining these with the measured equilibrium constant[55] give then for σ_p the values 2·0 and 1·6 respectively. This is in reasonable agreement with the substituted benzoic acid values presented above.

The facile 'dediazonization' or hydrolysis of the *p*-phenylene-bis diazonium salt[55, 60] is at first sight incompatible with the extreme electron-withdrawing character of the N_2^+ group, since electron-withdrawing substituents normally retard the rate of this phenol-forming reaction. However, the hydrolysis turns out to be pH dependent[55]. In fairly strong acidic media this special mechanism is suppressed and the tetrazonium salt now has the expected high stability.

The tetrazonium salt shows several very facile free radical reactions[61], notably reduction by alcohols, and it is clear (and not surprising) that the second diazonium group facilitates one-electron reduction of the first, although we have little to compare this with quantitatively, especially since in this reaction there is considerable net reduction of both diazonium groups. The details of chain initiation and termination proposed in this study of the alcohol reduction have been shown to be subject to a more reasonable interpretation by introducing a new termination mechanism[62].

Finally, we should interpret again the rather low σ (1·3) derived from the rate of coupling of the tetrazonium salt with 2-aminonaphthalene-6-sulphonic acid[28], based upon the value of ρ for this coupling of $+4{\cdot}26$ [63]. Some coupling rates of diazonium salts with various compounds have given curved Hammett plots[64], and this deviation may correspond to the predicted concave downward shape of sufficiently wide-range Hammett plots[65]. The deviation may also arise from a shift of rate-determining step in this known two-step reaction[66].

IV. CONCLUSIONS

The effect of the diazo group as a substituent has been shown to be not very large and of ambiguous direction, since it is both acid strengthening and base strengthening. The effects have not been detected except very close to the diazo group.

The effect of the diazonium ion group is quantitatively established, it has a very strong acid-strengthening, electron-withdrawing effect. It is, by virtue of its charge, a substituent with a strong solvent dependence of its substituent effect and one can therefore imagine some effects of unprecedented magnitude, but even in water it has more influence than any other known substituent.

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