
PYRAZOLONES, PYRAZOLIDONES, AND DERIVATIVES

Richard H. Wiley

University of Louisville, Louisville, Kentucky

Paul Wiley

Upjohn Laboratories, Kalamazoo, Michigan

1964

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**PYRAZOLONES, PYRAZOLIDONES,
AND DERIVATIVES**

This is the twentieth volume in the series

THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

A SERIES OF MONOGRAPHS

ARNOLD WEISSBERGER, *Consulting Editor*



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The Chemistry of Heterocyclic Compounds

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

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

ARNOLD WEISSBERGER

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Rochester, New York*

Preface

Perhaps one of the most unusual facets of pyrazole chemistry is the extensive literature on the pyrazolin-5-ones. Although this will probably come as no surprise to those who have had any interest in this class of compounds, the basic chemical reasons underlying this extensive literature, and the man-hours of chemical research which have gone into producing it, deserve careful consideration. There are very real practical and theoretical bases for the situation.

Historically, dyes and pharmaceuticals derived from pyrazolin-5-ones were among the first successful commercial synthetic organic chemicals in which interest has continued actively until the present. Ludwig Knorr's discovery in 1883 of antipyrine (2,3-dimethyl-1-phenyl-3-pyrazolin-5-one) and Ziegler's discovery in 1884 of the yellow dyestuff tartrazine: 4-(4-sulfophenylazo)-1-(4-sulfophenyl)-5-oxo-2-pyrazolin-3-carboxylic acid gave useful compounds before their structures were known. The value of these materials was immediately recognized and both are still in use. Much of the voluminous literature has resulted from studies directed toward modification of these structures to enhance their useful characteristics. A group of widely used pharmaceuticals including aminopyrine (4-dimethylamino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one); dipyrone (2,3-dimethyl-1-phenyl-5-oxo-2-pyrazolin-4-methylaminomethanesulfonic acid sodium salt); and sulfamipyrene (a dipyrone analog) were developed. This research has recently culminated in the discovery of the useful anti-inflammatory properties of phenylbutazone (4-butyl-1,2-diphenyl-3,5-pyrazolidinedione). In spite of the problems encountered in the undesirable side-reactions, principally agranulocytosis, produced by these drugs, interest in them has never abated and one feels confident in predicting the discovery of additional useful and improved drugs in this structural classification.

The development of new and improved dyes based on pyrazolinone structures has likewise led to modern developments of no inconsiderable magnitude. The use of tartrazine as an approved color for foodstuffs is of significance. The development of pyrazolinone dyes for use as magenta couplers and sensitizers in color photography and in metal chelate dye structures has established a renewed, modern interest in these dyes. The chelating characteristics, which will be of continuing theoretical structure interest in coordination chemistry, have been used in developing picrolonates (salts of 3-methyl-4-nitro-1-*p*-nitrophenyl-2-pyrazolin-5-one) of possible utility in analytical procedures.

The overwhelming deluge of chemical research arising from these utilitarian values has probably obscured the possibilities for fundamental research with these compounds. For the most part the structural problems that have been encountered are not complex. This is probably due in part to the fact that modern organic reaction techniques, such as radiation-induced transformations, modern structural concepts, such as molecular orbital theory and conformational analysis, and modern physical instrumentation, such as n.m.r., have not as yet been applied to the possibilities inherent in the chemistry of these compounds. It is also perhaps unusual that no pyrazolinone has been found to occur in nature. With the discovery in 1959 of β -(1-pyrazolyl)alanine in the seeds of *Citrullus vulgaris*, it would now appear probable that a pyrazolinone may likewise be found in some living tissue. This would certainly provide a new type of fundamental interest in the bio-organic chemistry of these materials. It might lead ultimately to a clue as to the mode of action of the pharmaceuticals—a problem about which there appears to be little or no current available information.

With the hope that the availability of the information on pyrazolinones presented in this volume might be of value in the furtherance of both fundamental and applied studies, the publishers and authors have considered it best to present this material as promptly as possible in the present volume rather than as part of the pyrazole volume for which it was originally intended. The authors are appreciative of this cooperation on the part of the publishers and it is hoped that users of this book will be aware that the immensity and sheer bulk of the literature has posed an unusual, but altogether interesting, challenge to all concerned in the preparation of this volume. The authors also wish especially to thank Miss Ollidene Weaver who did much of the typing of the manuscript in her spare time.

RICHARD H. WILEY
PAUL WILEY

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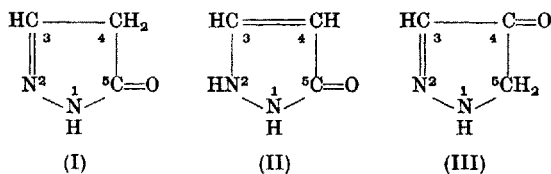
PART I
CHEMISTRY

CHAPTER I

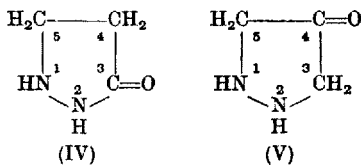
General

1. Introduction

Pyrazolinones and pyrazolidinones are oxo derivatives of pyrazolines and pyrazolidines, respectively, and are so named in *Chemical Abstracts* at present. However, the usual method of naming in the earlier literature is the pyrazolone-pyrazolidone system. Although a large number of tautomeric structures are possible for pyrazolinones, the usual assignment of ring structures is as shown in (I), (II) and (III). The *Chemical Abstracts* names for these are: (I) 2-pyrazolin-5-one, (II)



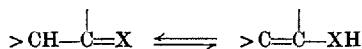
3-pyrazolin-5-one and (III) 2-pyrazolin-4-one. The names most frequently used in the literature for (I) and (II) are 5-pyrazolone and 3-pyrazolone, respectively. In many cases there has been no certain identification of a compound as a 2-pyrazolin-5-one or a 3-pyrazolin-5-one. Because of this it will be assumed that all pyrazolin-5-ones having no substituent at N-2 are 2-pyrazolin-5-ones unless this has been definitely shown to be incorrect. The basic ring structures for pyrazolidinones are (IV) and (V) but no compounds of type (V) have been



reported. Compounds of type (IV) are usually called pyrazolidones in the literature.

The nomenclature used in this discussion will generally be in accordance with *Chemical Abstracts*, although some trivial names will be used since these are very common among pyrazolinones and are frequently well known. Examples of such names are antipyrine, pyrazole blue and aminopyrine. The numbering is as shown in formulas (I)–(V).

As an aid to classification all compounds in which the tautomerism



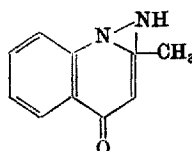
can theoretically exist will be considered as $>\text{CH}-\overset{\overset{|}{\text{C}}}{\text{=X}}$ compounds (X=O, S, Se, Te, NH, NR or NCOR). It is recognized that this will frequently be in disagreement with the actual structure which, if known, will be indicated in the discussion.

This review will cover all pyrazolinones and pyrazolidinones reported up to and including the 1956 *Chemical Abstracts* and will cover the more important publications which have appeared since. However, a number of publications dealing with applications, biological activities and analysis were omitted as they were regarded as being of insufficient significance for coverage. A rather extensive list of the compounds of these types which have been reported is included, although here again there are many omissions. A number of dyes were not included as their structure was uncertain. Some very complex dyes which would require considerable space for inclusion are omitted and a reference to them is given. In general, the large number of salts reported were not included and in particular all picrolonates were omitted. However, many of the complexes which pyrazolin-5-ones form so readily are discussed, although in some cases these may be of a salt-like nature. Compounds in which the oxo substituents are replaced by such groups as imino, thiono and seleno are considered in this review. The early literature, which is available from standard sources (Beilstein, Meyer-Jacobson) has not been exhaustively compiled.

2. Historical

The well-known German chemist, Ludwig Knorr, reported the preparation of the first pyrazolinone in 1883.⁸⁰⁵ This compound was 3-methyl-1-phenyl-2-pyrazolin-5-one prepared by the reaction of ethyl acetoacetate with phenylhydrazine. In the first publication no structure was proposed, but in a later publication⁸⁰⁶ structure (VI) was suggested.

In this same article synthesis of the widely used analgesic and antipyretic, antipyrine, was reported. This was one of the first synthetic

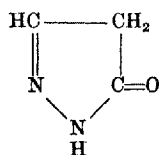


(VI)

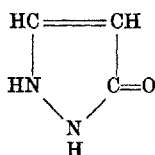
organic drugs. It was marketed and used before the correct structure for pyrazolinones was suggested by Knorr⁸⁰⁹ in 1887 and the name by Ruhemann.¹²³⁰

3. Structure

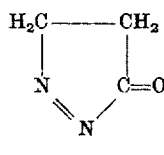
A short time after the discovery of pyrazolin-5-ones Knorr⁸⁰⁹ proposed the 2-pyrazolin-5-one and the 3-pyrazolin-5-one structures on the basis of analyses, methods of preparation and reactions. These structures in the main approximate the correct ones and in some cases are correct. However, a large number of structures are theoretically possible for most pyrazolin-5-ones and in many cases no one structure can be said to fit completely. The tautomeric isomers (VII)–(XIII) are possible for unsubstituted pyrazolin-5-ones:



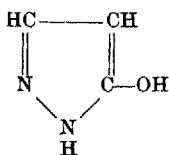
(VII)



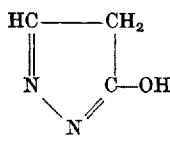
(VIII)



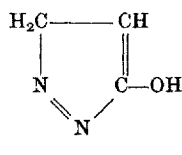
(IX)



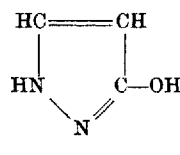
(X)



(XI)



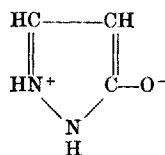
(XII)



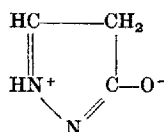
(XIII)

In addition a number of ionic tautomeric isomers can be envisaged which could make very important contributions to the over-all structure. These are (XIV)–(XVIII). Substitutions at N-1, N-2 and disubstitution at C-4 substantially alter the possibilities for various tautomeric

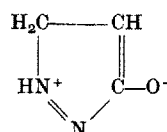
and resonance forms. Of the possible tautomeric forms shown, only (VII), (VIII) and (X) appear to exist to any extent although Valyashko



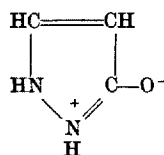
(XIV)



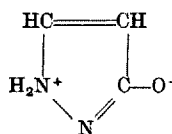
(XV)



(XVI)



(XVII)



(XVIII)

and Bliznykov¹⁵¹⁰ report diazo structures as present on the basis of rather complex ultraviolet absorption spectra. There is extensive evidence, both chemical and physical for these three structures. The presence of enolic forms is shown by the fact that one of the most common tests for 2-pyrazolin-5-ones is the use of ferric chloride to form a colored complex^{809, 1551} and by the ready formation of 5-alkoxy-pyrazoles from pyrazolinones.^{655, 811} Dmowska and St. Weil³⁷⁶ have claimed the isolation of the keto and enol forms of 4,4'-(3-nitrobenzylidene)bis(3-methyl-1-phenyl-2-pyrazolin-5-one) and keto and enol forms of similar compounds have been isolated.^{1134, 1135} Existence of the form (VIII) is shown by alkylation of 3-phenyl-2-pyrazolin-5-one to give 2-methyl-3-phenyl-3-pyrazolin-5-one.⁵⁴

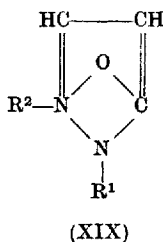
The structures of pyrazolin-5-ones have been very extensively studied using ultraviolet and infrared absorption spectra and such techniques have established unequivocally that (VII), (VIII) and (X) are the chief tautomeric contributors. Most of the workers in this field have emphasized the complexity of ultraviolet spectra due to the existence of tautomeric mixtures. Gomez⁵⁸⁴ has stated that no deduction can be drawn from the ultraviolet spectra of 1-methyl-3-phenyl-2-pyrazolin-5-one, 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one and its 4-dimethylamino analog because of the tautomeric equilibria present. The existence of an equilibrium between 2-pyrazolin-5-one and 3-pyrazolin-5-one structures has been proposed by Biquard and Grammaticakis⁹⁵ for 3-alkyl-1-aryl- and 1-aryl-3,4-dialkyl-2-pyrazolin-5-ones on the basis of ultraviolet absorptions. Gagnon and co-workers^{503, 505}

have been most active in this field and have drawn several conclusions from ultraviolet studies, some of which were in disagreement with infrared absorption spectra interpretations. These workers have found that pyrazolin-5-ones absorb ultraviolet light either in the neighborhood of 240–260 m μ with a log ϵ value of 4.0–4.4 or at 295–325 m μ with a log ϵ value of 3.3–4.0, or in both regions. The shorter wave length absorption is believed to be due to $>C=C<$ absorption while the longer is due to $>C=N-$. Thus type (VII) would show the longer wave length absorption, type (VIII) the shorter, and type (X) both, or a mixture of any two would show absorption at both wave lengths. 4-Alkyl-3-aryl-2-pyrazolin-5-ones absorb at the lower wave length only, indicating that they possess only structure (VIII). However, this conclusion was in disagreement with the finding that these compounds exhibited absorption in the infrared at 1600 cm.⁻¹ due to $>C=N-$ and at 3300 cm.⁻¹⁵⁰⁵ and showed no absorption attributable to carbonyl. Thus they must actually be of type (X). From the ultraviolet spectra 4-alkyl-1,3-diaryl-2-pyrazolin-5-ones were concluded to be a mixture of types, but the infrared spectra very clearly showed them to be type (VII) as there was only carbonyl and $>C=N-$ absorption. It would appear that the 1-arylpyrazolin-5-ones with no N-2 substituent are usually of type (VII), since Glauert and Mann⁵⁷⁸ found no imino or hydroxyl absorption in the infrared spectra of 1,4-diaryl-2-pyrazolin-5-ones. Recently^{366a} the infrared spectra of 3-methyl-, 3-trifluoromethyl-, 1,3-dimethyl-, 1-methyl-3-trifluoromethyl- and 1-phenyl-3-trifluoromethyl-2-pyrazolin-5-one have been studied. The presence of absorption bands at 2400–2700 cm.⁻¹ believed due to zwitterionic forms indicated that these compounds exist largely as form (XIV).

The effect of substitution on the structure of pyrazolinones is a very important one, because certain of the tautomeric forms then become impossible. For example, substitution at N-1 allows only structures (VII), (VIII) and (X). Substitution at N-2 would make (VIII) and (XIII) the only possible tautomers. A combination of N-1 and N-2 substitution leaves (VIII) as the only possibility. If there is substitution at N-1 and disubstitution at C-4, then only isomer (VII) is possible. There has been little investigation of the possibilities for tautomeric structures of N-2 substituted pyrazolinones. However, Kitamura⁷⁸⁸ has suggested that such compounds exist as a mixture of forms (VIII) and (XIII).

There has been considerable discussion of the situation in regard to the ionic structures. About fifty years ago Michaelis^{978, 983, 984, 1002, 1003} proposed (XIX) as the structure for 1,2-disubstituted pyrazolinones. In modern terminology this could correspond to structure (XIV).

Komada⁸⁴⁴⁻⁸⁴⁶ recently has used this structure to explain the structure of the tetrabromides of this type of pyrazolinones. Kitamura⁷⁸⁸



has used rather inconclusive chemical evidence in support of the existence of 3-pyrazolin-5-ones in form (XVII). Somewhat better evidence for the structural contributions of these resonance forms has been given in the form of dipole moments, ultraviolet data and bond lengths. Jensen and Friedinger⁷¹⁵ and Brown *et al.*²⁴⁵ have found abnormally high dipole moments for 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one and its thiono analog. This was considered to be due to contributions by forms (XIV) and (XVII) to the extent of about 35 per cent. A structure analogous to (XVII) has been proposed for 2-pyrazolin-5-thiones also on the basis of dipole moments.⁹³⁴ Valyashko and Bliznykov¹⁵⁰⁹ have found that 4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-ones have ultraviolet spectra very similar to that of 5-chloro-3-methyl-1-phenyl-pyrazole methochloride, indicating a considerable contribution by form (XIV). Krohs⁸⁶⁰ has demonstrated a considerable contribution from the carbonyl form, as shown by infrared absorption in the carbonyl region. This has been confirmed by other infrared studies, and it has been proposed on the basis of this that form (VIII) is the predominating one in some cases.^{366a} Romain¹²⁰⁸ has studied the bond lengths in 4-bromo-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one. These bond lengths indicate a resonance hybrid structure composed of forms (VIII) and (XIV) with some contribution from (XVII).

Chattaway and co-workers^{287-290, 294} have synthesized a number of 1-aryl-2-pyrazolin-4-ones which, as a rule, have been considered to have the 4-hydroxypyrazole structures. However, some of these must have the 2-pyrazolin-4-one structure due to disubstitution at C-5. Emerson and Beegle⁴²⁵ have synthesized some 2-pyrazolin-4-ones unsubstituted at N-1 permitting more possibilities for isomerism. These will be discussed later.

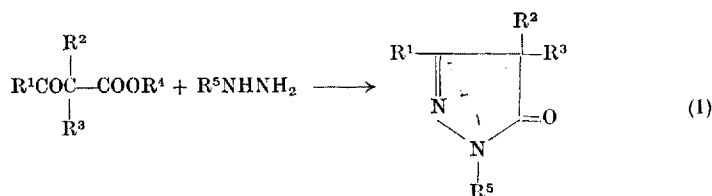
The pyrazolidinones (IV) present a number of possibilities for structural isomerism, but very little study of their structure has been made. It is generally assumed that they have the classical form (IV).

Certainly they would not be expected to have the tendency of 2-pyrazolin-5-ones to enolize, since they could not achieve an aromatic-like structure.

4. Synthesis

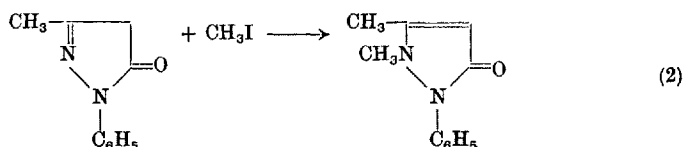
Only a few of the principal synthetic methods for pyrazolinones and pyrazolidinones will be discussed at this point. Other methods will be mentioned in connection with various classes of compounds. The procedures mentioned here will be discussed in greater detail at the appropriate places.

By far the most widely used synthesis for 2-pyrazolin-5-ones is the condensation of a β -ketoester with a hydrazine (eq. 1).^{6, 11, 64, 269, 303, 805}

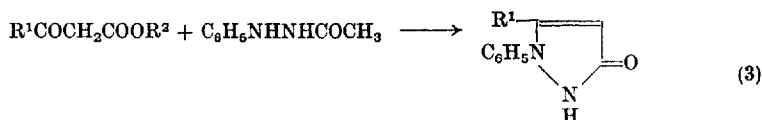


The R groups in this reaction can be almost anything, H, alkyl, aralkyl, aryl, heterocyclic and many others. Modifications of this procedure have employed β -thionoesters,^{1006, 1008} β -oximinoesters¹⁵⁵⁵ and β -ketoamides.^{99, 197, 1276}

Perhaps the most common procedure for preparing 3-pyrazolin-5-ones is alkylation of a 2-pyrazolin-5-one at N-2 as shown for the synthesis of antipyrine (eq. 2).⁸⁰⁶ Other alkylating agents such as dimethyl

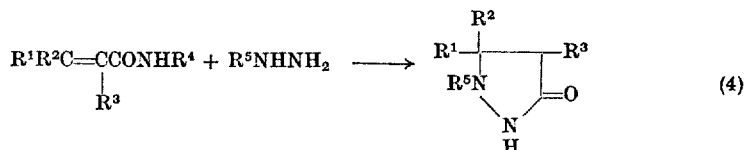


sulfate⁷⁸¹ can be used, and almost any 2-pyrazolin-5-one can be alkylated, although frequently *O*-alkylation occurs and also alkylation at N-1 if it has no substituent. Another useful synthesis of 3-pyrazolin-5-ones is the condensation of a β -ketoester with acetylphenylhydrazine (eq. 3). The acetyl group is lost and the phenyl group appears at

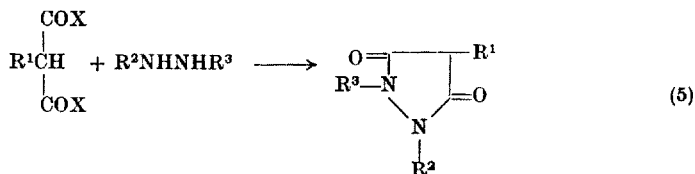


N-2.^{984, 988, 993} A modification of this consists of using a symmetrically substituted hydrazine to give 1,2-disubstituted-3-pyrazolin-5-ones.⁵⁴

The synthesis of pyrazolidinones is readily achieved by condensation of an α,β -unsaturated acid,¹⁵⁵⁰ ester^{1209, 1569} or amide⁷⁵⁸ with a hydrazine. In eq. 4 is shown the reaction for an amide.



The reaction of a malonic ester or chloride with hydrazines gives 3,5-pyrazolidinediones (eq. 5).^{188, 222, 248, 252, 1234}



5. Physical Properties

Most pyrazolinones and pyrazolidinones are solids, although many, some very complex, can be distilled as high-boiling liquids. 2-Pyrazolin-5-one is a liquid boiling at 163°. Reduction of the $>\text{C}=\text{N}-$ lowers this to 132°. Substitution on N-1 and N-2 gives a low-melting solid. However, substitution at C-3 or C-4 has a more pronounced effect, as for example in 3-methyl-2-pyrazolin-5-one, which melts at 215°. Alkyl substitution in pyrazolidinones does not have such a marked effect but does raise boiling and melting points. Almost all aryl substituted pyrazolinones and pyrazolidinones are solids, but many can be distilled.

The solubility of pyrazolinones and pyrazolidinones is so varied as to make generalizations of little value. The simpler ones, of lower molecular weight, are soluble in hot water and a few are even soluble in cold water. Almost all are soluble in polar organic solvents and many are soluble in ether and benzene. However, most are insoluble in petroleum ether.

Ultraviolet and infrared spectra have been considered in some detail in the section dealing with structure. Concerning the ultraviolet spectra it can be stated that, while there is considerable absorption by pyrazolinones and some pyrazolidinones, these absorptions are so complex, owing to tautomerism, that little can be deduced from them.

The infrared spectra are as would be expected. In some cases there are clear bands due to carbonyl and $>C=N-$ and in others the carbonyl band is missing but hydroxyl bands are present. Raman spectra of antipyrine and aminopyrine have been investigated.^{273, 1167}

Dipole moments have already been discussed in the section dealing with structure. They have been found to be quite high for the few 3-pyrazolin-5-ones studied. The only value reported for a 2-pyrazolin-5-one is considerably lower, being 2.54 for 3-methyl-2-pyrazolin-5-one.

A number of miscellaneous physical properties of antipyrine and a few of its derivatives have been studied. These are listed with references in Table I.

TABLE I. Physical Properties of Antipyrine Investigated

Physical Property	Reference
Crystal Form	844
Dielectric Constant	367
Dielectric Coefficient	367
Heat Capacity	1466
Latent Heat	668
Phase Diagram	669
Surface Activity	561

6. Chemical Properties

Only a few of the more important chemical properties of pyrazolinones and pyrazolidinones will be discussed in this section, since these will be covered more thoroughly in connection with the different classes.

The pyrazolinones are in general weak acids⁸⁰⁵ and many can be titrated with strong bases. The 2-pyrazolin-5-ones are stronger acids than the 3-pyrazolin-5-ones¹⁵²³ which are very weak. Most pyrazolinones are readily soluble in bases. The pyrazolidinones are not acidic, unless some special feature makes them so. The most extensive data on basicity have been provided by Veibel and co-workers^{1521, 1522, 1525} who have titrated a number of pyrazolinones with perchloric acid in acetic acid. The pK_b values range from 10.3 to 12.3, except for 4,4-disubstituted and 4-halogen substituted 2-pyrazolin-5-ones. The 4,4-disubstituted 2-pyrazolin-5-ones are so weak that they are essentially neutral, while the halogenated compounds have pK_b values of about 13.2.

Both 2-pyrazolin-5-ones and 3-pyrazolin-5-ones undergo substitution at C-4 in an aromatic fashion. Halogenation, nitration and coupling with diazonium salts occur readily. In 2-pyrazolin-5-ones such reactions

as condensation with aldehydes and ketones and alkylations occur readily at C-4. The pyrazolinone and pyrazolidinone rings do not have aromatic stability, although in many cases they can assume an aromatic-like structure. The ring is readily destroyed by acid or base hydrolysis and by oxidation. Pyrazolidinones react very much as do aliphatic hydrazides.

CHAPTER II

Pyrazolin-5-ones

1. Introduction

The pyrazolin-5-ones are classified and discussed according to their functional groups. Compounds having more than one pyrazolinone ring will be classified similarly to the monocyclic ones and discussed in the same section. All compounds which can theoretically assume the 2-pyrazolin-5-one structure, except those classified as 3,5-pyrazolidine-dione derivatives will be considered to be such. Only those for which this is impossible, i.e. 2-substituted pyrazolin-5-ones, will be considered 3-pyrazolin-5-ones. A number of compounds having no functional group on the pyrazolinone ring, which have been synthesized for study as coloring agents are listed in connection with the discussion of pyrazolinones used in photography. A number of very complex compounds of similar type are not included in this review, but references to them are given in the dye section. All compounds having no functional group attached to the pyrazolinone ring will be considered in the section dealing with alkyl, alicyclic, aralkyl, aryl and heterocyclic substituted pyrazolin-5-ones. All oximes are classified as nitroso compounds unless it is manifestly impossible to do so as in a case having the substituent =NOR. This would be listed in the section concerning amino-2-pyrazolin-5-ones. The 5-iminopyrazolines and the aminopyrazoles which in this discussion are classified as 5-iminopyrazolines are considered with the 2-pyrazolin-5-ones appropriate to their substitution, as are the 2-pyrazolin-5-thiones.

2. Unsubstituted Alkyl, Alicyclic, Aralkyl, Aryl and Heterocyclic Substituted Derivatives

A. 2-Pyrazolin-5-ones

(1) *Syntheses*

Syntheses of the 2-pyrazolin-5-one ring will be discussed in this section. Those syntheses of this class which depend upon introduction

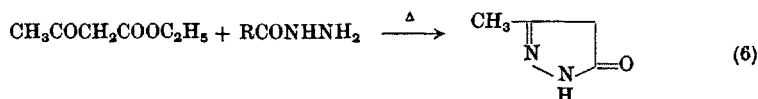
of a substituent into the already formed ring will be discussed under reactions. Compounds of this type are listed in Table II (see Appendix).

Methods for synthesis of 2-pyrazolin-5-ones are extremely numerous but the one most frequently used is that shown in eq. 1, the condensation of a β -aldehyde- or β -keto-ester with a hydrazine. The substituents on the ester and the hydrazine have been greatly varied. All types of alkyl, alicyclic, aralkyl, aryl and heterocyclic substituted esters have been used. In general the yields are the better the smaller the substituents R^2 , R^3 and R^4 . In the case in which R^2 and R^3 are benzyl, pyrazolinone formation does not occur when R^4 is phenyl.⁶⁴⁹ Also, if R^2 and R^3 are aryl, pyrazolinone formation fails. When R^3 is larger than methyl, formation of pyrazolinones is more difficult, although many more complex esters having one α -substituent or none have been used.⁶²⁹ Ethyl α,α -diethylacetoacetate does not form a pyrazolinone with hydrazine hydrate, but the corresponding methyl ester does.⁶¹ R^1 may be hydrogen, in which case the ester would be a β -aldehyde-ester,^{303, 813, 1636} or it may be alkyl,^{42, 53, 61, 97, 135, 572, 805, 1582} aryl,^{54, 469, 505} heterocyclic,^{10, 307, 682} alicyclic,²⁷⁴ or of other types.¹²⁴ It has been reported that cyclization of benzoylacetic esters to pyrazolinones is easier than is that of acetoacetic esters.⁷⁷⁷ Almost any monosubstituted hydrazine can be used to prepare a pyrazolinone. The simpler the substituent the better the yield usually is,⁵⁰⁵ though alkyl,^{250, 788} alicyclic,¹⁰¹ aralkyl,²⁵⁰ aryl^{25, 136, 229, 1251} and heterocyclic^{74, 91, 413, 833} hydrazines have been successfully employed. The conditions used in condensing β -ketoesters and hydrazines to form pyrazolinones are quite varied. The most widely used method is simply heating the ester and the hydrazine together without added catalysts. The temperatures used are most frequently 100–200°.^{250, 505, 805} Quite frequently the hydrazine is condensed with the ketoester to form a hydrazone under milder conditions than are used in the final cyclization step.⁵⁰⁵ A modification of this is to use an already prepared hydrazone.^{1100, 1490} Acidic^{25, 1372} and basic conditions are frequently used, particularly in the cyclization step. Under favorable circumstances the yields are very good. Gagnon and co-workers⁵⁰⁵ have prepared a series of 4-alkyl-3-phenyl-2-pyrazolin-5-ones in yields of 83–96 per cent, although yields of corresponding 1-phenyl compounds were much lower, varying from 50 to 81 per cent.

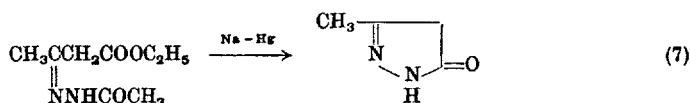
In summarizing this method of synthesis it can be said that it is so extremely general that almost any non-substituted or monosubstituted β -ketoester will react with almost any monosubstituted hydrazine to form a 2-pyrazolin-5-one.

A number of modifications of the β -ketoester-hydrazine synthesis

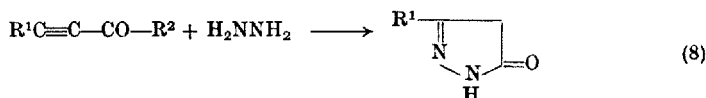
of pyrazolinones has been used. One of these modifications is the use of acid hydrazides (eq. 6).^{6, 96, 360} Under mild conditions the pyrazolinone



obtained has the acyl substituent on N-1, but at temperatures of 25° to 100° this substituent is lost. In addition to β -ketoesters, the corresponding amides and anilides have been employed in a number of cases^{197, 378, 872, 1030, 1276} under very similar conditions. The amides may or may not be substituted on the nitrogen atom. Mitra^{1008, 1007} has reported the use of β -thionoacetoacetates instead of acetoacetic esters to form pyrazolinones. The use of β -ketoesters in which R¹ or R² of eq. 1 is CH₃CO or C₂H₅OOC^{165, 358} gives pyrazolinones with elimination of the acyl substituent. A further modification of this synthesis is shown in eq. 7.

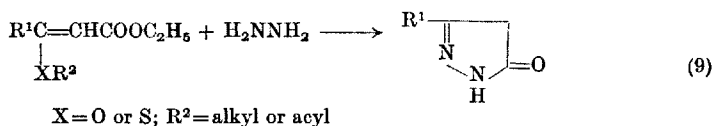


A number of syntheses of 2-pyrazolin-5-ones depend on the reaction of compounds, other than β -ketoesters, substituted in the β -position or of α,β -unsaturated acids, esters and amides. The most frequently used unsaturated compounds are those having a triple bond in the α,β -position.^{1023, 1024, 1075, 1548, 1680} R² can be HO,¹⁵⁵² RO^{1023, 1024, 1686} or H₂N (eq. 8).^{1023, 1024} A similar reaction is the condensation of ethyl

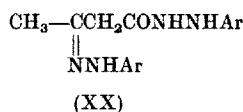


α -chlorocinnamate with hydrazine to give 3-phenyl-2-pyrazolin-5-one.⁶¹⁰ This probably goes through an acetylenic intermediate. The condensation of methyl crotonate, isocrotonic esters and methyl methacrylate with hydrazines gives as a side-product small yields of 2-pyrazolin-5-ones, the main products being pyrazolidinones.^{479, 1569} The pyrazolidinones are probably dehydrogenated to a slight extent to give the pyrazolinones. The reaction of β -alkoxy- α,β -unsaturated esters^{1023, 1024} and β -alkylthio- and β -acylthio- α,β -unsaturated esters¹⁰⁰⁷ with hydrazines to give pyrazolinones (eq. 9) proceeds quite readily. The

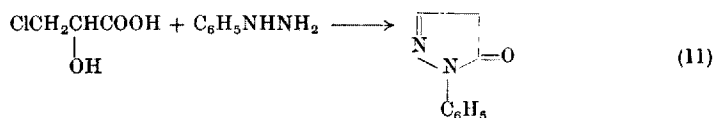
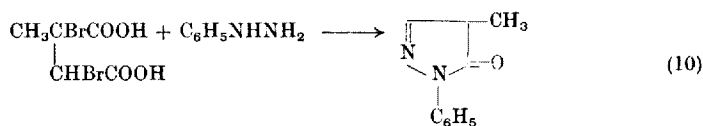
reaction of ketene with arylhydrazines forms 2-pyrazolin-5-ones.^{723, 885}



The first product formed is the hydrazone of the corresponding acetoacethydrazide (XX). This then cyclizes to the desired product at ele-

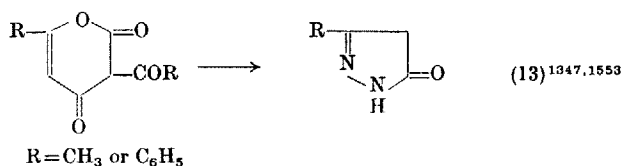
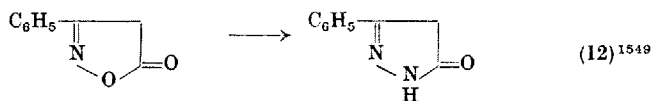


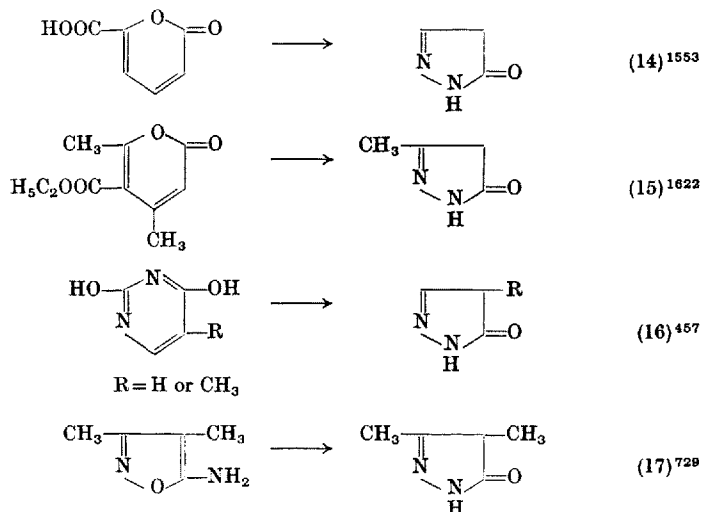
vated temperatures. The reaction of phenylhydrazine with β -halogenated acids to give pyrazolinones as shown in eqs. 10 and 11 has been reported.^{446, 858} These reactions probably occur by removal of water



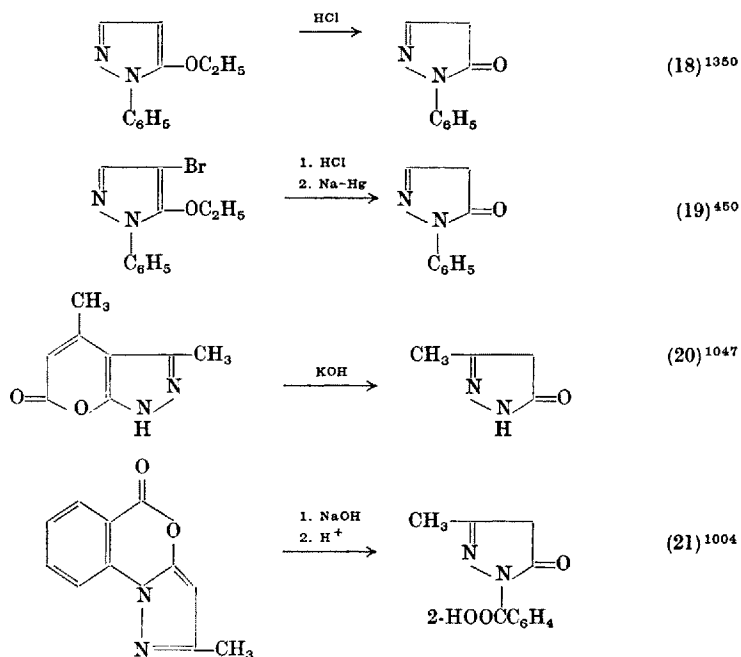
or hydrogen bromide to give an unsaturated intermediate. It has been shown that such an intermediate, methyl β -chloroisocrotonate, reacts with hydrazine hydrate to give 3-methyl-2-pyrazolin-5-one.⁴⁷⁹

A number of heterocyclic systems react with hydrazine to give pyrazolinones. These are shown in eqs. 12-17 and are of little synthetic utility.

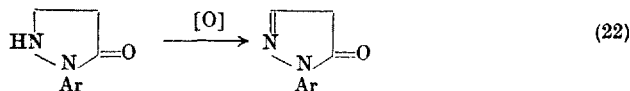




Various pyrazole systems having appropriate substituents in the 5-position can be converted into pyrazolinones. The most frequently used synthesis of this type is hydrolysis of 5-alkoxypyrazoles which is shown with others in eqs. 18-21.

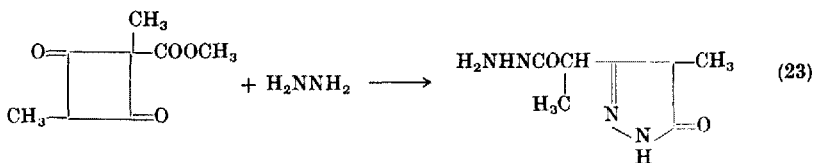


The oxidation of 2-arylpyrazolidinones (eq. 22) to pyrazolinones occurs readily and yields as high as 95 per cent have been reported.⁶⁸ The reagents used were ferric chloride,^{68,1351} bromine^{816,1569} or calcium hypochlorite.¹⁵⁶⁹



The decarboxylation of 5-oxo-2-pyrazolin-3- and 4-carboxylic acids has been used frequently to prepare 2-pyrazolin-5-ones. In the case of the 4-carboxylic acids decarboxylation usually occurs in boiling water.^{308,532,1228,1230} The 3-carboxylic acids decarboxylate by pyrolysis, at somewhat higher temperatures, or by heating with sodium carbonate or calcium carbonate.^{508,1544,1546}

A rather unusual synthesis of pyrazolinones from a cyclobutane



derivative has been reported (eq. 23).¹²⁷⁷ This probably involves cleavage of the 1,3-dione to a β -ketohydrazide which cyclizes.

(2) Physical Properties

The 2-pyrazolin-5-ones are almost all solids, but a few are liquids. Their melting points vary a great deal and many melt with decomposition although some are sufficiently thermally stable to be distilled at temperatures above 200°. For many, more than one melting point has been reported and it is usually impossible to decide from the published data which is the correct one.

The solubilities of these compounds vary greatly, but in general they are insoluble in nonpolar solvents and soluble in polar ones and frequently can be crystallized from hot water.

Both acidic and basic properties are possessed by 2-pyrazolin-5-ones.⁸⁰⁷ They dissolve readily in ammonia and sodium carbonate solutions. The $\text{p}K_a$ values reported⁵⁰⁵ are 6.2–11.0, compounds unsubstituted at N-1 being somewhat stronger acids than are those

substituted at N-1. Veibel and co-workers^{1522,1524} have reported that 2-pyrazolin-5-ones have pK_b values of 10–13, indicating very weak basicity. Only those compounds which can assume the betaine form shown in (XIV) (p. 6) can be titrated with acid. No basic properties are shown by those compounds in which disubstitution at C-4 precludes the existence of this form.

A number of studies of ultraviolet and infrared absorption spectra of 2-pyrazolin-5-ones have been made.^{95,505,506,578} The ultraviolet spectra show maxima in the neighborhood of 250 $m\mu$ with $\log \epsilon$ values of 4.10–4.40 and at about 310 $m\mu$ with $\log \epsilon$ values of 3.90, or in both of these regions of the spectrum. The shorter wave length absorption is attributed to the presence of $>C=N-$ and the longer wave length absorption to $>C=C<$. Infrared absorption occurs at 1600 $cm.^{-1}$ in all cases owing to the $>C=N-$ absorption and either at 3300 $cm.^{-1}$ for compounds existing in the enol form, or at 1700–1710 $cm.^{-1}$ for compounds having the carbonyl form. From the spectral data it has been concluded that 2-pyrazolin-5-ones having aryl substitution at N-1 generally exist in the oxo forms (VII) and (VIII) (p. 5) unless substitution prevents formation of the (VIII) type. If N-1 is unsubstituted, the form (X) predominates. However, recently de Stevens and co-workers^{366a} have reported somewhat different findings for infrared spectra of 2-pyrazolin-5-ones having H, alkyl and aryl at N-1 and alkyl groups at C-3. Their results led them to suggest the form (XIV) as the principal one for these compounds.

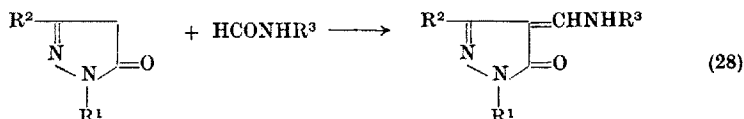
A study of the absorption of 2-pyrazolin-5-ones by silver bromide has been made by Stolyarova and Chel'tsov.¹³⁴⁸ These workers found that there was absorption of a unimolecular layer of pyrazolinones with the heterocyclic rings parallel to the absorbent surface.

(3) Chemical Properties

The most outstanding chemical property of 2-pyrazolin-5-ones is the activity of the hydrogen atoms at C-4. This position is very reactive, undergoing the characteristic condensations and substitutions of the active methylene group. Aldehydes and ketones react readily at this position, giving in the simpler cases a mixture of products as shown in eq. 24.^{22,34,110,296,311,333,633,702,809,980,1123,1241,1250,1263,1288,1351} This type of reaction is generally true of aldehydes, but in the case of ketones where one R is aryl only the monopyrazolinone product is obtained.¹¹²⁸ Some more active aldehydes such as formaldehyde²⁴ and chloral^{107,895} do not eliminate water but form, as one of the products, a hydroxyalkyl

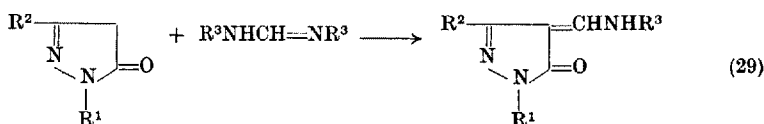
which have been most frequently condensed with 2-pyrazolin-5-ones have been aromatic ones and a very large number of these have been used.

Ridi and Checchi^{1188, 1189} have studied the condensation of formamides with 2-pyrazolin-5-ones. This condensation occurs at a temperature of 160–200° and appears to be an aldol condensation followed by dehydration (eq. 28). R¹ may be hydrogen, alkyl or aryl, while R²

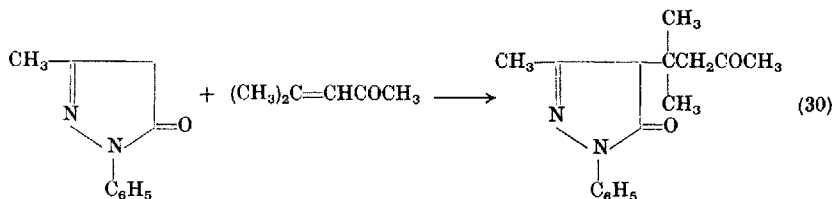


has been only alkyl and aryl. R³ has been either hydrogen or aryl. Acetamide and other amides also react in this way with 2-pyrazolin-5-ones.^{1188, 1192, 1193} The compounds synthesized in this manner are shown in Table II, Section G. It is not completely certain that the 4-substituent is as shown in eq. 28. It may be the isomeric form, R³N=CH. One of the products frequently obtained in this reaction is a 4,4'-methylidynbispyrazolinone, formed by the reaction of the first product with the starting material with elimination of ammonia or an amine.

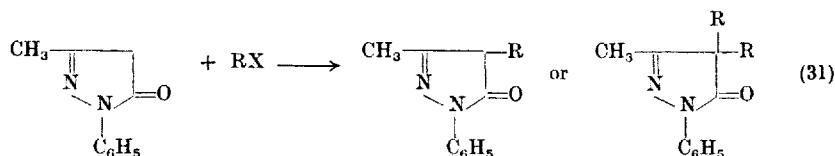
A reaction analogous to the condensation of amides with 2-pyrazolin-5-ones is the reaction of amidines first reported by Dains (eq. 29).^{348, 349} This has been extended by Ogata, Tauno and Nishida¹⁰⁷⁰ to vinylogs of amidines of the type C₆H₅NH(CH=CH)₂CH=NC₆H₅.



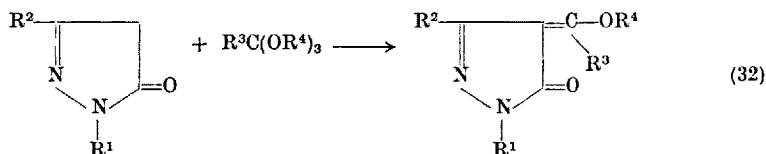
If α,β -unsaturated ketones are condensed with 2-pyrazolin-5-ones the reaction is a Michael addition (eq. 30)^{686, 721} resulting in alkylation.



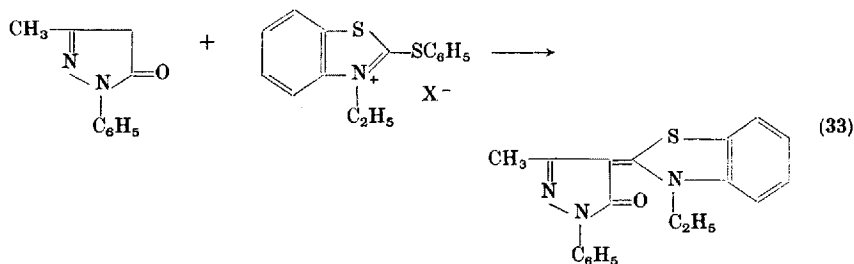
The alkylation of 2-pyrazolin-5-ones at C-4 occurs readily (eq. 31)^{113, 1321} with compounds having reactive halogen atoms. An example



of this is the alkylation of 3-methyl-1-phenyl-2-pyrazolin-5-one with methyl iodide and sodium methoxide to give the corresponding 4,4-dimethyl compound.⁸⁰⁹ However, this reaction may give alkylation at N-2 or O-alkylation and as a rule it is easier to alkylate at these positions than it is at C-4 when aliphatic halides are used. Indeed, in the case of 3-methyl-1-phenyl-2-pyrazolin-5-one the N-2 alkylation occurs to a much greater extent than does exclusive alkylation at C-4, the products being 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one and 1-phenyl-2,3,4-trimethyl-3-pyrazolin-5-one. Various triaryl carbinols and ethers of such carbinols alkylate 2-pyrazolin-5-ones in the presence of acids to give 4-triarylmethyl-2-pyrazolin-5-ones.^{567, 570} A somewhat similar reaction is that of orthoesters (eq. 32).⁷⁶⁴ 2-Methyl-4-chloroquinoline also alkylates 2-pyrazolin-5-ones at C-4.⁹⁷¹

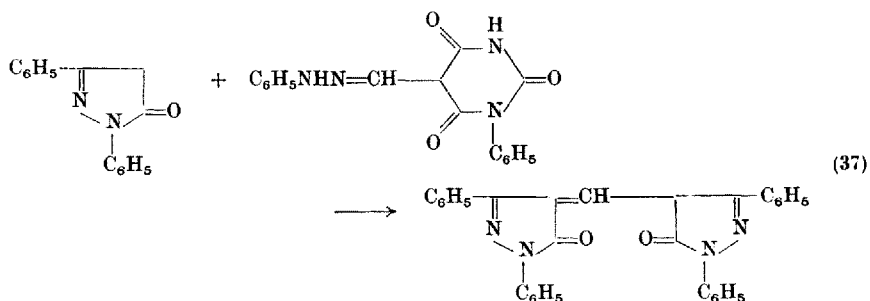
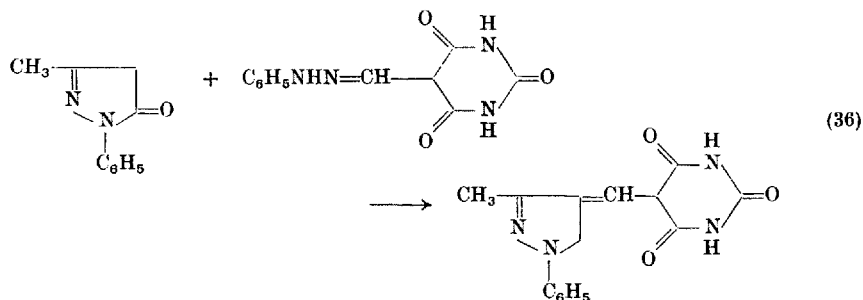
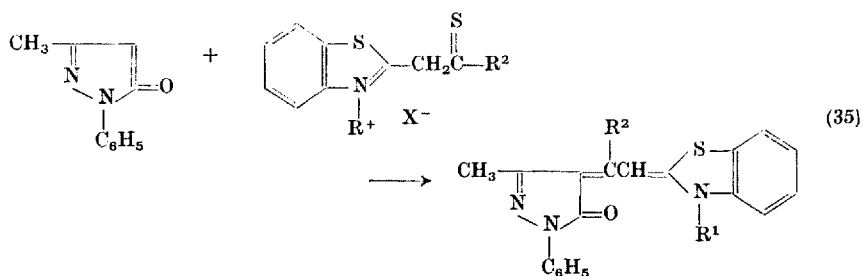
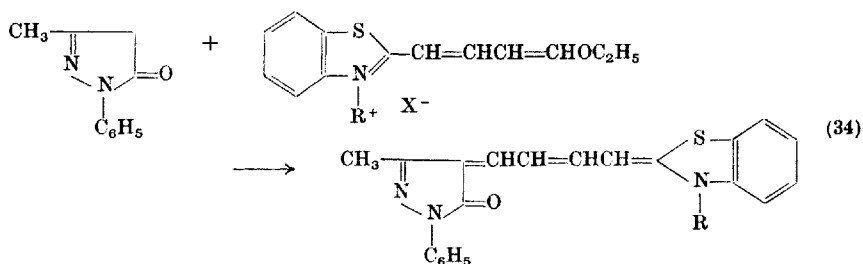


A very important reaction in the synthesis of merocyanine dyes is the alkylation of 2-pyrazolin-5-ones with various heterocyclic rings as illustrated in eqs. 33-35.^{166, 238, 239} 2-Pyrazolin-5-ones other than the



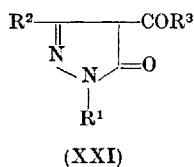
one shown here can be used, and a large variety of heterocyclic compounds such as quinolines, benzoxazoles and numerous others have been employed. The anion may be halogen or *p*-tosyl.

The hydrazones of 5-formylbarbituric acid react with 2-pyrazolin-5-ones in a fashion rather similar to that of aldehydes and ketones

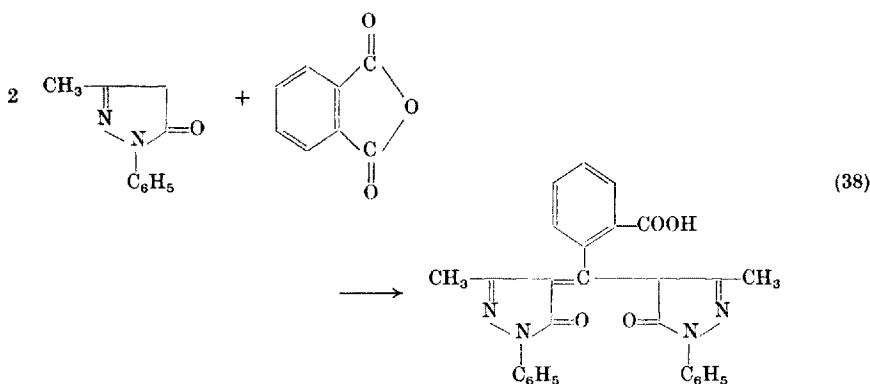


(eqs. 36 and 37).¹¹⁸⁸ Apparently it cannot be predicted which of these two types of reaction will occur.

2-Pyrazolin-5-ones can be readily acylated at C-4 with acid chlorides,¹¹⁰ esters¹⁶⁴¹ and anhydrides.¹²⁷⁹ Very few reactions with acid chlorides and esters have been reported but the product is the ketone (XXI), as expected. Phthalic anhydride reacts with two moles

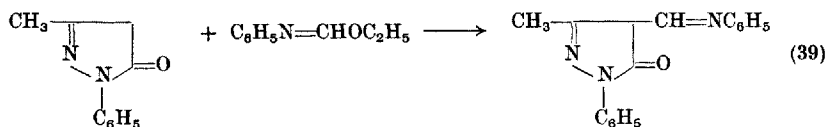


of 2-pyrazolin-5-one according to eq. 38. Perhaps the first step in this

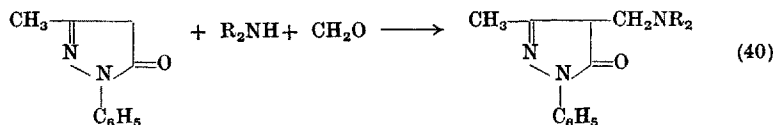


reaction is acylation, followed by reaction of a second molecule of pyrazolinone with the ketone first formed.

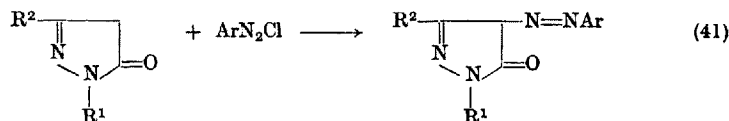
Another reagent which alkylates 2-pyrazolin-5-ones is ethyl isoformanilide, the products being 4-anilinomethylidene-2-pyrazolin-5-ones (eq. 39).^{823, 824} Similar products have been obtained by Losco and Passerini¹⁰⁸⁹ by reaction of isonitriles with 2-pyrazolin-5-ones.



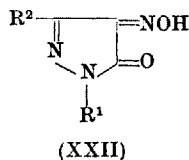
As would be expected, 2-pyrazolin-5-ones undergo the Mannich reaction readily (eq. 40).¹⁰⁹⁸



A variety of functional groups can be introduced directly into the 4-position of 2-pyrazolin-5-ones. Perhaps the most important of these is the arylazo group which is introduced by reaction with diazonium salts (eq. 41).^{333, 809, 813} This reaction has been used to prepare a vast



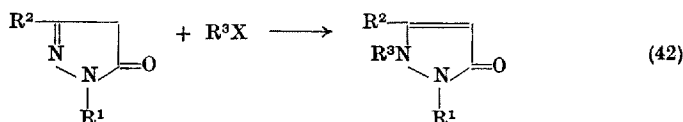
number of azo dyes, many of which have been of considerable commercial importance. It will be discussed in more detail in connection with pyrazolinone dyes and preparation of azo derivatives. Another reaction of commercial importance is that of 2-pyrazolin-5-ones with aromatic amines in the presence of oxidizing agents to form color couplers which are 4-arylimino-2-pyrazolin-5-ones (eq. 172).^{244, 1538} The same kind of product is obtained by the reaction of 4-arylidene-2-pyrazolin-5-ones with aromatic amines. The net result is replacement of the arylidene group with the arylimino group.¹²⁵⁵ Halogenation at the 4-position also occurs readily with phosphorus pentachloride,^{333, 809} phosphorus tribromide³³³ or bromine.^{333, 809, 816} The phosphorus halides form 4,4-dihalogenated derivatives. Direct bromination with an equivalent of bromine gives 4-bromo-2-pyrazolin-5-ones, but excess of bromine gives the 4,4-dibromo and even some tribromo compound. 2-Pyrazolin-5-ones react with nitrous acid to give nitroso derivatives which exist usually as the corresponding oximes (XXII).^{333, 809, 816} Nitration with



dilute nitric acid forms 4-nitro-2-pyrazolin-5-ones.^{61, 333, 806} A 4-formyl group can be introduced by using the Reimer-Tiemann reaction. Sulfonation of 3-methyl-1-phenyl-2-pyrazolin-5-one with 20 per cent oleum at 10–15° results in formation of the corresponding 4-sulfonic acid.⁶⁸⁴ Higher temperatures cause not only sulfonation of the heterocyclic ring, but sulfonation of the phenyl group. A cyano group can be introduced into the 4-position of 2-pyrazolin-5-ones by reaction with cyanogen bromide in the presence of aluminum chloride.²⁴ These substitutions are much more difficult if an alkyl substituent is present in the 4-position, although in some cases such a group is eliminated. 4-Triaryl-methyl-2-pyrazolin-5-ones react with diazonium salts with replacement

of the triarylmethyl substituent by the arylazo group.⁵⁶⁷ Of course, 4,4-dialkyl-2-pyrazolin-5-ones do not react with these substituting reagents. These reactions are discussed further in sections devoted to preparation of the various types of compounds arising from such reactions.

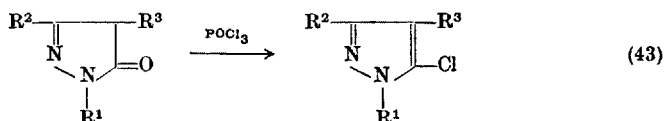
As already mentioned, it is possible for 2-pyrazolin-5-ones to react with alkylating agents at N-2 and at the oxygen atom in addition to C-4. If there is no substituent at N-1, this position can also be alkylated. Most alkylations give a mixture of the possible products. However, by alkylation at temperatures of 100–130°, with or without basic catalysts, 2-pyrazolin-5-ones can be converted to 2-alkyl-3-pyrazolin-5-ones in excellent yields (eq. 42). This reaction has been extensively studied



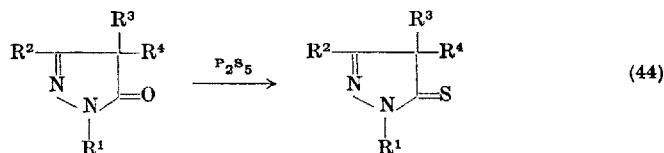
because, in the case of 3-methyl-1-phenyl-2-pyrazolin-5-one and methyl iodide, the product is the commercially important analgesic and antipyretic, antipyrine. The most widely used procedure for carrying out this reaction is the use of methyl iodide and methanol at 100°. ⁸⁰⁶ Methylation has also been accomplished by use of methyl sulfate and sodium hydroxide,¹¹⁰ methyl *p*-toluenesulfonate and sodium methoxide,⁵⁴ dimethyl sulfate,^{94,985} methyl iodide at 130°, ¹⁴⁷⁵ diazomethane,⁹⁴ and methyl iodide and sodium methoxide.¹²⁰⁵ Alkylation under similar conditions with alkylating agents having longer carbon chains, such as ethyl iodide,¹²⁰⁵ propyl bromide,¹³²¹ benzyl chloride ¹³²¹ and 2-dialkylaminoethyl chlorides²⁴⁹ has been successful. Nef¹⁰⁵⁶ has reported that alkylation of 3-methyl-1-phenyl-2-pyrazolin-5-one with methyl iodide and sodium methoxide occurs at C-4 with no N-2 alkylation, at N-2 with no C-4 alkylation, and at both positions. In 2-pyrazolin-5-ones lacking a 1-substituent alkylation occurs to give 1-substituted 2-pyrazolin-5-ones,^{54,1205} usually with little or no *O*-alkylation, and alkylation with alkylchloroformates leads to substitution only at N-1.⁶¹ Somewhat more drastic conditions form 5-alkoxypyrazoles.^{811,1321}

Acylation of 2-pyrazolin-5-ones having no substituent at N-1 occurs readily with such agents as acetyl chloride,^{1499,1598} acetic anhydride,^{1499,1598} benzoyl chloride^{1056,1598} and aryl sulfonyl chlorides.¹¹⁹⁹ The usual product is a 1-acyl-2-pyrazolin-5-one, but acylation may also occur on oxygen, or both on oxygen and at N-2.¹⁵⁹⁸

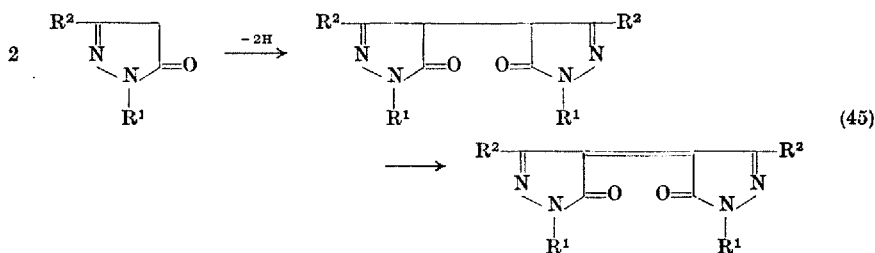
The reaction of 2-pyrazolin-5-ones with phosphorus oxychloride to give 5-chloropyrazoles (eq. 43) is a very general one.^{51, 307, 985, 992, 1003, 1205}



The reaction requires temperatures of 100–150° and all pyrazolinones of this type undergo it. The oxygen of 2-pyrazolin-5-ones can also be replaced by sulfur if phosphorus pentasulfide at about 130–150° is used (eq. 44).^{759, 1343} This reaction is widely used for preparation of 2-pyrazolin-5-thiones.



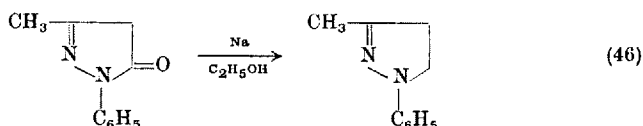
The hydrogen atoms on C-4 of 2-pyrazolin-5-ones are readily attacked by mild oxidizing agents. The products of this reaction are bispyrazolinones (eq. 45) when such oxidizing agents as phenyl



hydrazine^{333, 636, 809, 818, 991} or nitrous acid are used.⁸⁰⁹ The use of ferric chloride in limited amounts gives the bispyrazolinones in which the two rings are connected by a single bond,¹⁵⁸² but larger amounts of ferric chloride give further oxidation and in the product the two pyrazolinone rings are attached to each other by double bonds⁸⁰⁹ as shown in eq. 45. Oxidation of 2-pyrazolin-5-ones having a 1-aryl substituent with *t*-butylhydroperoxide¹⁵²⁶ or oxygen in neutral solution¹⁵²⁸ leads to bispyrazolinones, as shown in the first step of eq. 45. In contrast to this, the use of *t*-butylhydroperoxide in the presence of sodium alkoxides¹⁵²⁶ or of oxygen in acid media¹⁵²⁸ converts the 2-pyrazolin-5-one to the corresponding hydroxy compound. These are excellent

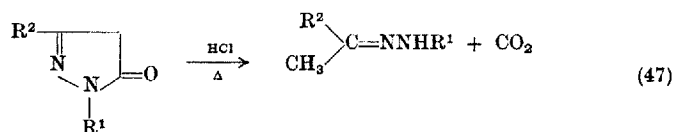
preparative methods for 4-hydroxy-2-pyrazolin-5-ones. Shirai and Yashiro¹²⁹⁹ have found that some 2-pyrazolin-5-ones can be converted to bispyrazolinones merely by recrystallization from hot water. 4,4-Disubstituted-2-pyrazolin-5-ones do not undergo the oxidative dimerization, except in the cases of those substituted with a 4-arylidene group which are oxidized by phenylhydrazine.¹⁰⁹⁰ These compounds apparently react by replacement of the ArCH= by hydrogen from the phenylhydrazine and the unsubstituted pyrazolinone thus arising is oxidized. Strong oxidizing agents, such as potassium permanganate, completely destroy the 2-pyrazolin-5-one ring, forming pyruvic acid, water, nitrogen and carbon dioxide.¹⁵⁴⁹

The heterocyclic ring of 2-pyrazolin-5-ones is quite stable to catalytic reduction. Aromatic substituents present can be reduced to cyclohexyl groups by means of various hydrogenation catalysts without reduction of the heterocyclic ring.^{161, 859, 1280} The carbonyl function of 2-pyrazolin-5-ones is subject to reduction by various chemical reagents. Treatment of 3-methyl-1-phenyl-2-pyrazolin-5-ones with zinc results in reduction to the corresponding pyrazole,⁸⁰⁹ but somewhat more drastic conditions cause complete decomposition of the heterocyclic ring, giving aniline and acetonitrile.⁸⁰⁹ Reduction of the same compound with sodium and alcohol forms the corresponding pyrazoline (eq. 46).⁸⁰⁹ The



use of sodium and amyl alcohol on 2-pyrazolin-5-ones forms 5-hydroxy-pyrazolines,⁵³ as does reduction with lithium aluminum hydride.¹⁵⁰⁵

Although 2-pyrazolin-5-ones are relatively stable to acid hydrolysis, those having 1-(dinitrophenyl) or 1-(trinitrophenyl) substituents are decomposed, forming arylhydrazones (eq. 47).⁷⁷⁷



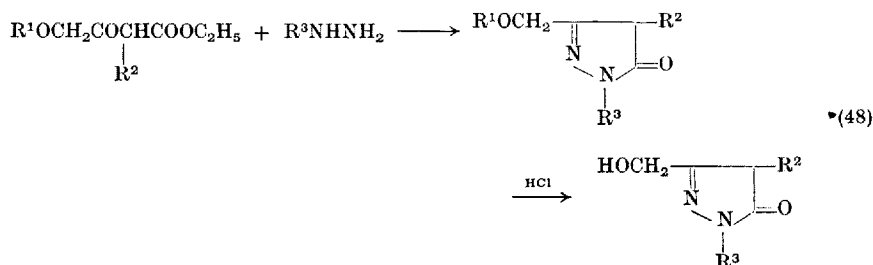
Hydrolysis of 2-pyrazolin-5-ones with 33 per cent sodium hydroxide solution also destroys the ring.¹²⁸⁶ The hydrolysis products were not identified with certainty, but it was thought that acetic and propionic acids were among them.

2-Pyrazolin-5-ones form a variety of complexes with various metals

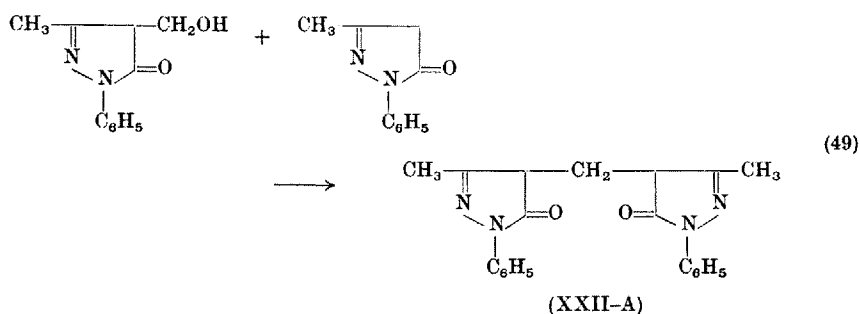
and metal salts.^{393, 394, 482} 3-Methyl-1-phenyl-2-pyrazolin-5-one has been reported to form complexes with iron, cobalt, silver, cupric oxide, cupric iodide, silver iodide, ferric iodide, cobalt iodide and beryllium chloride. These complexes actually are salts of the enolic form of the pyrazolinone in many cases, although in others the only bonds may be those formed by donation of the electrons by the $C=N-N<$ group.³⁹⁴ In some cases both types of linkages are present. The compounds formed usually have the number of molecules of 2-pyrazolin-5-one corresponding to the valence of the metal atom present.

(4) *Hydroxyalkyl Types*

Most of the syntheses of α -hydroxyalkyl and α -alkoxyalkyl-2-pyrazolin-5-ones have been discussed in connection with the reactions of 2-pyrazolin-5-ones. However, there is one synthesis by which compounds of this type are obtained directly. This is by reaction of the appropriate alkoxy- or phenoxymethylacetoacetic esters with hydrazines (eq. 48).^{532, 1314, 1315, 1316, 1562} The reactions of these compounds



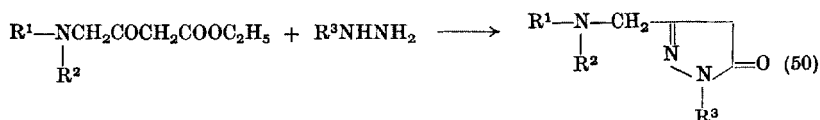
are the general ones for 2-pyrazolin-5-ones and for hydroxy and alkoxy functions except for the condensation of 4-hydroxymethyl-2-pyrazolin-5-ones with another pyrazolinone to give bis(2-pyrazolin-5-ones) (eq. 49).²⁴



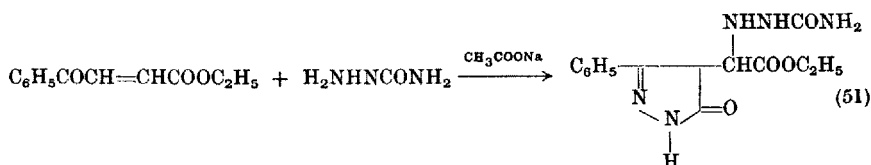
The α -hydroxyalkyl and α -alkoxyalkyl-2-pyrazolin-5-ones are listed in Table II, Section F.

(5) *Aminoalkyl Types*

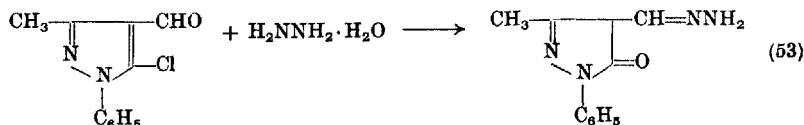
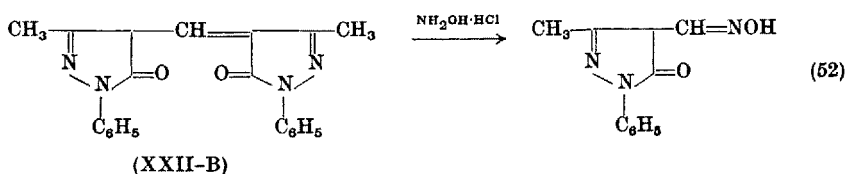
A number of syntheses of compounds having nitrogen on a carbon attached to 2-pyrazolin-5-one rings have already been mentioned, but several others are known. The most important of these is the reaction of 4-formyl- or 4-acyl-2-pyrazolin-5-ones with hydroxylamine, hydrazines, semicarbazide and similar chemicals.^{559, 1641} These compounds can also be obtained by direct synthesis from an appropriate β -ketoester or derivative and a hydrazine (eq. 50).^{138, 512, 1100} An interesting syn-



thesis of this type of compound is that shown in eq. 51.¹¹⁷⁹ Presumably condensation of one molecule of semicarbazide with the ketone carbonyl



is followed by cyclization to the C-3 of the ester with elimination of ammonia after addition of a second molecule of semicarbazide. Two other syntheses of these compounds are shown in eqs. 52 and 53.^{925, 1206}



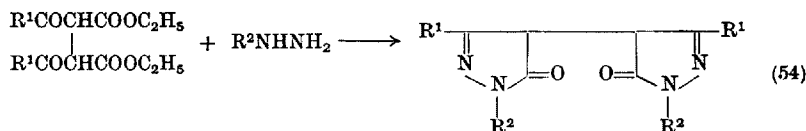
The reactions of these derivatives are typical of the functional groups present.

Compounds having nitrogen on a carbon atom which is attached to a 2-pyrazolin-5-one ring are listed in Table II, Section G.

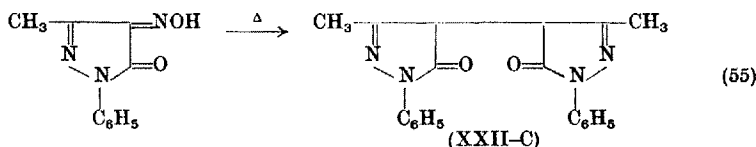
(6) *Bis(2-pyrazolin-5-ones)*

A large number of 2-pyrazolin-5-ones exist in which two or more such rings are combined. These are almost all combined symmetrically, that is the same positions in the two rings are linked, and the vast majority are combined in the 4,4'-positions, although many are connected at the 3,3'-positions and some by way of the 1,1'-positions. Those 4,4'-bispyrazolinones in which the two rings are directly connected are listed in Tables III and IV. Those having atoms between the rings are listed in Tables V-VII. The 3,3'-bispyrazolinones are listed in Table VIII and the 1,1'-bispyrazolinones in Table IX.

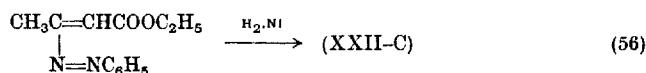
The most widely used synthesis of 4,4'-bis(2-pyrazolin-5-ones) is mild oxidation of monocyclic 2-pyrazolin-5-ones, which has already been discussed in the section devoted to reactions of 2-pyrazolin-5-ones (eq. 45). These compounds can also be synthesized by reaction of α,α' -diacylsuccinic esters with hydrazines (eq. 54).^{357,807,815} A number



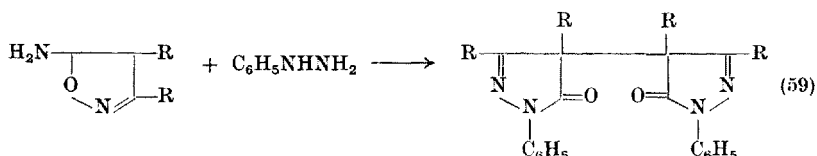
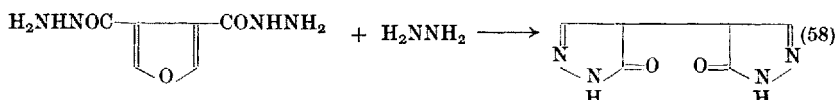
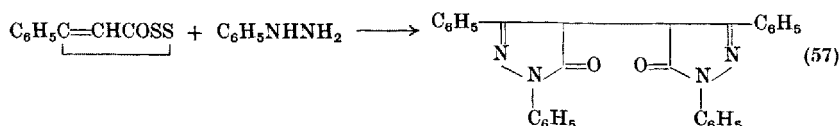
of miscellaneous dimerizations of 2-pyrazolin-5-ones and 3-pyrazolin-5-ones have been reported to give 4,4'-bis(2-pyrazolin-5-ones). 3-Methyl-1-phenyl-2-pyrazolin-5-one reacts with various acylanilides¹¹⁹² and with sodium ethoxide¹⁶⁴⁵ to give dimers. Ethyl groups are introduced at the 4,4'-positions by the use of sodium ethoxide. Heating a 4-oximino-2-pyrazolin-5-one has been reported to give a dimer in which the 4-substituent has been eliminated (eq. 55).⁹²⁵ According to van



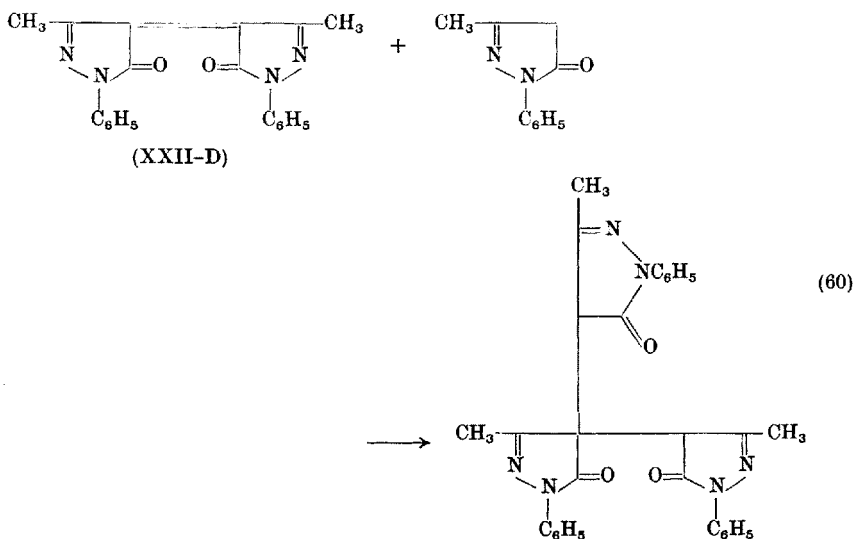
Alphen¹⁵¹³ it is also obtained by the reductive cyclization of a crotonic ester (eq. 56). The replacement of a 4-imino function in a 2-pyrazolin-5-one by a 2-pyrazolin-5-one lacking a 4-substituent also leads to a



dimer.¹⁵³⁸ Hydrazines react with various heterocyclic compounds to give 4,4'-bis(2-pyrazolin-5-ones). These reactions are shown in eqs. 57-59.^{129, 725, 729} Ridi and co-workers¹¹⁹⁴ have treated various pyrazolo-



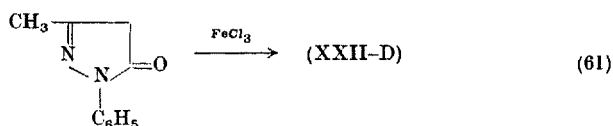
2-pyrones and phenylmethyltartonylurea and imide with phenylhydrazine to give 4,4'-bis(3-methyl-1-phenyl-2-pyrazolin-5-one). A variety of other 4,4'-bis(2-pyrazolin-5-ones) can be converted into the type being



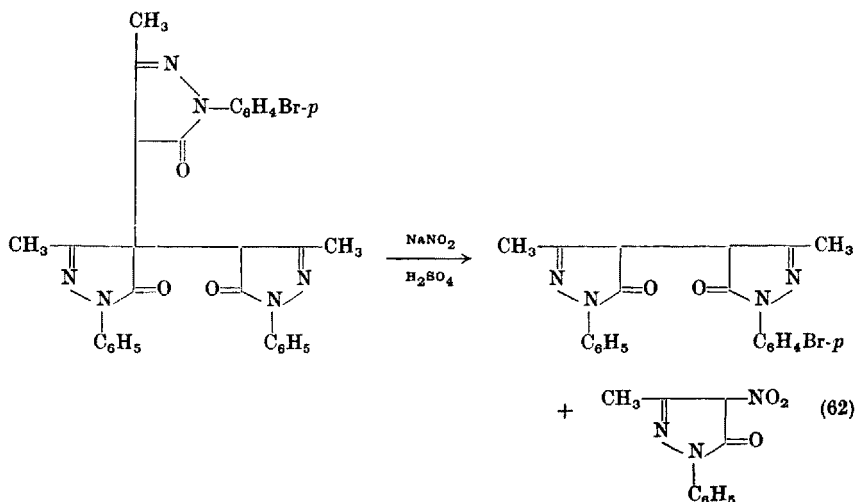
discussed here. 4-Benzylidene-4,4'-bis(3-methyl-1-phenyl-2-pyrazolin-5-one) reacts with azobenzene or phenylhydrazine to give 4,4'-bis(3-methyl-1-phenyl-2-pyrazolin-5-one).^{1090, 1091} Of particular interest is

the addition of various compounds having active methylene to the 4,4'-bis(2-pyrazolin-5-ones) connected by a double bond since this leads in some cases to trimers.^{1607,1609,1613,1614} This reaction is shown in eq. 60.

Only a very few 4,4'-bis(2-pyrazolin-5-ones) linked by a double bond have been prepared. The parent compound of this series, 4-(3-methyl-1-phenyl-5-oxo-2-pyrazolin-4-ylidene)-3-methyl-1-phenyl-2-pyrazolin-5-one (XXII-D), is known as pyrazole blue.^{323,807,809,816,1090,1091} It was so named by Knorr because of its great resemblance to indigo blue. All these compounds are strongly colored. The usual synthesis is by ferric chloride oxidation of monomeric 2-pyrazolin-5-ones (eq. 61)^{296,809} or by oxidation of the corresponding bis compounds



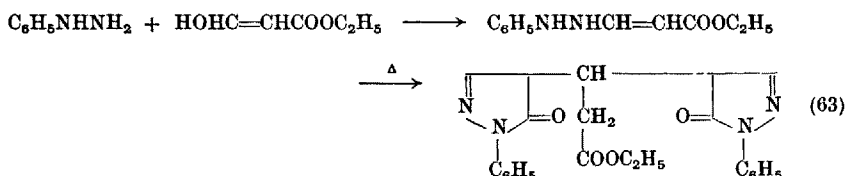
linked by a single bond with ferric chloride, nitrous acid, nitric acid or various nitriles.^{296,333,1090} The product in eq. 61 is pyrazole blue. Other methods of synthesis are treatment of 4-(3-methyl-1-phenyl-2-pyrazolin-5-ylidene)-3-methyl-1-phenyl-2-pyrazolin-5-one with bromine in alkali,³²³ heating of 4-bromo-3-methyl-1-phenyl-2-pyrazolin-5-one



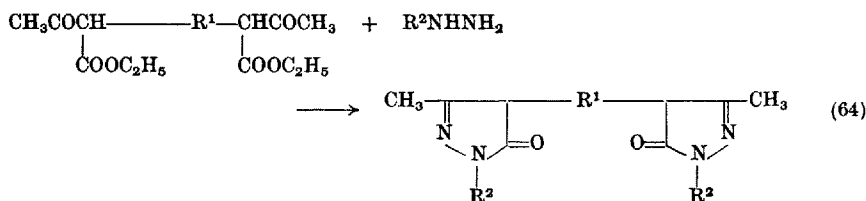
with alcohol⁸⁰⁹ and degradation of trimers.^{1607,1608} The trimer degradation procedure gives unsymmetrical compounds of the pyrazole blue type (eq. 62). The double bond connecting the rings in these

compounds reacts as do normal olefins and in addition undergoes additions with compounds having active hydrogen^{1607,1608} or with such compounds as hydrogen cyanide.¹⁶¹²

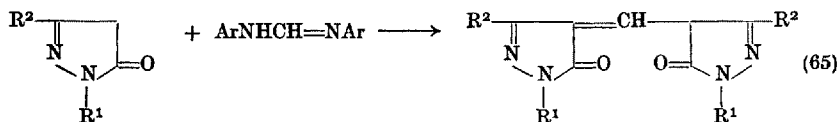
4,4'-bis(2-pyrazolin-5-ones) linked by carbon chains have been prepared in a multitude of ways, several of which have been mentioned in the discussion concerning reactions of 2-pyrazolin-5-ones. The only method of any importance is the condensation of 2-pyrazolin-5-ones with aldehydes and ketones (eq. 24, p. 20) and this has already been discussed. An interesting modification of this is the use of an anil as a substitute for the aldehyde.¹⁰⁹⁴ The anil functions similarly to the aldehyde. A second modification in which the aldehyde is generated in the course of the reaction has also been used (eq. 63).¹³⁵¹ Another



method used to some extent for the synthesis of 4,4'-bis(2-pyrazolin-5-ones) is the reaction of bis- β -ketoesters with hydrazines (eq. 64).^{451,513,514,1154} The reaction of 2-pyrazolin-5-ones with amidines to

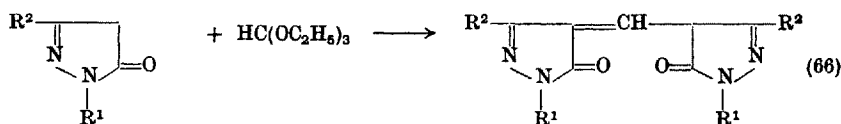


give substitution at the 4-position has already been mentioned. In addition to such products this reaction often gives 4,4'-methylidynebis(2-pyrazolin-5-ones) (eq 65).^{1070,1186} A reaction which appears

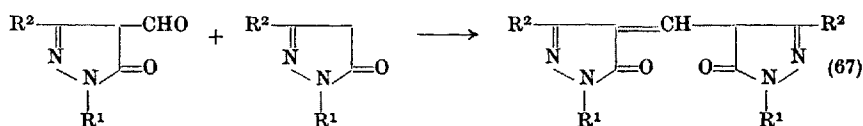


to be very similar to this and gives the same type of product is the condensation of 2-pyrazolin-5-ones with 1-phenyl-1,2-dihydro-4,6-diamino-1,3,5-triazines.³⁰⁰ The synthesis of 4,4'-methylidynebis(2-pyrazolin-5-ones) has usually been achieved by condensation of

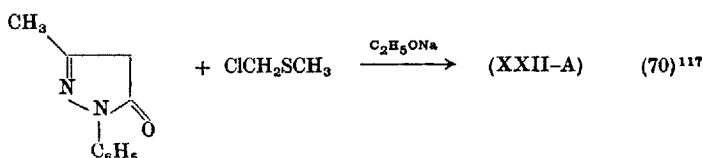
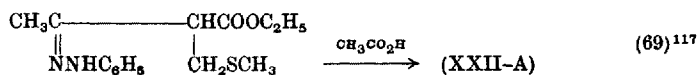
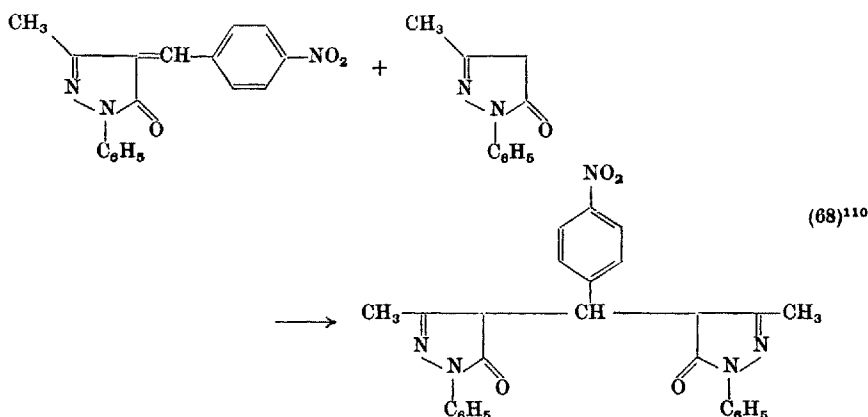
2-pyrazolin-5-ones with ethyl orthoformate^{611, 1188, 1669} (eq. 66) or by the condensation of 5-oxo-2-pyrazolin-4-carboxaldehydes with

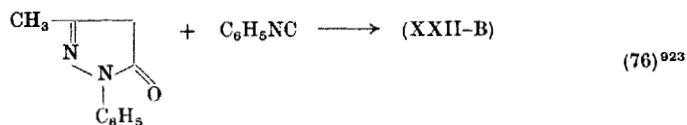
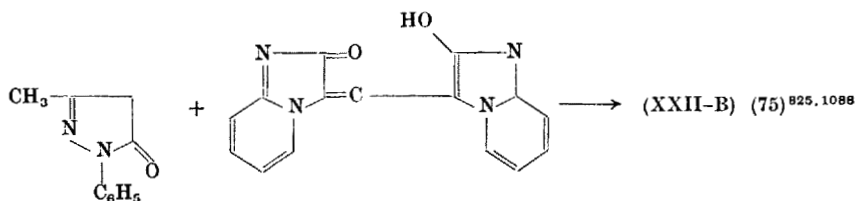
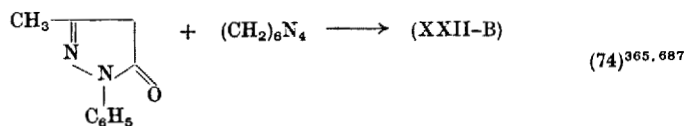
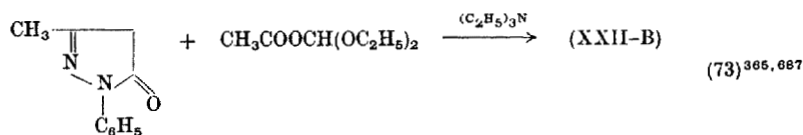
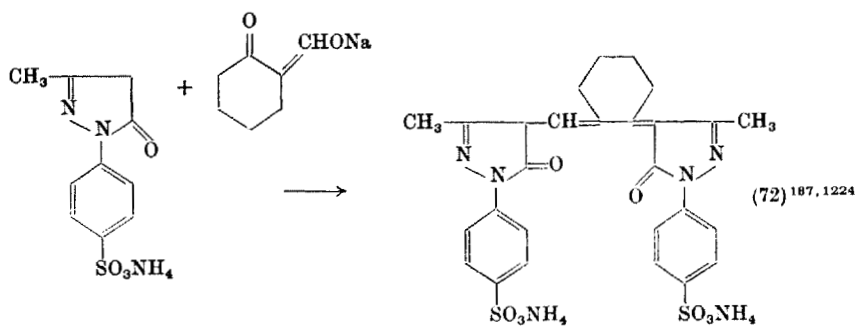
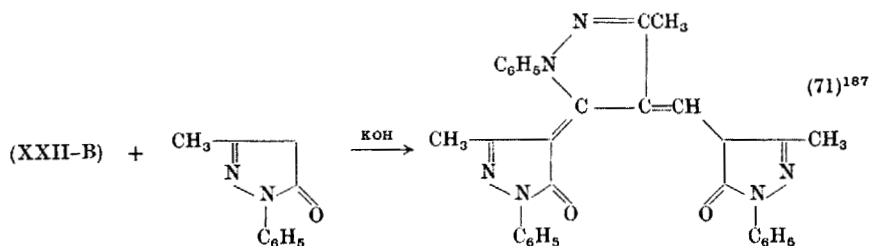


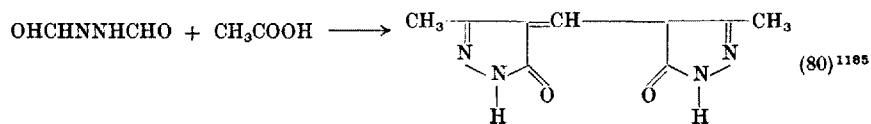
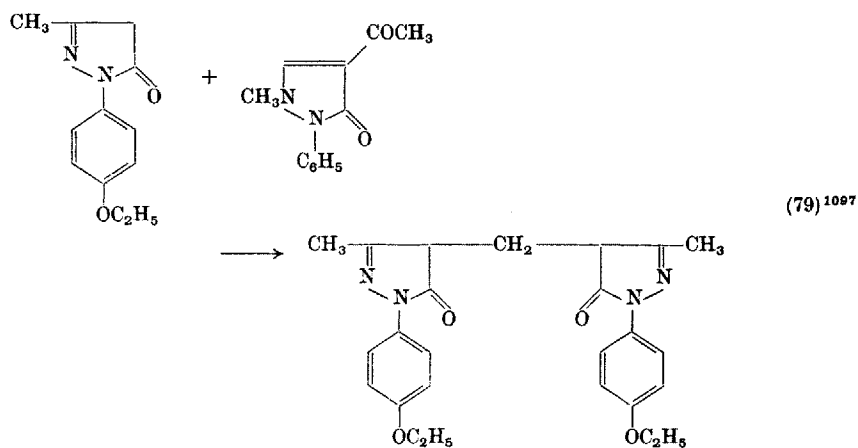
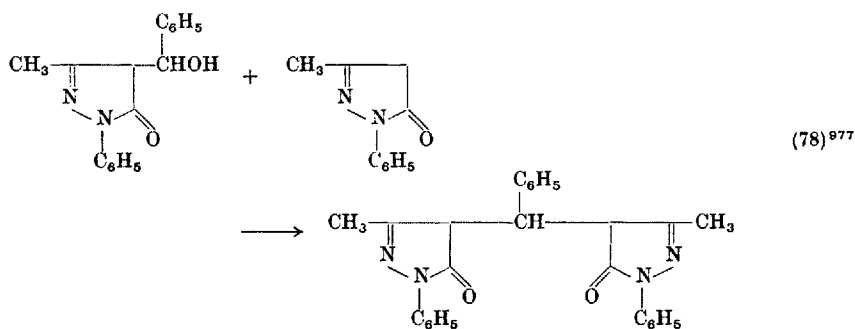
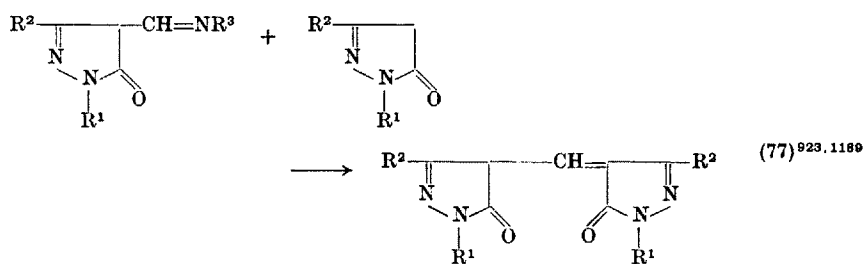
2-pyrazolin-5-ones (eq. 67).^{926, 1093, 1185} The latter condensation can be modified by boiling the aldehyde alone in water which causes partial

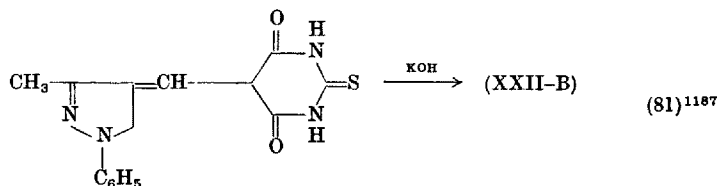


hydrolysis of the formyl group. The reactants shown in eq. 67 are then present and can react to form the bis compound. A variety of miscellaneous methods of preparing such compounds is given in eqs. 68-81.

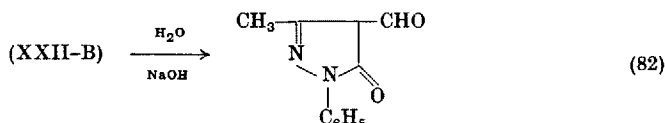








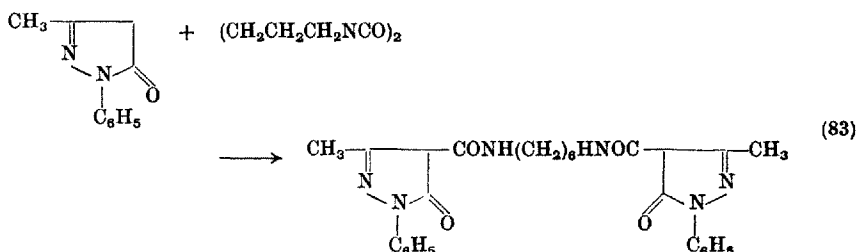
4,4'-Arylidenebis(2-pyrazolin-5-ones) can be decomposed by heat or acid to give 4,4'-methylidynebis(2-pyrazolin-5-ones).^{93,1036} In one case 4,4'-methenylbis(3-methyl-1-phenyl-2-pyrazolin-5-one) was reported as the product.²² The melting point given was 177°. This was undoubtedly the 4,4'-methylidyne compound which melts at 185°. The 4,4'-methenylbis compound, which melts at 220°, has been repeatedly reported as melting at 180–185° owing to its easy loss of hydrogen to give the 4,4'-methylidynebis compound. In some cases this heat degradation of 4,4'-arylidenebispyrazolinones converts them back into the mono-2-pyrazolin-5-ones.¹⁰³⁶ The degradation of bis(2-pyrazolin-5-ones) to mono compounds is also brought about by heating with formamide.¹¹⁸⁹ 4,4'-Methylidynebis-(2-pyrazolin-5-ones) are readily converted by treatment with hydroxylamine into the corresponding 5-oxo-2-pyrazolin-4-carboxaldehyde oxime⁹²⁵ or by hydrolysis with base to the 4-carboxaldehyde (eq. 82).⁹²⁶ The bromination of 4,4'-



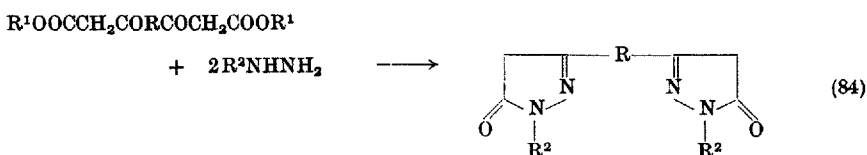
methylidynebis(3-methyl-1-phenyl-2-pyrazolin-5-one) has been reported by Ziegler and Sauermilch.¹⁶⁹² Bromination replaced the only remaining C-4 hydrogen by bromine. Hydrogen bromide could not be eliminated, but heating with alcohol replaced the halogen by hydrogen. The condensation of a series of 2-pyrazolin-5-ones with aryl aldehydes in 70 per cent acetic acid at elevated temperatures has been described as giving the enol form of 4,4'-arylidenebis(2-pyrazolin-5-ones).¹¹³⁵ The corresponding keto forms can be converted into the enols by heating in alcohol.

A few 4,4'-bis(2-pyrazolin-5-ones) are known in which the linking chain contains nitrogen atoms. These are Schiff bases and amides. 5-Oxo-2-pyrazolin-4-carboxaldehydes react with diamines having two primary amino groups to form 4,4'-bispyrazolinones.¹¹⁹⁰ The amides are synthesized by reaction of bisisocyanates with 2-pyrazolin-5-ones

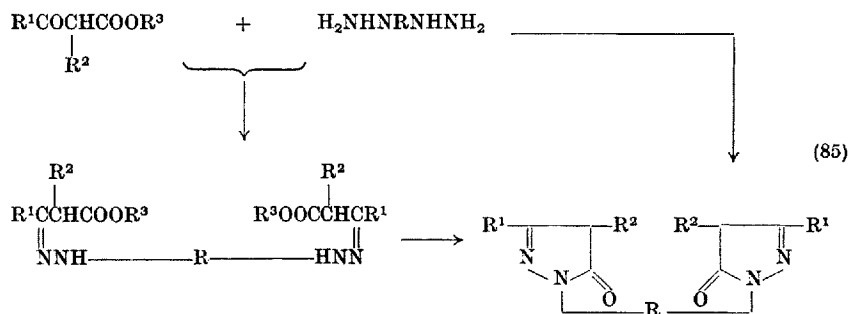
(eq. 83).¹¹¹¹ This reaction is of particular interest because it illustrates the great activity of the hydrogen atoms at C-4.



The 3,3'-bis(2-pyrazolin-5-ones) in which the rings are connected by carbon chains (Table VIII) are usually prepared by condensation of a hydrazine with an appropriate β,β' -dioxodiester (eq. 84).^{419, 462, 1222, 1225} Such bispyrazolinones linked by a carbonyl group have been prepared by pyrolysis of the calcium salt of 5-oxo-2-pyrazolin-5-one.¹⁵⁴⁹

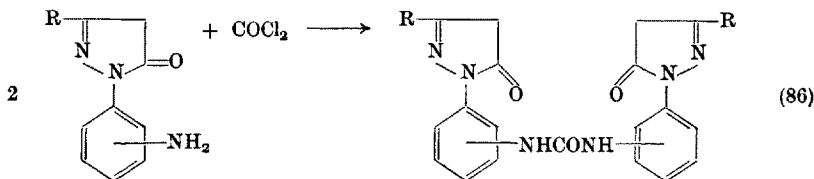


The 1,1'-bis(2-pyrazolin-5-ones) (Table IX) have been prepared by three methods. Two of these are variants on the familiar β -ketoester condensation with hydrazines but in these cases compounds having two hydrazine moieties are used.^{116, 212, 255, 459, 1037} These two methods are illustrated in eq. 85. The R in the hydrazines used in the direct con-



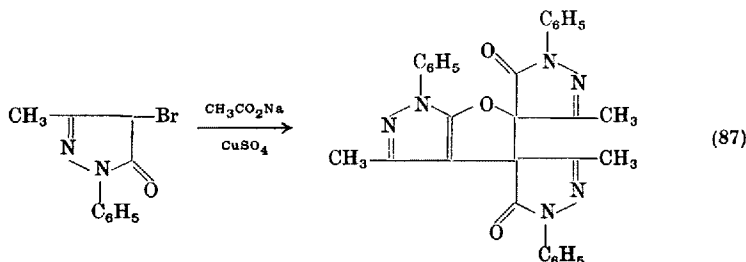
densation is usually aryl. The commonly used hydrazine when going through the bishydrazone has been carbazide¹⁶³² or a similar com-

pound.²⁵⁵ The reaction of phosgene with 1-(X-amino-phenyl)-2-pyrazolin-5-ones also forms 1,1'-bis(2-pyrazolin-5-ones) (eq. 86).^{152, 511}



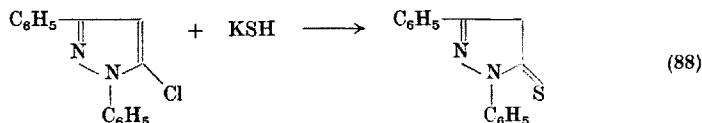
The 1,1'-bispyrazolines undergo the usual reactions of 2-pyrazolin-5-ones.

Westoö has reported the synthesis of complex bispyrazolinones which he has called furlones.^{1608, 1610, 1611} These have two 2-pyrazolin-5-one rings connected through a dihydrofuran ring which in turn is fused with a pyrazole ring. These were prepared by condensation of 4-halogenated-2-pyrazolin-5-ones, together, with 1-aryl-2-pyrazolin-5-ones, or with pyrazole blue (XXII-D) in the presence of a base and copper sulfate (eq. 87). These compounds are listed in Table X.



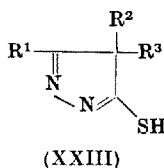
B. 2-Pyrazolin-5-thiones

The reaction of 2-pyrazolin-5-ones with phosphorus pentasulfide forms 2-pyrazolin-5-thiones (eq. 44).^{759, 990, 1343} The reactants are usually heated at the temperature of boiling xylene. A second method used in the preparation of such compounds is the reaction of 5-chloropyrazoles with potassium hydrogen sulfide (eq. 88).^{977, 990, 1003}

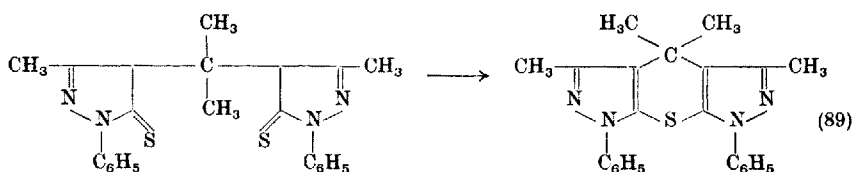


The properties of these compounds are very similar to those of the 5-oxo analogs. They are usually colorless but are yellow if substituted

in the 4-position. Acidic and basic properties are both present. Kendall and Ruffin⁷⁵⁹ claim that 3,4,4-trialkyl-2-pyrazolin-5-thiones exist as mercapto pyrazoles having the structure (XXIII).

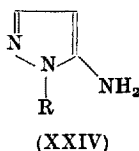


Reactions of 2-pyrazolin-5-thiones at the 4-position are quite similar to those of the 5-oxo analogs. Condensation of one mole of the pyrazolinthione with one mole of ketone or aldehyde to form 4-alkylidene- or arylidene-2-pyrazolin-5-thiones occurs.⁹⁹⁰ Coupling with diazonium salts forms 4-azo compounds⁹⁹⁰ and nitrosation occurs.⁹⁹⁰ Alkylation or acylation ordinarily attacks the sulfur atom to give 5-mercaptopyrazoles.^{977, 990} Oxidation with mild oxidizing agents such as iodine or nitrous acid forms a disulfide,⁹⁹⁰ but the use of hydrogen peroxide gives a sulfonic acid, according to Michaelis,⁹⁹⁰ or replacement of the sulfur by oxygen, according to Kitamura.⁷⁸⁵ Mercaptides are formed with mercuric oxide or mercuric salts.⁹⁹⁰ The 4,4'-bis(2-pyrazolin-5-thiones) cyclize very readily to form a tricyclic compound with elimination of hydrogen sulfide (eq. 89).⁹⁹⁰ The 2-pyrazolin-5-thiones are listed in Table XI.



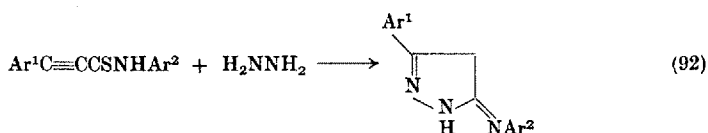
C. 5-Imino-2-pyrazolines

It is probable that most of the 5-imino-2-pyrazolines exist as the corresponding aminopyrazoles (XXIV). Gagnon, Boivin and Trem-



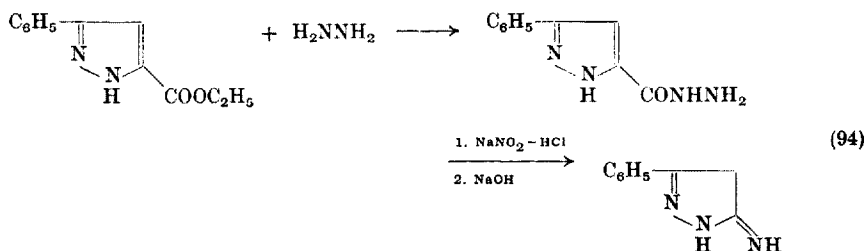
bley⁵⁰⁶ have studied the ultraviolet absorption spectra of these compounds and concluded that the usual structure is the aminopyrazole

The principal methods of preparation of these compounds are very similar to those used for the 5-oxo- compounds, except that nitriles, and in some cases amides, are used instead of esters, acids or acid derivatives. β -Ketonitriles,^{342, 344, 838, 1562} β -aldehydonitriles,¹²⁷ β -iminonitriles,^{90, 324, 996, 1010, 1285, 1542} α,β -unsaturated trithiones¹²⁹ and α,β -acetylenic nitriles¹⁰²⁵ are condensed with hydrazines. In many cases the intermediate hydrazones have been isolated and cyclized.^{86, 132, 310, 996, 1011, 1285, 1287} These reactions are shown in eqs. 90 and 91. Worrall and co-workers^{1655, 1856} have reported the condensation of aromatic acetylenic amides with hydrazines to give 5-imino-2-pyrazolines (eq. 92). Presumably the amides react like the iminothioacids, hydrogen


$$\text{C}_6\text{H}_5\text{C}=\text{CHC}\text{SS} + \text{C}_6\text{H}_5\text{NHNH}_2 \longrightarrow \begin{array}{c} \text{C}_6\text{H}_5 \\ \parallel \\ \text{N} \diagdown \\ \quad \text{N} \diagup \\ \quad | \\ \text{C}_6\text{H}_5 \\ \quad \text{NH} \end{array} \quad (93)$$

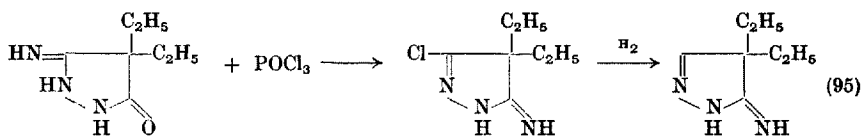
Several methods for the synthesis of 5-imino-2-pyrazolines depend upon the amination of a pyrazole ring. 5-Chloropyrazoles react with aniline to give the corresponding 5-amino compound.^{826, 1002} The chloropyrazoles can be prepared and amination accomplished in one

step by treatment of 2-pyrazolin-5-one with phosphorus oxychloride and aryl amines at the same time.^{827, 828} Also reduction of a 5-nitropyrazole has been used.¹⁰⁸⁶ Ethyl 3-phenylpyrazole-5-carboxylate has been converted into a hydrazide, then to an azide, and finally, by a Curtius rearrangement, to the amino compound (eq. 94).¹⁰⁸⁶ Also amides can be rearranged to give iminopyrazolines.¹⁰⁴⁶



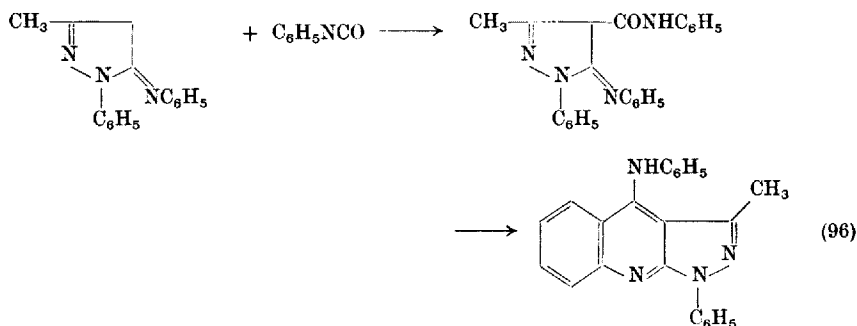
Cusmano^{340, 341, 345} has converted 5-alkyl- and 5-arylisoxazole-3-carboxylic acids into 5-imino-2-pyrazolines by treatment with phenyl hydrazine. Musante has also used this procedure.¹⁰⁴³⁻¹⁰⁴⁵ This reaction goes by way of β -ketonitrile intermediates and gives very poor yields.⁸⁶

The decarboxylation of 1,3-diphenyl-5-imino-2-pyrazolin-3-carboxylic acid gives 1,3-diphenyl-5-imino-2-pyrazoline.⁵⁰⁶ Druey and Schmidt³⁹¹ have taken advantage of the selective replacement of an oxo group by chlorine over that of an imino group to prepare 5-imino-2-pyrazolines (eq. 95).



The reactions of 5-imino-2-pyrazolines are very similar to those of the 5-oxo analogs, except for reactions specifically involving the 5-imino group as its amino tautomer. For example, condensations with aromatic aldehydes occur to form 4,4'-arylidenebis(5-imino-2-pyrazolines). Michaelis⁹⁹⁶ has prepared compounds of this type from 3-methyl-1-phenyl-5-imino-2-pyrazoline in which the arylidene groups and melting points are respectively: $\text{C}_6\text{H}_5\text{CH}$, 66° ; $2\text{-NO}_2\text{C}_6\text{H}_4\text{CH}$, 89° ; $\text{X-HOC}_6\text{H}_4\text{CH}$, 120° ; $4\text{-CH}_3\text{C}_6\text{H}_4\text{CH}$, 219° . However, reaction with aldehydes or ketones can also occur at the amino group to give Schiff bases or alkylation.¹⁰¹¹ Ketones such as acetoacetic ester used in vigorous conditions give pyrazolopyrimidines.³²⁹ Halogenation,^{996, 1056}

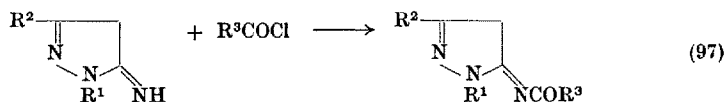
nitration,¹⁶⁵⁶ nitrosation,^{340, 1002, 1010} and coupling with diazonium salts⁹⁹⁶ occur at C-4 as expected. The nitrosation products are usually oximes. The condensation of phenyl isocyanate with the 5-imino-2-pyrazolines occurs to give the 4-carboxyanilides (eq. 96).⁸²⁶ These com-



pounds then readily cyclize to quinoline derivatives. Phenyl isothiocyanate, N,N'-diphenylurea and N,N'-diphenylthiourea also react in this way. *p*-Nitrophenylsulfenyl chloride reacts with 3-methyl-1-phenyl 5-imino-2-pyrazoline to give 3-methyl-4-(4-nitrophenylmercapto)-1-phenyl-5-imino-2-pyrazoline.³²⁵

Druey and Schmidt³⁹¹ have reported that alkylation of N-1 unsubstituted 4,4-dialkyl-5-imino-2-pyrazolines with dimethyl sulfate occurs at the N-1 position.

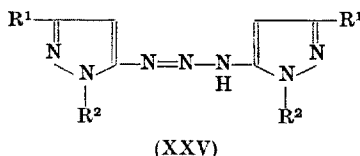
As illustrated in eq. 97, the acylation of 5-imino-2-pyrazolines



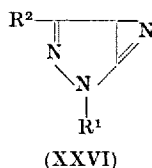
occurs on the 5-imino group rather than at C-4 as in the 5-oxo analogs. However, the use of diethylmalonyl chloride gives acylation at both positions.³²² Aliphatic acid chlorides,³⁹¹ aliphatic anhydrides,³²⁵ aromatic acid chlorides³⁴⁰ and sulfonyl chlorides³²⁵ have been used as acylating agents. Carbon disulfide reacts with the imino group to give a bispyrazolylthiourea.⁹⁹⁶ Nitrous acid diazotizes the 5-imino group,⁹⁹⁶ another argument for its existence in the tautomeric amino form. If insufficient nitrous acid to diazotize all of the 5-imino-2-pyrazolines is used, the resulting diazonium salt couples with undiazotized material, giving an iminoazo compound (XXV). The diazonium salt also couples with phenols.

Moureu and Lazennec¹⁰²⁵ were unable to hydrolyze 3-alkyl-5-imino-2-pyrazolines to the 5-oxo analogs, but Cusmano³⁴⁰ claims to

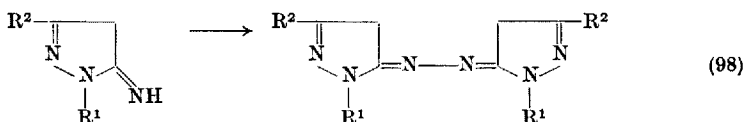
have hydrolyzed the imino group of 4-nitroso-1,3-diphenyl-5-imino-2-pyrazoline to an oxo group using acid conditions.



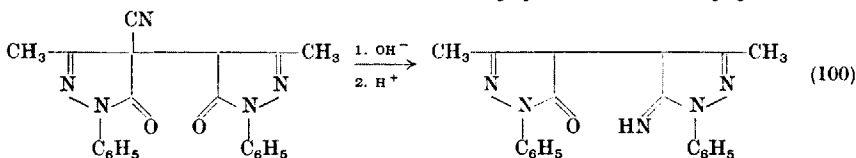
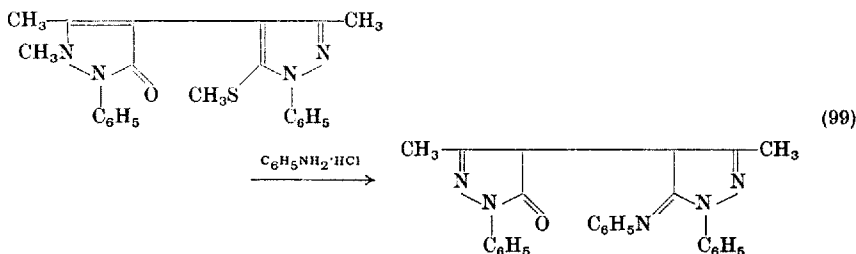
Michaelis^{99b} has reported that oxidation of various 5-imino-2-pyrazolines with hydrogen peroxide or nitrous acid gives what were called azipyrazoles of type (XXVI). It seems highly unlikely that these



products actually had the structure proposed. It may be that the compounds formed were 5,5'-bis(5-imino-2-pyrazolines), as indicated in eq. 98, although the evidence is not completely consistent with this interpretation. 5-Imino-2-pyrazolines are listed in Table XII.



A few bis(2-pyrazolin-5-ones) having one or both 5-oxo groups replaced by imino groups have been prepared. The preparation of those having one imino group is shown in eqs. 99 and 100. Those linked



through the nitrogen atoms of the 5-imino group are listed in Table XIII. The usual preparation is reaction of a 5-imino-2-pyrazoline having no substituent on the 5-imino nitrogen with oxalic acid³²² or phosgene.³⁰¹

D. 3-Pyrazolin-5-ones

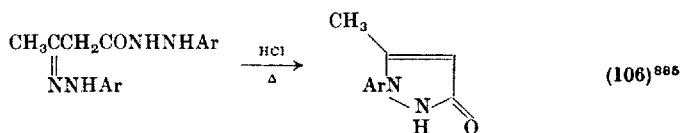
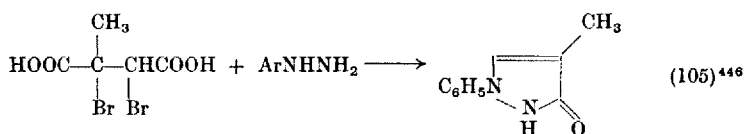
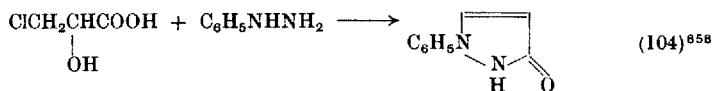
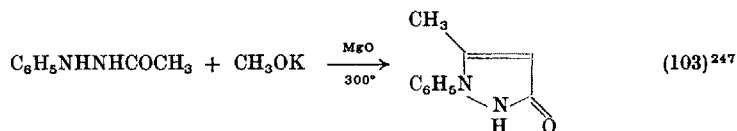
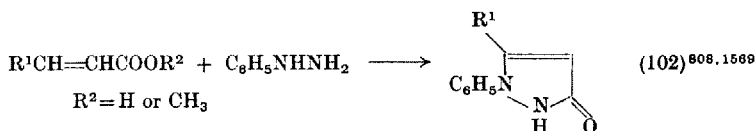
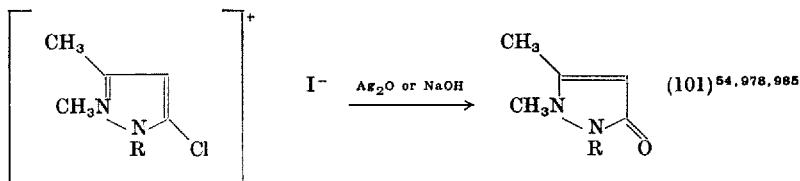
(1) *Syntheses*

As has been mentioned previously (eq. 42, p. 26) the method most frequently used to synthesize 3-pyrazolin-5-ones is alkylation of 2-pyrazolin-5-ones at N-2. In general this can be used only for synthesis of 2-alkyl-, 2-aralkyl- and 2-heteroalkyl-3-pyrazolin-5-ones. The earliest workers used methyl iodide in methanol at temperatures of 100–130°. ^{806, 818, 992} Other methylating agents used have been dimethyl sulfate at temperatures of 100–130°, ^{113, 362, 781, 1173} dimethyl sulfate with base, ¹¹⁰ diazomethane, ⁹⁴ methyl iodide, ^{141, 1475} methyl iodide in the presence of sodium methoxide, ¹²⁰⁵ methanol and dry hydrogen chloride at 140° ¹⁵⁰⁸ and methyl *p*-toluenesulfonate in the presence of base. ^{102, 1198, 1205} A number of other short-chain alkyl halides, such as ethyl iodide, allyl chloride and isopropyl chloride with and without added base have been used. ^{250, 1205, 1447} Benzyl chloride ^{54, 250} and xanthhydrol ⁴⁵⁷ give 2-aralkyl-3-pyrazolin-5-ones. A variety of heteroalkyl chlorides have been condensed with 2-pyrazolin-5-ones using sodamide as the condensing agent. ²⁴⁹ The yields in these alkylations vary considerably, but in general the more complex the alkyl or aralkyl halide used the lower the yields. Methylation has been reported in yields of 85 per cent, ⁷⁸¹ but benzylation occurs only to the extent of 15 per cent. ²⁵⁰ The usual yields appear to be 40–65 per cent. The chief side reaction occurring is *O*-alkylation to give 5-alkoxypyrazoles. Of course, if there is only hydrogen at N-1, alkylation frequently occurs there also. ⁵⁴

As shown in eq. 3 (p. 9) the reaction of acyl arylhydrazines with β -ketoesters forms 2-aryl-3-pyrazolin-5-ones. ^{679, 849, 984, 988, 1001} The acyl group is lost in the cyclization and these products have no N-1 substituent. Formyl-, acetyl- and benzoylhydrazines may be used. This is a very frequently employed method for preparation of 2-aryl-3-pyrazolin-5-ones. The condensing agents generally used have been phosphorus trichloride, phosphorus oxychloride and phosphorus pentachloride. A modification of this, also mentioned earlier, has been the condensation of a symmetrically substituted hydrazine with a β -ketoester to give 1,2-disubstituted-3-pyrazolin-5-ones. ^{54, 370} The sub-

stituents on N-1 and N-2 may be both alkyl or both aryl, although very few 1,2-diaryl-3-pyrazolin-5-ones are known.

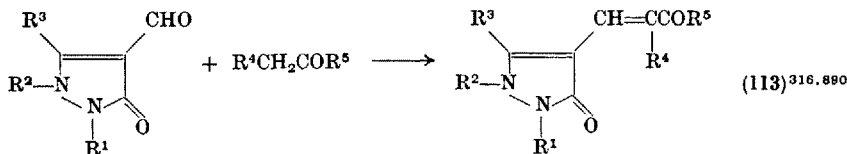
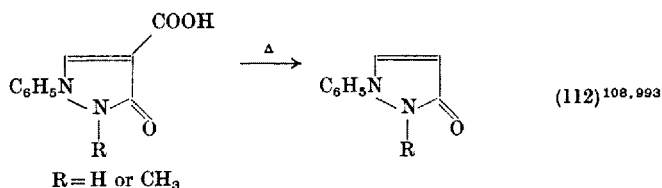
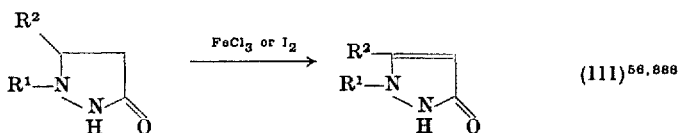
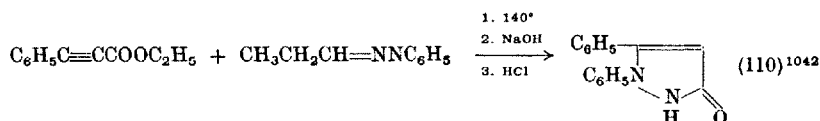
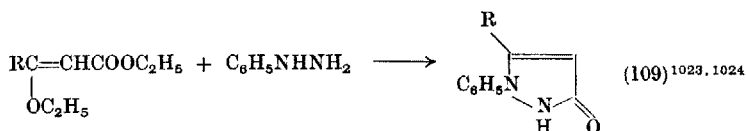
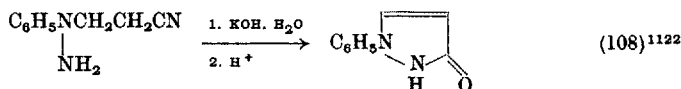
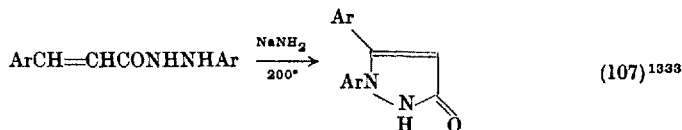
A large number of other syntheses of 3-pyrazolin-5-ones have been reported, although most are not of importance as practical methods of preparation. These are illustrated in eqs. 101-113.



Lecher, Parker and Conn⁸⁸⁵ report that the cyclization of the hydrazone hydrazone, as in eq. 106, is the preferred synthesis for 2-aryl-3-methyl-3-pyrazolin-5-ones.

A number of 4-heterocyclic-3-pyrazolin-5-ones have been prepared using the appropriate 4-substituted pyrazolinone in the usual reactions

to form the particular heterocyclic ring. For example, 4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one has been condensed with 1,4-diketones to form pyrazolinones substituted by pyrroles.⁴⁵² Isatin has



been used in the Pfitzinger reaction with 4-acetyl-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one to give pyrazolinones substituted by quinolines.⁹⁰³

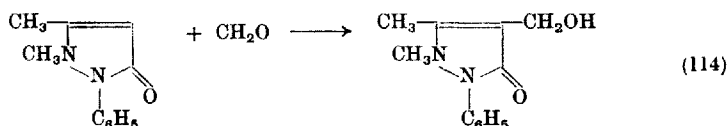
(2) Properties

Like the 2-pyrazolin-5-ones, most of the 3-pyrazolin-5-ones are solids with a wide range of melting points. Among the 3-pyrazolin-5-ones having only alkyl, heterocyclicalkyl and aryl substituents a number having four substituents are very high boiling liquids. Those having fewer substituents are all solids, as are those substituted by aralkyl and heterocyclic groups. Solubility varies greatly and no generalizations can be made.

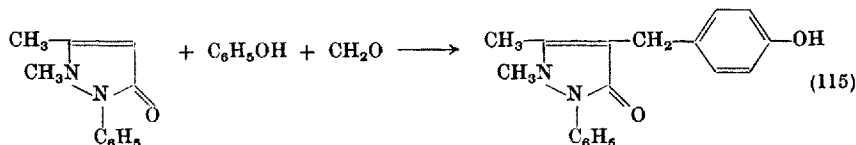
In contrast to the 2-pyrazolin-5-ones, the 3-pyrazolin-5-ones are basic, but usually are not acidic⁸⁰⁷ or only very weakly so.¹⁵²⁴ It does appear that 3-pyrazolin-5-ones having no N-1 substituent are more acid than those substituted at N-1,⁸⁸⁵ presumably because they can tautomerize to the lactim structure (XIII). The basic nature of 3-pyrazolin-5-ones is demonstrated by their ability to form stable hydrochlorides, picrates, methiodides and other salts.^{801, 818, 984} The infrared and ultra-violet absorption of 3-pyrazolin-5-ones has been discussed previously in connection with the structures of these compounds.

The vast majority of reactions undergone by 3-pyrazolin-5-ones occur at the 4-position. These pyrazolinones react by direct substitution, very much as do activated benzene rings. Such reactions as halogenation, nitrosation, sulfonation, acylation, the Mannich reaction and many others give 4-substituted-3-pyrazolin-5-ones.

3-Pyrazolin-5-ones react with formaldehyde to give 4-hydroxymethyl-3-pyrazolin-5-ones (eq. 114).¹⁷ In the presence of phenols

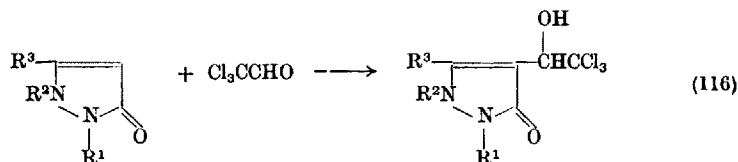


further condensation occurs, forming 4-benzyl-3-pyrazolin-5-ones (eq. 115).^{20, 21} The phenol condenses in the para position. A similar reaction occurs with dialkylanilines.¹⁴⁸³ The Mannich reaction is also a reaction

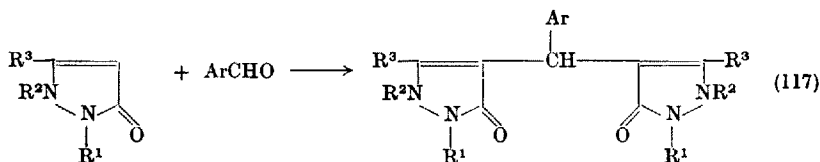


with formaldehyde, but in the presence of amines and is readily undergone by 3-pyrazolin-5-ones. With aliphatic amines the products are 4-dialkylaminomethyl-3-pyrazolin-5-ones,^{110, 637, 945} but aniline gives a

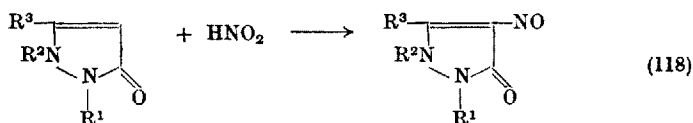
4-arylaminomethyl derivative.¹⁴⁸³ When methylaniline is used a bispyrazolinone is also obtained by reaction at the amino group and at the 4-position of the aromatic ring.¹⁴⁸³ Hydroxylamines react analogously to dialkylamines with 3-pyrazolin-5-ones and formaldehyde.¹⁴⁸² Reactions of 3-pyrazolin-5-ones with chloral^{902, 1190} are entirely analogous to their reactions with formaldehyde. This is illustrated in eq. 116. The reaction of aromatic aldehydes with 3-pyrazolin-5-ones is



analogous to the reaction of such aldehydes with 2-pyrazolin-5-ones, except that the products are always bispyrazolinones,^{21, 809, 988, 992} as shown in eq. 117.



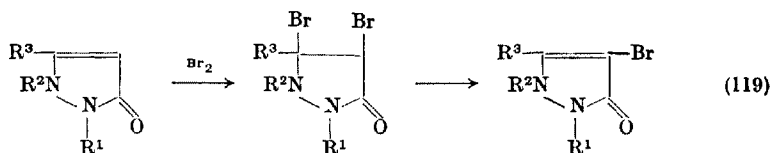
Nitrosation of 3-pyrazolin-5-ones is quite easy, commonly occurring in the 4-position (eq. 118). The usual reagent is nitrous acid,^{145, 781, 809, 860, 984, 992, 1174} prepared *in situ* by the use of sodium



nitrite and acid. However, nitrogen trioxide has also been used successfully.¹⁰⁰¹ If a substituent is present in the 4-position and the 3-position is vacant, nitrosation occurs to give a 3-nitroso-3-pyrazolin-5-one.⁹⁷²

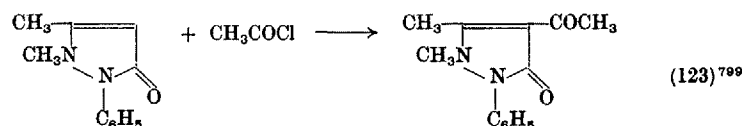
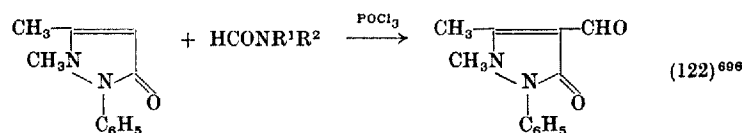
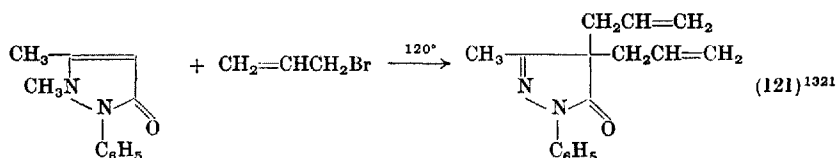
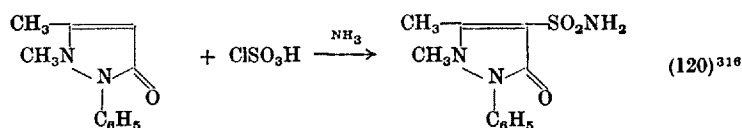
Halogenation of 3-pyrazolin-5-ones with elemental chlorine, bromine, and iodine occurs readily to form the corresponding halogenated compounds.^{540, 809, 988, 1001, 1056} In the case of bromine, addition frequently occurs to give the 3,4-dibromo derivatives (eq. 119) which lose hydrogen bromide very readily and the usual product is the 4-bromo-3-pyrazolin-5-one.^{809, 818, 1024, 1320} Various other agents also react with 3-pyrazolin-5-ones to introduce halogen at C-4. Chlorination occurs with sodium hypochlorite⁷⁹⁵ and phosphorus pentachloride.¹⁰⁰¹

N-Bromosuccinimide brominates 3-pyrazolin-5-ones but an excess brominates alkyl groups in the 3-position.^{362,899} Iodination occurs by treatment of 3-pyrazolin-5-ones with mercuric chloride followed by iodine.¹⁰⁰¹



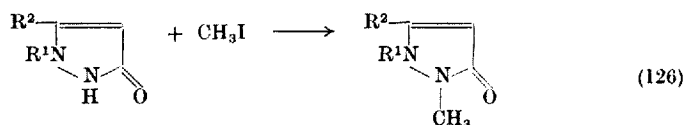
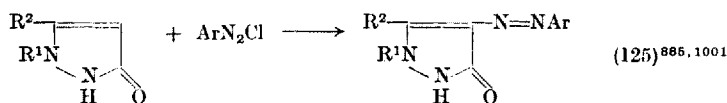
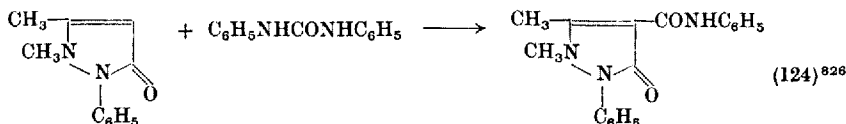
3-Pyrazolin-5-ones react with concentrated nitric acid^{809,860,888,992,1001} or an excess of nitrous acid^{984,992,1001} to form 4-nitro-3-pyrazolin-5-ones. Presumably the excess of nitrous acid first nitrosates and this product is oxidized to the nitro compound.

A variety of miscellaneous reactions which occur by substitution at C-4 are illustrated in the following equations. None of these reactions

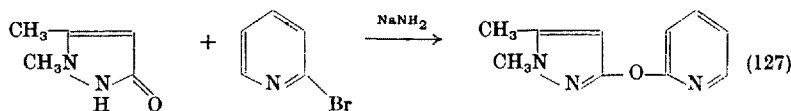


has been used, or investigated, extensively. Benzyl chloride has also been used in reaction (121) and only one benzyl moiety is introduced. Reaction (125) may also give 3-substitution if the 4-position is blocked.⁹⁷²

Those 3-pyrazolin-5-ones which have no N-1 substituent can be alkylated at this position by use of methyl iodide in methanol^{888, 988} or dimethyl sulfate (eq. 126).¹⁰⁰¹ *O*-Methylation occurs as a side-

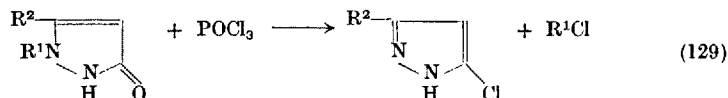
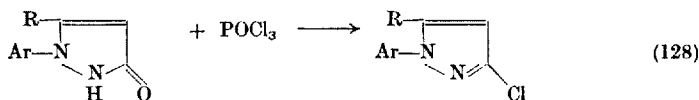


reaction. Krohs⁸⁶⁰ has reported that halogenated pyridines, pyrimidines and thiazoles in the presence of sodamide react with the oxygen rather than the nitrogen (eq. 127). An analogous reaction occurs between such



3-pyrazolin-5-ones and benzenesulfonyl chloride and acyl chlorides to give *O*-acylpyrazoles.^{988, 1001}

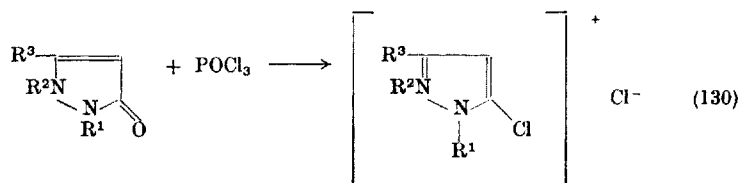
The reaction of phosphorus oxychloride with 3-pyrazolin-5-ones is rather similar to the reaction with 2-pyrazolin-5-ones in that oxygen is replaced by halogen. In those cases in which there is no substitution at N-1 and aryl substitution occurs at N-2, chloropyrazoles are formed,



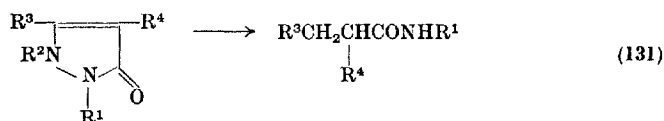
as shown in eq. 128.^{984, 988, 1001} This reaction takes a different course when the N-2 substituent is alkyl or aralkyl.^{700, 795} In these cases the N-2 substituent is eliminated (eq. 129). In cases in which both nitrogen

atoms are substituted, the 3-pyrazolin-5-one is converted to a quaternary salt of a 5-chloropyrazole (eq. 130).⁷⁸⁹

The 3-pyrazolin-5-one ring is stable to mild catalytic reductions, such as reduction with low pressure hydrogen in the presence of platinum or palladium catalyst.^{532, 860} However, under extremely drastic conditions, hydrogen at a pressure of 1000 atmospheres and a tem-

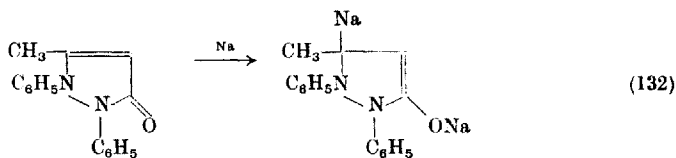


perature of 180° and nickel catalyst, ring cleavage occurs⁸⁵⁹ with elimination of one nitrogen atom and formation of anilides (eq. 131).



Hot acid destroys the ring system of 3-pyrazolin-5-ones.^{700, 807} Various products have been reported from this reaction, depending upon substituents in the pyrazolinone ring and conditions. Destruction of the 3-pyrazolin-5-one ring system with base⁷⁰⁰ leads to a β -ketoanilide.

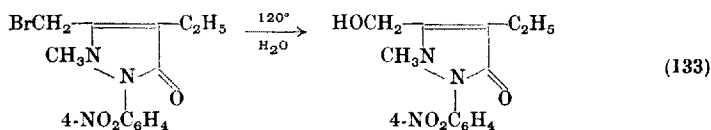
The reaction of zinc with 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one has been reported by Knorr⁸⁰⁷ to give benzene, aniline and unidentified products. Heymons and Rohland⁶⁴⁷ treated 1,2-diphenyl-3-methyl-3-pyrazolin-5-one with metallic sodium, obtaining addition of sodium at the 1,4-position of the conjugated system present (eq. 132).



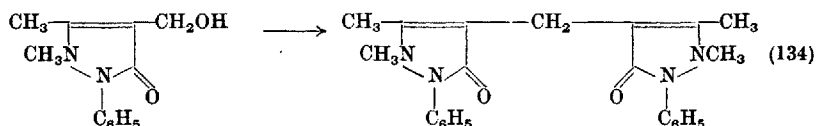
The compounds discussed in the previous sections are listed in Sections A, B, C, and D of Table XIV.

3-Pyrazolin-5-ones having 3- and 4- α -hydroxyalkyl substituents are prepared in a number of ways. Two of these, alkylation of the corresponding 2-pyrazolin-5-one at N-2 and reaction of 3-pyrazolin-5-ones with aliphatic aldehydes, have already been mentioned. The

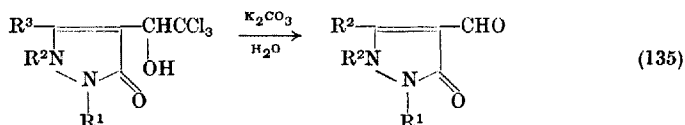
reduction of 4-acyl substituents will be discussed in the section dealing with such 3-pyrazolin-5-ones. A fourth method used has been the hydrolysis of 3-bromomethyl-3-pyrazolin-5-ones at elevated temperatures (eq. 133).^{532, 697} The reactions of these compounds are those of



alcohols and esters and of 3-pyrazolin-5-ones, except for a few special ones. 4-Hydroxymethyl-3-pyrazolin-5-ones in mild acid solution form 4,4'-bis(3-pyrazolin-5-ones) (eq. 134).⁹⁷⁰ The alcohols obtained by con-

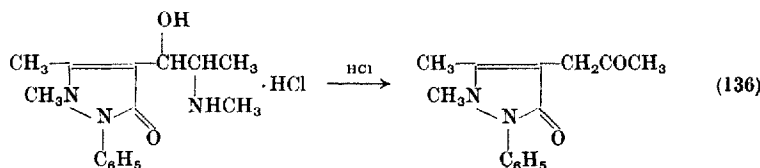


densing chloral with 3-pyrazolin-5-ones decompose in the presence of potassium carbonate to give the corresponding 4-carboxaldehydes (eq. 135).^{107, 196, 889} This is the principal method used for preparation



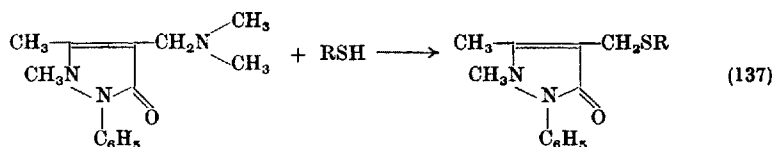
of such aldehydes. These compounds are listed in Table XIV, Section E.

Bodendorf and Ziegler¹¹³ have reported the conversion of a 4-(1-hydroxy-2-methylaminopropyl)-3-pyrazolin-5-one into a 4-(2-oxopropyl)-3-pyrazolin-5-one in the presence of acid (eq. 136).

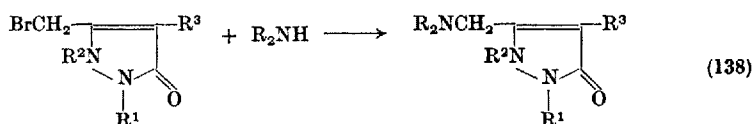


Only a few α -alkylthiomethyl-3-pyrazolin-5-ones are known.¹¹²⁷ These have been prepared by reaction of mercaptans with 4-dimethylaminomethyl-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (eq. 137). These compounds are listed in Table XIV, Section E.

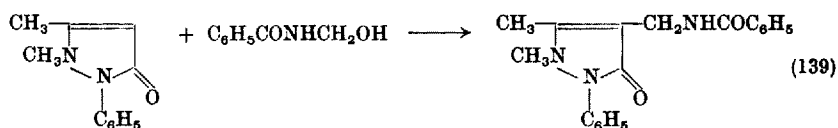
The most frequently used method of preparation of compounds having nitrogen attached to a carbon atom which is substituted on the 3-pyrazolin-5-one ring is reaction of hydroxylamine, amines, hydrazines, hydrazides, etc., with 5-oxo-3-pyrazolin-4-carboxaldehydes.



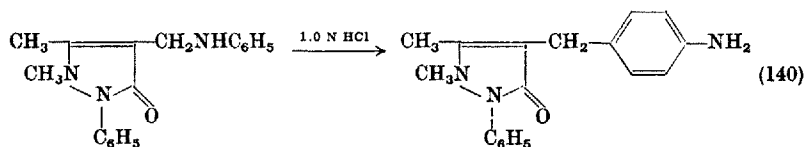
This will be discussed in more detail in the section devoted to the reactions of the 4-carboxaldehydes. A frequently used method for preparing 4-dialkylaminomethyl-3-pyrazolin-5-ones is the Hoffmann method for preparing amines (eq. 138).^{697, 1318, 1319} A rather interesting



synthesis of 4-benzamidomethyl-3-pyrazolin-5-ones has been published by Monti.¹⁰¹⁴ *N*-Methylolbenzamide was condensed with 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (eq. 139).

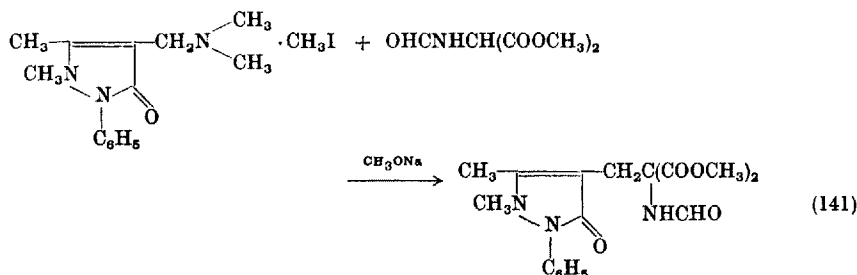


The reactions of these compounds are for the most part normal for such functional groups. The only unusual one reported is the rearrangement shown in eq. 140.^{110, 1483} Hellmann and Schumacher⁶³⁸ have



reported that 4-dimethylaminomethyl-3-pyrazolin-5-ones can react as alkylating agents. Nitro- and formamidomalonic esters react with these

pyrazolinones by elimination of dimethylamine and introduction of the 5-oxo-3-pyrazolin-4-methyl system into the malonic ester (eq. 141).

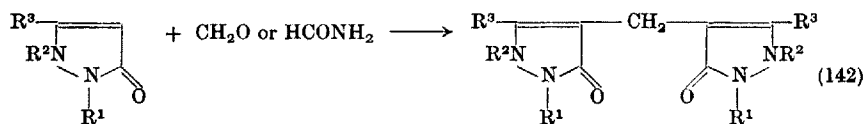


This reaction is quite analogous to such alkylations with gramine. These compounds are listed in Table XIV, Section F.

(3) *Bis(3-pyrazolin-5-ones)*

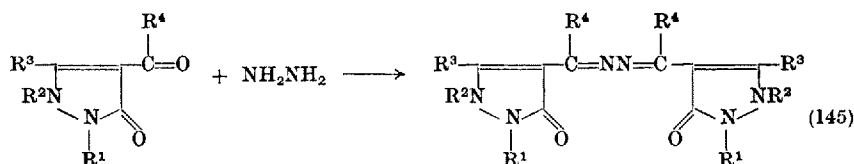
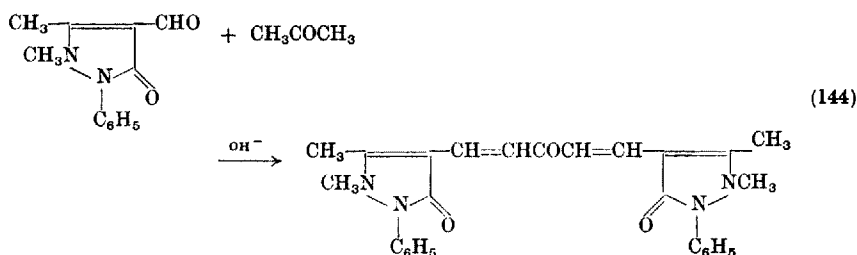
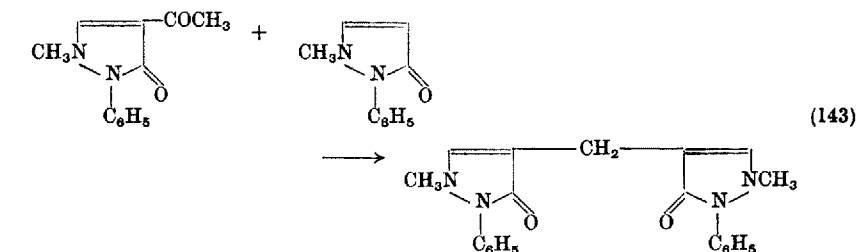
Only a very few 4,4'-bis(3-pyrazolin-5-ones) are known in which the rings are linked directly. These are prepared by methylation of 4,4'-bis(2-pyrazolin-5-ones)^{807, 809} or by treatment of the methiodides of 4-(5-chloropyrazol-4-yl)-3-pyrazolin-5-ones with alkali.⁹⁹¹ These compounds are listed in Table XV.

Bis(3-pyrazolin-5-ones) in which the linking chain is not attached to the pyrazolinone nucleus by functional groups are listed in Tables XVI and XVII. Most of these compounds have as the linking chain an arylidene group and are prepared by the reaction of 3-pyrazolin-5-ones with aryl aldehydes,^{566, 568, 569, 807, 1001, 1133} as shown in eq. 117 (p. 50). Some aliphatic aldehydes have also been used in this reaction.⁴⁰⁹ 3-Pyrazolin-5-ones react with formaldehyde or formamide to form the corresponding bis compounds (eq. 142).^{910, 1192} Under basic conditions

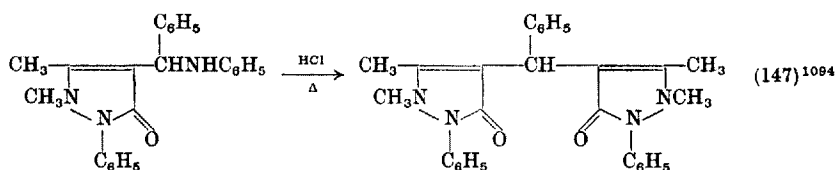
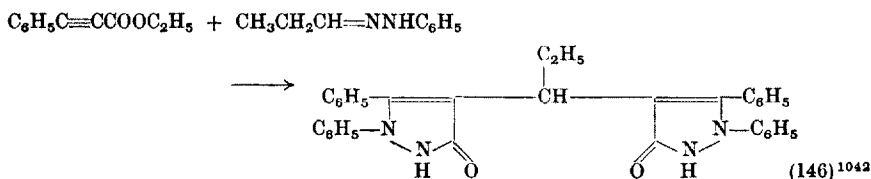


4-hydroxymethyl-3-pyrazolin-5-ones condense to form bispyrazolinones (eq. 134),^{107, 481, 896} apparently by partial elimination of the 4-hydroxymethyl group and the condensation of this product with unchanged starting material. Bis(2-pyrazolin-5-ones) can be converted into the corresponding 3-pyrazolin-5-ones by alkylation at N-2,¹¹⁶ as is done so frequently in the mononuclear series. 4,4'-Methylenebis(3-pyrazolin-5-ones) have been prepared by reduction of the corresponding ketone with

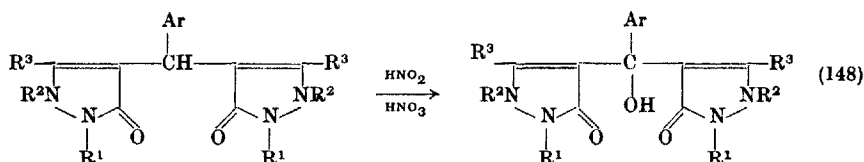
zinc and acid.⁷⁴⁰ A variety of 3-pyrazolin-5-ones having a 4-acyl substituent react with various reagents to form bis(3-pyrazolin-5-ones).^{316,799,902} These preparations are illustrated in eqs. 143–145. The



Mannich reaction using primary amines, when applied to 3-pyrazolin-5-ones, forms bispyrazolinones.⁹⁴⁵ Two more preparations of such compounds are shown in eqs. 146 and 147.

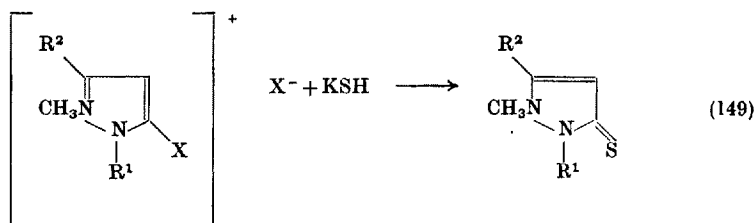


Very little investigation of the reactions of bis(3-pyrazolin-5-ones) has been done, but presumably the typical reactions occurring at C-4 in the mononuclear compounds would not occur. Ginzburg and co-workers^{568,568,569} have published a number of papers concerned with oxidation of 4,4'-arylidenebis(3-pyrazolin-5-ones). A mixture of nitrous and nitric acids was used as the oxidant and the tertiary carbon atom connecting the pyrazolinone rings was oxidized to a carbinol (eq. 148). Pyrolysis of 4,4'-(4-dimethylaminobenzylidene)bis(2,3-dimethyl-1-phenyl-3-pyrazolin-5-one) in the presence of carbon dioxide at 175–180° has been reported¹¹³³ to cause loss of hydrogen.



E. 3-Pyrazolin-5-thiones and -5-selenones

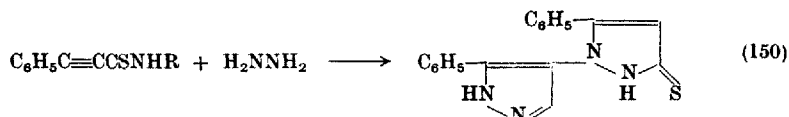
A large number of 3-pyrazolin-5-thiones and a few 5-seleno analogs (Table XVIII) have been prepared. Almost all of these have been synthesized by reaction of the methochloride or methiodide of a 3- or 5-halogenated pyrazole with potassium hydrogen sulfide,^{844, 984, 986, 988, 992} potassium sulfide, sodium sulfide⁹⁸¹ or potassium hydrogen selenide.⁹⁸⁶ This method of synthesis is illustrated in eq. 149 for a 5-halopyrazole.



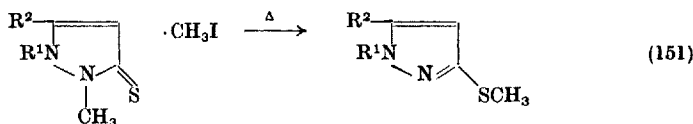
In one case the substituents on the nitrogen atoms were both phenyl.⁷⁸⁹ Two other methods of synthesis of the 3-pyrazolin-5-thiones have been reported. Michaelis⁹⁹² has claimed the conversion of 1,2-dimethyl-3-phenyl-3-pyrazolin-5-one to the thione analog by reaction with potassium hydrogen sulfide. Worrall¹⁶⁵³ has reported the synthesis shown in eq. 150.

Although comparatively little has been published concerning the properties and reactions of 3-pyrazolin-5-thiones and -5-selenones, it is apparent that in general they are very similar to the comparable oxo

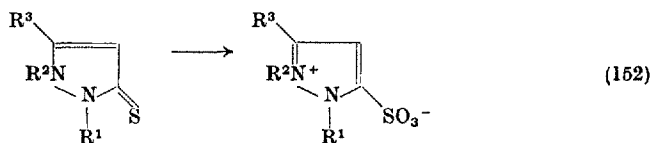
compounds. These compounds are basic, forming stable salts with mineral acids.^{978, 984, 988} They undergo nitration at C-4 and presumably would react similarly in other electrophilic substitutions. Reaction with



halogens gives a perhalide having four atoms of halogen per molecule of pyrazolinone.^{988, 992} These then lose halogen readily to leave a dihalo derivative, which is probably the corresponding 4,5-dihalo-3-pyrazolidinethione or -3-pyrazolidineselenone. Alkylation of the sulfur or selenium atom occurs by heating the methiodide (eq. 151)^{984, 988, 992} or other



alkyl iodides. The 3-pyrazolin-5-thiones are capable of oxidation at the sulfur atom and several such oxidation products have been reported. Kitamura^{785, 789} has found that oxidation of 2,3-dimethyl-1-phenyl-3-pyrazolin-5-thione with hydrogen peroxide gives 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one. Komada⁸⁴⁵ has oxidized the same compound with chlorine, hydrogen peroxide, sodium hypochloride and perbenzoic acid to give what was called a dioxide, the structure of which was not reported. The oxidation of various 3-pyrazolin-5-thiones with peroxide^{785, 789} or with chlorine^{978, 985, 988, 1001} gives what was called a trioxide. It is possible that this is a zwitterion as shown in eq. 152. A

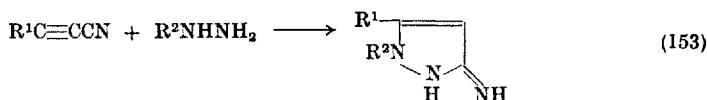


few 5-oxo-5'-thiono-, 5,5'-thiono- and 5,5'-selenobis(3-pyrazolines) have been prepared by methods used for the mono compounds and they are listed in Table XV.^{785, 986, 991}

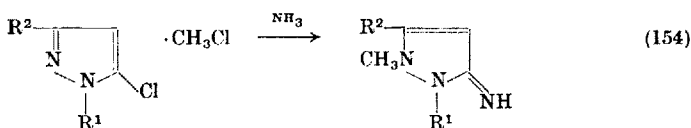
F. 5-Imino-3-pyrazolines

A number of 5-imino-3-pyrazolines are known and are listed in Table XIX. Those which have no substituent at N-1 can exist as

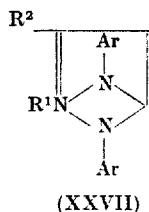
aminopyrazoles and probably are in this tautomeric form. Most preparative methods for these compounds depend upon conversion of chloropyrazoles or 3-pyrazolin-5-ones to 5-imino-3-pyrazolines, although they can be formed directly from noncyclic compounds. This is shown in eq. 153.¹⁰²⁵ Michaelis has prepared 5-imino-3-pyrazolines by



reaction of the methochlorides of chloropyrazoles with ammonia or amines (eq. 154).^{985, 996, 1352} From an analogous reaction with aryl-

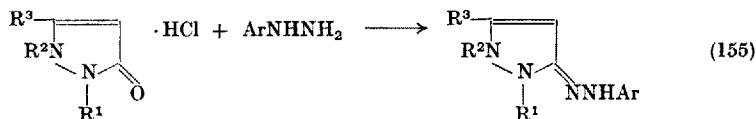


amines Michaelis¹⁰⁰² suggested that the products were of the type (XXVII). It seems much more likely that these were 5-arylimino-3-

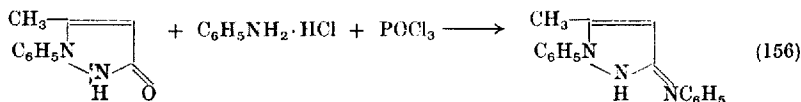


pyrazolines. 5-Imino-3-pyrazolines can also be prepared by treatment of 5-imino-2-pyrazoline methiodides with sodium hydroxide.⁹⁹⁶

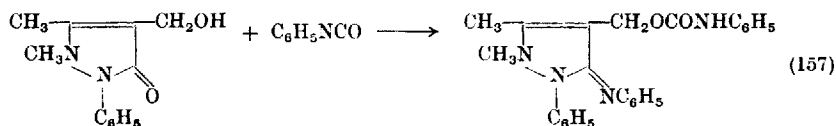
3-Pyrazolin-5-one hydrochlorides react with hydrazines at about 100° to form 5-imino compounds (eq. 155).⁹⁸³ A similar reaction has



been reported for 3-pyrazolin-5-thiones.¹⁶⁵³ Other syntheses are shown in equations 156⁸²⁶ and 157.⁴⁰² Very little has been published concerning reactions and properties of these compounds.



A few 5-imino- and 5,5'-iminobis(3-pyrazolines) are listed in Table XV. These are prepared by reaction of the appropriate chloropyrazole methiodide with ammonia.⁹⁹¹

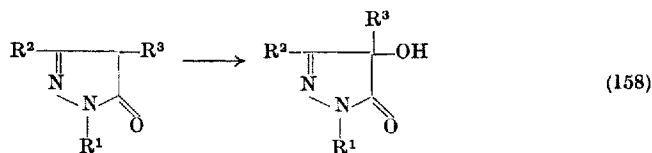


3. Hydroxy and Mercapto Derivatives

A. 2-Pyrazolin-5-ones

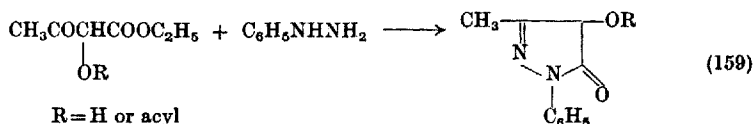
Both 3-hydroxy- and 4-hydroxy-2-pyrazolin-5-ones can exist theoretically and quite a number of 4-hydroxy compounds are known. The 3-hydroxy-2-pyrazolin-5-ones are tautomeric with 3,5-pyrazolidinediones which probably exist principally as the 3-hydroxy isomers. However, for the purposes of this discussion these compounds will be considered as diones.

The most widely used and certainly most general procedure for preparation of 4-hydroxy-2-pyrazolin-5-ones is that developed by Veibel, Linholt and Westoo.¹⁵²⁵⁻¹⁵²⁸ Usually oxidations of 2-pyrazolin-5-ones lead to formation of bispyrazolinones. These workers found that oxidation of 1-substituted-2-pyrazolin-5-ones in alkaline solutions gave very good yields of the 4-hydroxy analogs (eq. 158). Oxidizing agents

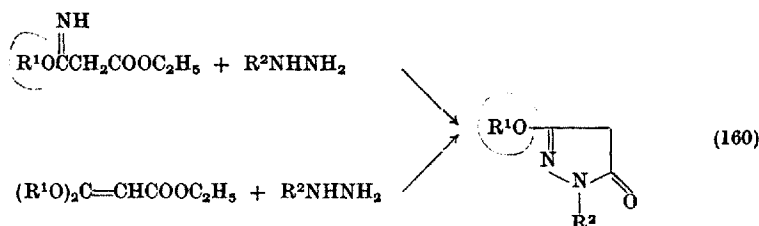


used were hydroperoxides and oxygen. Acid media were also found to suppress the formation of bis(2-pyrazolin-5-ones). Various other methods have been used for preparation of 4-hydroxy-2-pyrazolin-5-ones but none extensively. Thoms and Schmupp¹⁴⁹¹ have used catalytic reduction of 2-pyrazolin-4,5-diones. The 4-oxo group is reduced to hydroxyl in preference to other unsaturated centers. Bülow and Haas,²⁶² in reducing 4-phenylazo- and 4-nitro-2-pyrazolin-5-ones with zinc and acetic acid, obtained as side-products 4-hydroxy-2-pyrazolin-5-ones. The oxidation of 4,4'-bis[3-methyl-1-(4-nitrophenyl)-2-pyrazolin-5-one] with ferric chloride forms the corresponding mononuclear 4,4'-di-hydroxy compound.⁶⁹⁰ The condensation of α -acyloxy- β -ketoesters with

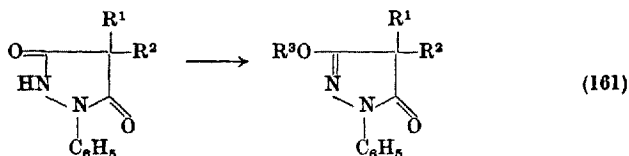
an equivalent of phenylhydrazine gives rise to a 4-acyloxy-pyrazolinone, but excess phenylhydrazine forms the 4-hydroxy analog (eq. 159).³⁷²



3-Alkoxy-2-pyrazolin-5-ones have been prepared by two methods. In one of these a hydrazine is condensed with a β -substituted ester (eq. 160).^{598, 1143} The second is *O*-alkylation of a 4,4-disubstituted-1-

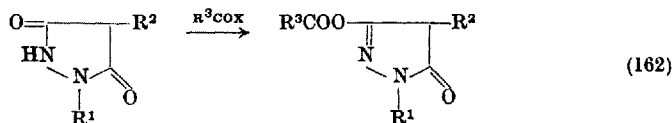


substituted-3,5-pyrazolidinedione (eq. 161). The reagents used have



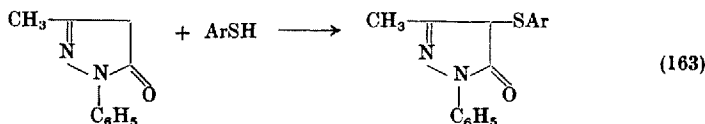
been diazomethane⁴¹ and methyl iodide and potassium hydroxide.⁹⁹⁴ With diazomethane *N*-alkylation also occurs. The only example with an alkoxy group in the 4-position found in the literature is 4-hydroxy-4-methoxy-3-methyl-1-(4-nitrophenyl)-2-pyrazolin-5-one, obtained by repeated crystallization of the corresponding 4,4-dihydroxy compound from methanol.⁶⁹⁰

One method of preparing acyloxy-2-pyrazolin-5-ones has already been mentioned (eq. 159). The second method is acylation of 3,5-pyrazolidinediones having no *N*-2 substituent (eq. 162). The acylations



have been achieved by use of acetic anhydride,¹²³⁴ benzoyl chloride⁹⁹⁸ and by trans-esterification.²⁰⁰

A number of 4-arylmercapto-2-pyrazolin-5-ones have been prepared by reaction of a 2-pyrazolin-5-one with aryl mercaptans (eq. 163).^{27,28} It was concluded that the first reaction was oxidation of the



mercaptan to a disulfide which then reacted with the pyrazolin-5-one. In support of this theory it was found that disulfides give the same reaction. The same types of compounds were also prepared by reaction of 4-bromo-3-methyl-1-phenyl-2-pyrazolin-5-one with the sodium salts of various mercaptans.^{27,28} Takahashi and Yoshii¹⁴⁷⁴ have treated 6-ethoxy-5-methyl-6-carbethoxypyrido-[2,3:2',3']-*p*-thiazine with hydrazine and obtained a 4-arylmercapto-2-pyrazolin-5-one. This is scarcely a practical synthetic method. α -Arylmercapto- and α -acylmercaptoacetoacetic esters react with hydrazines to give sulfur-containing substituents at C-4.²⁷

This group of compounds is listed in Table XX.

A few bis(2-pyrazolin-5-ones) having alkoxy substituents are known and are listed in Table III. These are prepared by addition of alcohols to the double bond connecting the pyrazolinone rings in pyrazole blue.

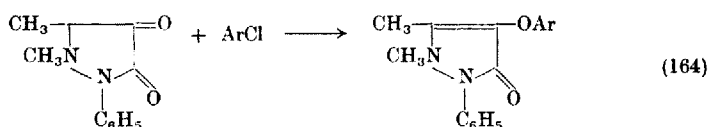
A few 4,4'-bis(2-pyrazolin-5-ones) in which the rings are linked by sulfur atoms are known. The linking group is almost always disulfide and is prepared by oxidation of 2-pyrazolin-5-ones substituted in the 4-position with mercaptoaryl groups.⁵⁷⁸ These compounds are listed in Table VII.

The few 3-acyloxy-5-imino-2-pyrazolines known are prepared by acylation of 5-imino-3-pyrazolidinones.^{391,594,1599} Crippa and Gaudmeri³² have treated 3-methyl-1-phenyl-5-imino-2-pyrazoline with *p*-nitrophenylsulfenyl chloride to obtain a 4-arylmercapto compound. These compounds are listed in Table XII.

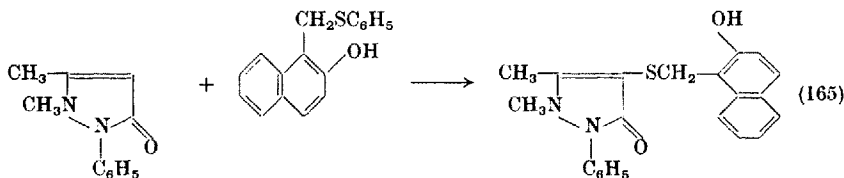
B. 3-Pyrazolin-5-ones

The two possible hydroxy-3-pyrazolin-5-ones (3-hydroxy and 4-hydroxy) are isomeric with pyrazolidinediones, the former with 3,5-pyrazolidinediones and the latter with 3,4-pyrazolidinediones. In conformity with the usage of this discussion the hydroxy-3-pyrazolin-5-ones will be considered as the isomeric diones. However, the derivatives of the hydroxyl groups will be considered in this section. Konek

and Szasz⁷⁸³ have methylated 4-acyloxy-3-methyl-1-phenyl-2-pyrazolin-5-ones at N-2 with methyl iodide to give the 4-acyloxy-3-pyrazolin-5-ones. Treatment of 3,5-pyrazolidinediones having no substituent at the 4-position with diazomethane has been used by Arndt and co-workers⁴¹ to give 3-methoxy-3-pyrazolin-5-ones. It is necessary to have a 2-substituent. 3-Acyloxy-3-pyrazolin-5-ones have been prepared in a similar fashion by acylation of 3,5-pyrazolidinediones.^{200, 1048} A number of 4-acyloxy-3-pyrazolin-5-ones have been synthesized by the reaction of 2,3-dimethyl-1-phenyl-3,4-pyrazolidinedione with various chlorinated aromatic compounds (eq. 164). The halogen in the aromatic halide was

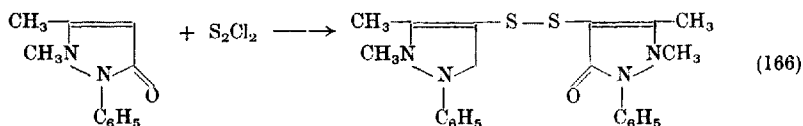


usually quite active, for example picryl chloride. The preparation of sulfur analogs of these compounds according to eq. 165 has been



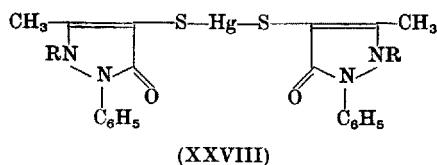
reported by Poppelsdorf and Holt.¹¹²⁷ These compounds are listed in Table XXI. The only bis(3-pyrazolin-5-one) having alkoxy or aryloxy substituents has been prepared as shown in eq. 164, except that a disubstituted aromatic compound was used.⁷⁴⁴ This compound is included in Table XVI.

Bis(3-pyrazolin-5-ones) having the 4,4'-positions connected by a disulfide bridge have been prepared by the action of sulfur dichloride on 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (eq. 166).^{8, 848} The same



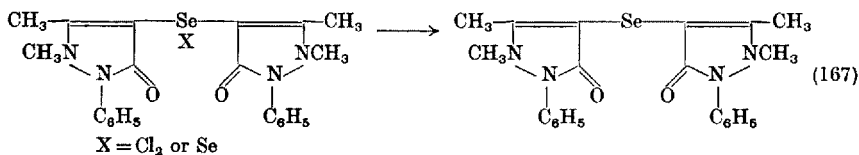
type of compound is formed as a by-product in the reaction of 4-bromo-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one with potassium thiocyanate to form the 4-thiocyano compound⁷⁴² and also by treatment of the 4-thiocyano compound with acid, base or heat.⁷⁴² The disulfides shown as

products in eq. 166 have been reported by Konek⁸⁴⁸ to react with mercury to give products of the type (XXVIII). A few bis(3-pyrazolin-



5-ones) in which the pyrazolinone rings are linked by selenium in the 4,4'-positions are known. Preparation of these is by the reaction of mono-3-pyrazolin-5-ones with selenium,⁵⁴⁵ selenium dioxide,⁵⁴⁵ selenium dichloride⁸⁵⁰ or selenium tetrachloride.⁸⁵⁰ In the first two cases the bridge is one selenium atom; in the third there is a mixture of selenide

and a two-atom bridge of the type $\begin{array}{c} \text{---Se---} \\ \downarrow \\ \text{Se} \end{array}$. In the last case the bridge is a dichloroselenide function. These last two types of bridge systems



can be converted into monoselenides by base, acid or heat treatment (eq. 167). These bispyrazolinones are listed in Table XVI.

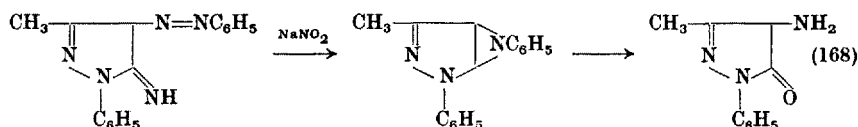
4. Amino, Imino, Hydrazino, Azo and Related Derivatives

A. 2-Pyrazolin-5-ones

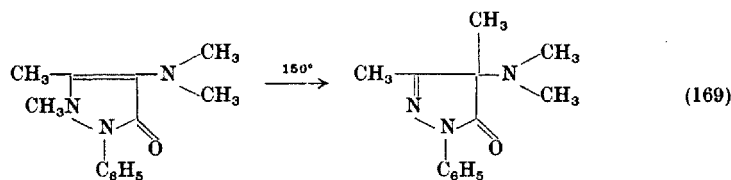
All functional groups having nitrogen attached to the pyrazolinone nucleus are considered in this section except nitroso, nitro and some oximes. Only those oximes which cannot be considered as tautomeric with the nitroso group are discussed here. Hydrazones are in this section. These compounds are listed in Tables XXII and XXIII.

All of these derivatives of 2-pyrazolin-5-ones have a nitrogen atom substituted at the 4-position as the 3-nitrogen-substituted-2-pyrazolin-5-ones are tautomeric with the 5-imino-3-pyrazolidinones and are considered as such in this discussion. The 4-nitrogen-substituted-2-pyrazolin-5-ones are not usually prepared by cyclization directly to the desired pyrazolinone ring but rather by modification of already formed pyrazolinones. The methods used are usually those employed in

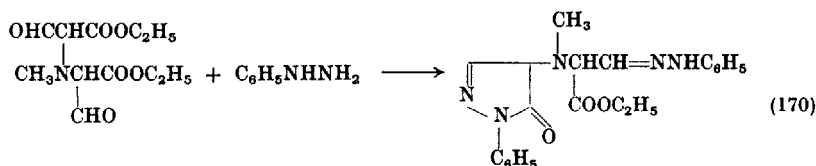
preparing such derivatives in aliphatic or aromatic compounds. For example, 4-amino-2-pyrazolin-5-ones in which the amine is primary are prepared by reduction of 4-oximino-, 4-nitro- or 4-azo-2-pyrazolin-5-ones. For the reduction of oxime^{52, 992} and nitro-groups^{478, 480} stannous chloride has been commonly used. Azo compounds have been reduced catalytically with hydrogen⁶⁷⁰ and with a zinc and acid mixture.³⁹⁷ Michaelis and co-workers⁹⁹⁶ have reported the oxidation of 4-phenylazo-3-methyl-1-phenyl-5-imino-2-pyrazoline to a fused pyrazolinone-azirane system as shown in eq. 168 and subsequent



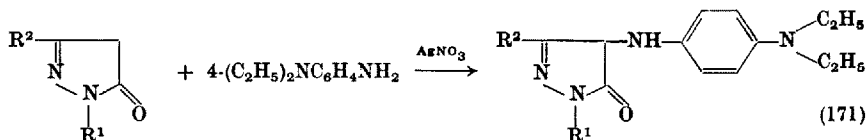
reduction of this to the 4-amino-2-pyrazolin-5-one which was isolated only as its oxidation product, rubazonic acid. The structure proposed for the intermediate seems most unlikely. Four methods have been reported for the direct preparation (i.e., with no amino intermediate) of secondary and tertiary 4-amino-2-pyrazolin-5-ones. Only one product has been synthesized by each of these routes. Maeda⁹³⁸ has heated 2,3-dimethyl-4-dimethylamino-1-phenyl-3-pyrazolin-5-one (aminopyrine) in the presence of salicylic acid or barbitol causing rearrangement of the 2-methyl substituent to the 4-position (eq. 169). In the



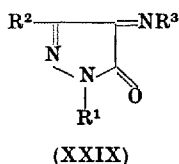
oxidation of 3-methyl-1-phenyl-2-pyrazolin-5-one with nitrobenzene Perroncito¹¹⁰⁷ has found that the principal product is the expected bispyrazolinone, but 4-anilino-3-methyl-1-phenyl-2-pyrazolin-5-one is also formed. This may occur through reaction of nitrobenzene reduction products formed by oxidation of some of the 3-pyrazolin-5-one. The cyclization of a tertiary amino β -aldehydoester to a pyrazolinone has been reported (eq. 170).¹⁵³⁷ Itano⁶⁹⁵ has used a method for preparation



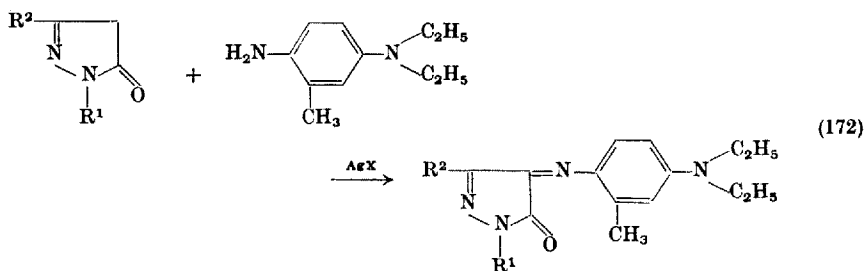
of such compounds that may be fundamentally the same as that of Perroncito, the reaction of an amine with a 2-pyrazolin-5-one in the presence of an oxidant (eq. 171).



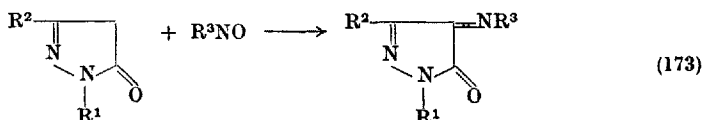
4-Imino-2-pyrazolin-5-ones of the type (XXIX) have become very important in the field of color photography and will be discussed in



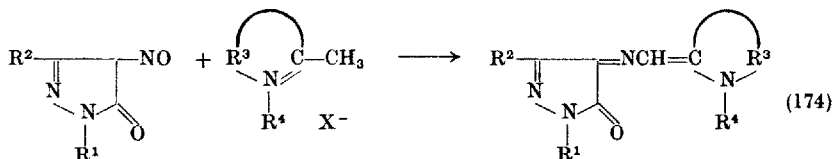
more detail in respect to this use. They have been particularly investigated at Eastman Kodak by Weissberger and Vittum who oxidized an alkaline solution of a 2-pyrazolin-5-one and 2-amino-5-diethylaminotoluene with silver nitrate or silver chloride (eq. 172) to obtain the



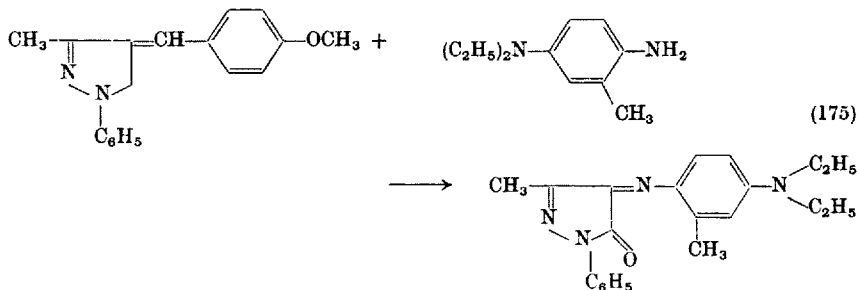
desired 4-iminopyrazolinones. Gerbeaux⁵¹⁹ has used the same procedure and in addition has used potassium ferricyanide and sodium hypochlorite as oxidizing agents. Mann and Haworth⁹⁴³ and Gerbeaux⁵¹⁹ have taken advantage of the active hydrogen atoms in the 4-position of 2-pyrazolin-5-ones for the preparation of the imino derivatives. Various aromatic nitroso compounds were condensed with 2-pyrazolin-5-ones (eq. 173). Brooker and White²⁴⁰ have prepared this same type



of compound by reaction of 4-nitroso (or oximino)-2-pyrazolin-5-ones with quaternary salts of heterocyclic compounds having active hydrogen on a methyl substituent (eq. 174). Similar products are obtained by

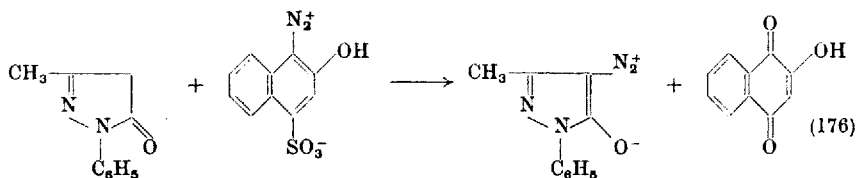


the reaction of 4-benzylidene-2-pyrazolin-5-ones with aromatic amines.¹²⁵⁵ The benzylidene group is replaced by an arylimino group (eq. 175).

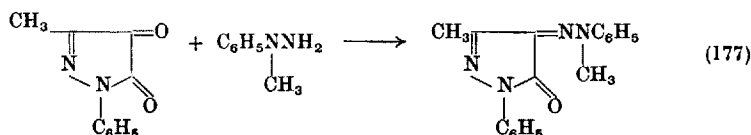


Synthesis of 4-amino-2-pyrazolin-5-ones is usually achieved by treatment of an α -amido- β -aldehyde- or β -ketoester with hydrazines according to the classical method for preparation of 2-pyrazolin-5-ones. Variants on this procedure consist of using an α -amidoester which has β -substituents whose reaction is equivalent to that of a β -carbonyl substituent. Such compounds are D-benzylpenicilloic acid α -methyl ester,¹⁰²⁷ ethyl phenylpenaldate²⁴³ and the acetal of an α -amido- β -formyl ester.^{59, 243} Cornforth has isomerized 2-phenyl-4-hydrazino-methylidyneoxazolidone to 4-benzamido-2-pyrazolin-5-one. The same compound was obtained by treatment of 1-ethoxyvinyl-2-phenyl-oxazolidone with phenylhydrazine.³¹⁹

The synthesis of 4-azo-3-methyl-1-phenyl-2-pyrazolin-5-one is shown in eq. 176.¹¹⁴⁴ The 4-hydrazones of 2-pyrazolin-4,5-diones have

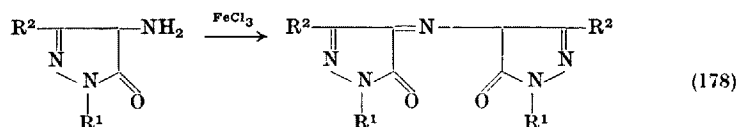


been prepared by Auwers and co-workers⁵² who used the reaction of a hydrazine with the 4,5-dione (eq. 177). This same compound was



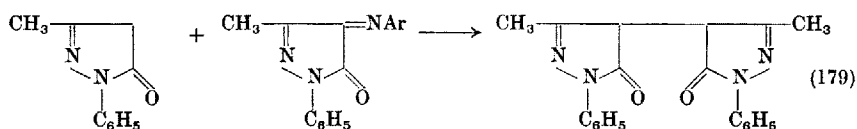
synthesized by methylation of 3-methyl-4-phenylazo-1-phenyl-2-pyrazolin-5-one and by cyclization of the bis(phenylmethylhydrazone) of ethyl α,β -diketobutyrate. These compounds are listed in Table XXI.

The 4-amino-2-pyrazolin-5-ones react as do other amines. They can be alkylated with alkyl halides⁹⁹² and react with aldehydes to form Schiff bases.^{633, 992} Oxidation of these amino compounds with ferric chloride leads to the rubazonic acids (eq. 178) in which two 2-pyrazolin-



5-one rings are connected at the 4,4'-position by nitrogen having no hydrogen.

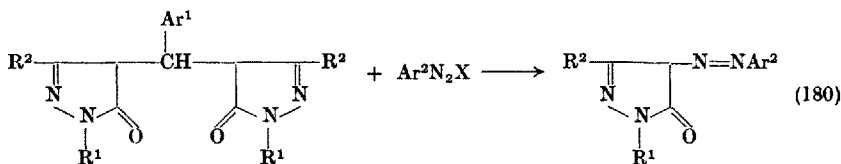
Rubazonic acid itself is 4-(3-methyl-1-phenyl-5-oxo-2-pyrazolin-4-ylideneamino)-3-methyl-1-phenyl-2-pyrazolin-5-one. 4-Arylimino-2-pyrazolin-5-ones are readily reduced to the corresponding 4-arylamino-2-pyrazolin-5-ones.¹⁵³⁸ 2-Pyrazolin-5-ones react with 4-arylimino-2-pyrazolin-5-ones to give bispyrazolinones (eq. 179).¹⁵³⁸



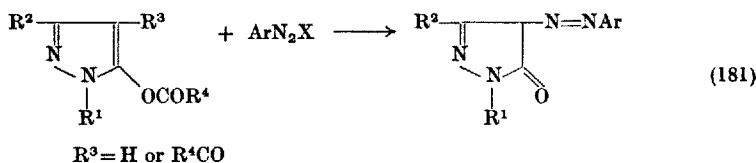
4-Arylazo-2-pyrazolin-5-ones are strongly colored and have good dyeing properties. These compounds have been prepared in vast numbers for use in dyeing all types of fabrics and are of great importance in the dye industry. They will be discussed fully from this viewpoint in the section dealing with pyrazolinone dyes. The 4-arylazo-2-pyrazolin-5-ones are listed in Table XXIII.

Of the many methods which have been used for preparing 4-arylazo-2-pyrazolin-5-ones by far the most important is the direct coupling of a diazonium salt with a 2-pyrazolin-5-one (eq. 41).^{77, 809, 813, 818, 980, 1251} This reaction goes extremely readily with

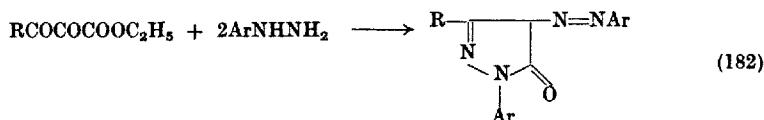
practically all 2-pyrazolin-4-ones having no 4-substituent. Coupling occurs with any aromatic amine capable of forming a diazonium salt and under a wide variety of conditions. Even 4-substituted-2-pyrazolin-5-ones have been reported to react with diazonium salts by replacement of the 4-substituent to form a 4-arylaazo-2-pyrazolin-5-one. Substituents replaced have been triarylmethyl,⁵⁶⁷ acyl⁵⁹¹ and halogen.¹⁵¹⁴ 4,4'-Arylidenebis(2-pyrazolin-5-ones) react with diazonium salts to form 4-arylaazo compounds (eq. 180).^{1255, 1351} A variation of this procedure is



reaction of a 5-acyloxypyrazole with a diazonium salt.⁵⁹¹ This reaction hydrolyzes the ester linkage and, if an acyl substituent is present at the 4-position, replaces it to form 4-arylaazo-2-pyrazolin-5-ones (eq. 181).

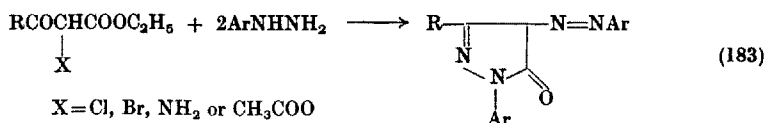


A method frequently used and capable of a large number of variations is the cyclization of α -substituted- β -ketoesters, amides or hydrazides with hydrazines to 4-arylaazo-2-pyrazolin-5-ones. One variant of this is the treatment of an α,β -diketoester with hydrazine (eq. 182).^{627, 1573, 1574, 1576} Instead of the ester, hydrazides of α,β -diketoacids

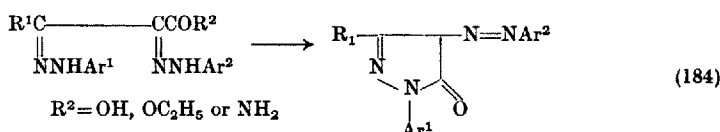


have been used.⁹⁹ A very similar synthesis is the use of an α -oximino- β -ketoester and a hydrazine.⁹⁹ Also quite similar is the cyclization of an α -hydrazone of an α,β -diketoester^{255, 259, 262, 314, 732} or α,β -diketoamide²⁶¹ with a hydrazine. The bishydrazones of α,β -diketoesters also react with hydrazines to form 4-arylaazo-2-pyrazolin-5-ones.^{255, 257} It is not necessary that the α -substituent be unsaturated. α -Amino- β -ketoesters,¹⁵³⁵ α -chloro- β -ketoesters^{1513, 1514} and α -acyloxyster³⁷² have

also been used (eq. 183). Apparently an oxidation of a hydrazino to an azo function occurs in the course of the reaction.

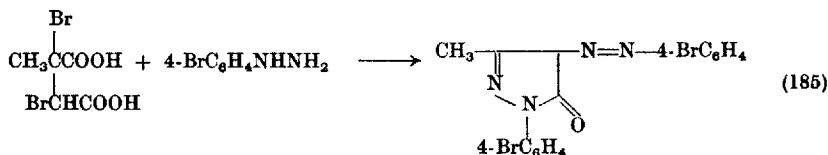


Cyclization of a variety of bishydrazones of α,β -diketoacids,^{52,285} α,β -diketoesters^{52,264,397,732,782} and α,β -diketoamides,³⁵² using either acid, base or heat, to 4-arylo-2-pyrazolin-5-ones has been reported (eq. 184). In this reaction the aryl groups have usually been the same



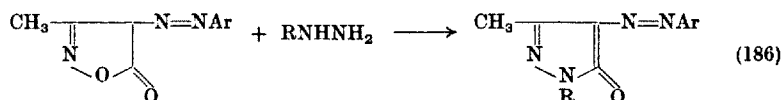
although Kleene⁷⁸² has used different aryl groups. Another modification of this reaction is due to Chargaff and Magasanik,²⁸³ who report that oxidation of the 1,2-bisphenylhydrazone of mesoxaldehyde gave rise to 4-phenylazo-1-phenyl-2-pyrazolin-5-one.

Fichter⁴⁴⁶ has reported an arylazopyrazolinone as one of the products from the reaction of α,α' -dibromo- α -methylsuccinic acid with *p*-bromophenylhydrazine (eq. 185).

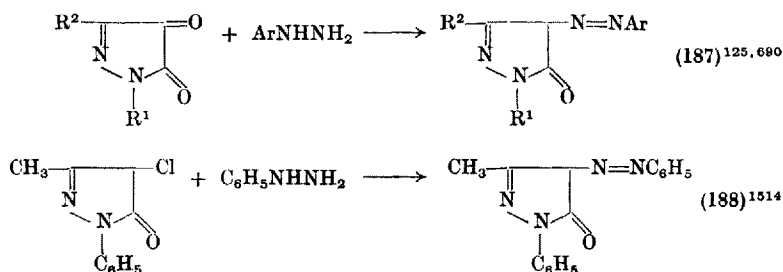


Huebner and Link⁶⁷⁰ have prepared 4-arylo-2-pyrazolin-5-ones by the reaction of hydrazines with 4-hydroxycoumarin, 3,3'-methylenebis(4-hydroxycoumarin) and with 2,3,4-triketochroman derivatives. In the case of the 4-hydroxycoumarins oxidation by phenylhydrazine occurs to give the bisphenylhydrazone of an α,β -ketoester. The reaction then proceeds as previously discussed for such compounds.

Bülow and Hecking²⁶³ have treated 4-aryloisoxazolidones with hydrazines to form 4-arylo-2-pyrazolin-5-ones (eq. 186) and other heterocycles undergo similar transformations.¹¹⁸



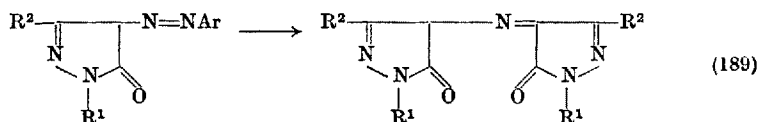
A number of 2-pyrazolin-5-ones having substituents at C-4 react with arylhydrazines by replacement of the substituent to give 4-aryloazo derivatives. These syntheses are illustrated in eqs. 187 and 188.



Ridi¹¹⁸⁵ has reported that the reaction of 2,3-dimethyl-1-phenyl-4-nitroso-3-pyrazolin-5-one with phenylhydrazine gives 4-phenylazo-3-methyl-1-phenyl-2-pyrazolin-5-one. This may occur by replacement of the methylphenylhydrazine moiety in the 3-pyrazolin-5-one by phenylhydrazine. The 4-oximino-2-pyrazolin-4-one could then react with phenylhydrazine to give the reported product.

Although in this discussion the 4-arylozo-2-pyrazolin-5-ones have been written as 5-oxo compounds, it is likely that they exist largely in the tautomeric enol form.²⁶²

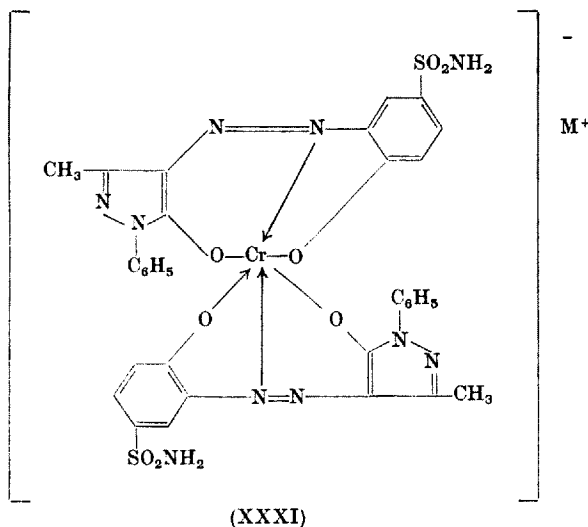
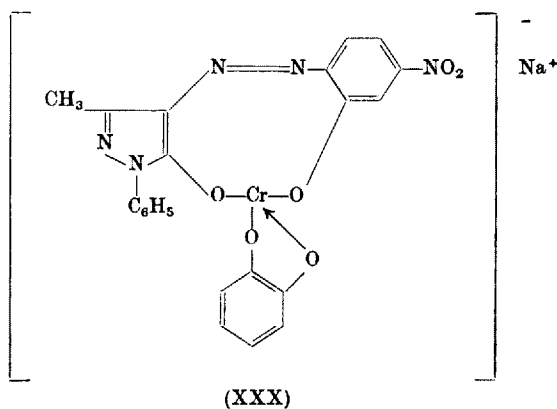
The methylation of 4-arylozo-2-pyrazolin-5-ones has already been mentioned.⁵² Nitration occurs with replacement of the 4-arylozo group.²⁶² Reduction occurs readily but two different paths are followed. As mentioned earlier, 4-amino-2-pyrazolin-5-ones can be obtained by catalytic reduction⁶⁷⁰ and with zinc and hydrochloric acid.³⁹⁷ However, reduction with zinc and acetic acid leads to rubazonic acids (eq. 189).



The conditions which determine the course of this reduction are not known.

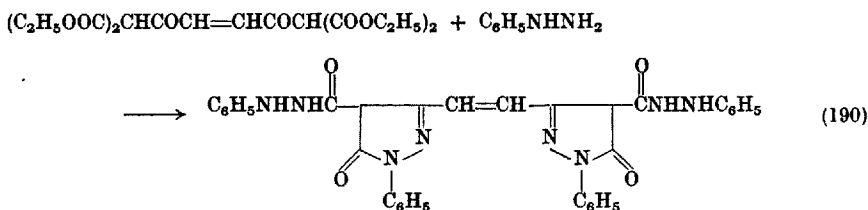
The most important reactions of 4-arylozo-2-pyrazolin-5-ones are those with various salts to form metal complexes. These products are of great importance in the dye industry and will be discussed more completely in the section devoted to dyes. Chromium complexes are prepared by reaction of a 4-arylozo-2-pyrazolin-5-one with inorganic compounds^{213, 1457} including chromium sulfate⁴⁷⁵ and chromium trifluoride,¹⁶¹⁶ with organic chromium compounds, such as chromium

formate⁸⁶⁵ and chromium complexes with salicylic acid.²⁰⁷ Copper,²¹³ nickel,²¹³ lead,²¹³ zinc¹⁶¹⁶ and cobalt¹⁶⁸⁰ have also been used. The aromatic moiety of the arylazo group usually has a hydroxyl or carboxyl group *ortho* to the azo linkage. The complexes thus obtained with chromium contain either one or two molecules of the dye per atom of



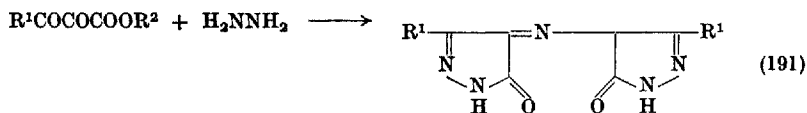
metal. The metal atoms react with the C-5 oxygen of the pyrazolinone ring in its enol form and with the hydroxyl group of the aromatic ring to form more or less covalent bonds. There is also electron donation by other oxygen atoms and by the azo nitrogen atoms to the metal atom. The structure (XXX) has been proposed for 1 : 1 complexes^{1117, 1259} and (XXXI) for 2 : 1 complexes.¹²⁵⁹

Amino-substituted bis(2-pyrazolin-5-ones) have been prepared in which the rings are linked by carbon chains or by nitrogen atoms. The former are listed in Tables VIII and IX and the latter in Tables VII and VIII. In most of those cases in which carbon chains link the two rings the amino substituents are introduced as they are in mono-pyrazolinones.^{255,494} Eisner, Elvidge and Linstead⁴¹⁹ have prepared some amino bis(2-pyrazolin-5-ones) by direct cyclization (eq. 190).



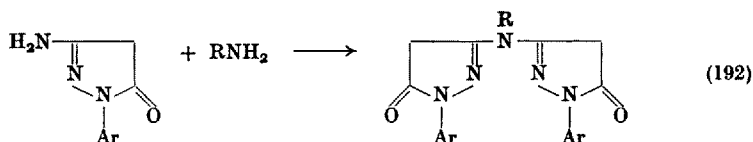
Some 1,1'-bis(4-arylideneamino-2-pyrazolin-5-ones) have been prepared by Furuya and Ueno⁴⁹⁴ by treating bis(2-pyrazolin-5-ones) with oxidizing agents in the presence of arylamines.

The best known series of amino bis(2-pyrazolin-5-ones) is the rubazonic acid series. In this case the two rings are linked by a single nitrogen atom. The preparation of rubazonic acid itself by oxidation of 4-amino-3-methyl-1-phenyl-2-pyrazolin-5-one with ferric chloride has already been mentioned (eq. 178).⁸⁰⁹ This is a general method for the preparation of rubazonic acids,^{333,397,611} although other oxidizing agents are sometimes used.⁴⁸⁰ Votocek and Wichterle¹⁵⁶⁷ have reported the isolation of a rubazonic acid analog as a side-product in the reduction of 4-oximino-3-phenyl-1-(2-phenethyl)-2-pyrazolin-5-one to the corresponding amine using zinc and acetic acid. The reduction of 4-phenylazo-2-pyrazolin-5-one has also been found to give a rubazonic acid.¹⁵⁵² Wohl and Doll¹⁵⁷⁶ have prepared rubazonic acid analogs by the reaction of an α,β -diketoester with hydrazine (eq. 191) and a some-

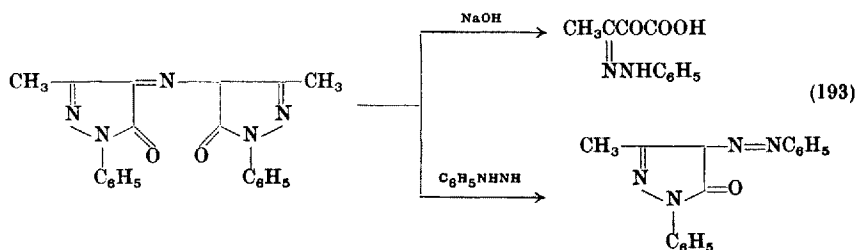


what analogous method has been reported by Wislicenus and Grob.¹⁶⁴² Moureu, Choivin and Petit¹⁰²² have obtained a very low yield of a rubazonic acid by the reaction of ethyl α -bromocinnamate with phenylhydrazine. 4,4'-Bis(2-pyrazolin-5-ones) linked by a single azo group and by $-\text{N}=\text{N}-\text{R}-\text{N}=\text{N}-$ have been reported, although these compounds are very few. Diazotization of 4-amino-2-pyrazolin-5-ones

followed by coupling with an appropriate acetoacetic ester derivative and cyclization gives 4,4'-azobis(2-pyrazolin-5-ones).¹⁰⁶² von Walther and Rothacker¹⁵⁸⁴ have claimed that the reaction of 4,4-dichloro-3-methyl-1-phenyl-2-pyrazolin-5-one and 3-methyl-1-phenyl-2-pyrazolin-5-one in the presence of hydrazine gives the same type of product. The compounds having two azo groups in the chain are prepared by coupling of tetrazotized diamines with acetoacetic esters followed by cyclization to 2-pyrazolin-5-ones,⁷⁶⁷ coupling of tetrazotized diamines with pyrazolinones,^{727, 1245, 1359} or a combination of these.²⁵⁹ Priewe and Poljak¹¹⁴⁷ reduced 5-oxo-2-pyrazolin-4-oximes with hydrogen or sodium hyposulfite and obtained 4,4'-bis(5-oxo-2-pyrazolin-4-yl)hydrazines. Oxidation of these compounds gave 4,4'-azo derivatives. 3,3'-Imino bis(2-pyrazolin-5-ones) have been prepared by condensation of 3-amino-1-aryl-2-pyrazolin-5-ones (1-aryl-5-imino-2-pyrazolidinones) with ammonia or amines (eq. 192).^{595, 596}



The most interesting of the aminobispyrazolinones are the rubazonic acids having the $=N-$ linkage. These compounds are quite strong acids, although no quantitative data on this are available. As would be expected, reduction of the extranuclear $C=N-$ occurs readily with stannous chloride to give the corresponding tertiary amine. Rubazonic acid is decomposed completely by sodium hydroxide and reverts to a monomer (eq. 193) upon treatment with phenylhydrazine.^{809, 992} The

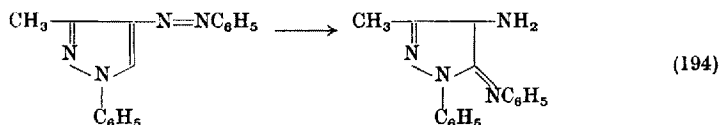


3,3'-iminobis(2-pyrazolin-5-ones) react with formaldehyde and ethyl orthoformate at the reactive 4,4'-positions to give tricyclic compounds.⁵⁹⁵ If there is no substituent on the linking nitrogen atom, reaction with dimethyl sulfate causes methylation at this nitrogen.⁷⁰⁵

Treatment with chlorosulfonic acid gives sulfonation in the benzene ring, when present.⁷⁰⁵

Michaelis and co-workers⁹⁹⁰ have prepared 3-methyl-1-phenyl-4-phenylazo-2-pyrazolin-5-thione by coupling of the corresponding pyrazolinthione with phenyldiazonium chloride.

5-Imino-2-pyrazolines having nitrogen substituents at the 4-position have been reported by Michaelis and co-workers.^{995, 996, 1002} The 4-amino compounds have been prepared by reduction of 4-oximino analogs¹⁰⁰² and by reduction of arylazopyrazoles⁹⁹⁵ (eq. 194) with



mild reducing agents, such as sodium hydrosulfite. These amino compounds react with ketones and isocyanates as do other amines. 4-Arylazo-5-imino-2-pyrazolines have been prepared as are the 5-oxo analogs.⁹⁹⁶ These compounds are listed in Table XII.

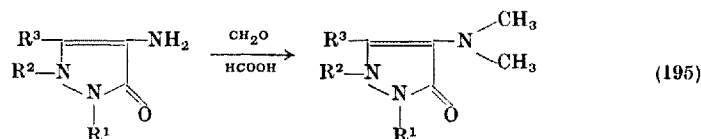
B. 3-Pyrazolin-5-ones

3-Pyrazolin-5-ones having nitrogen substituents in the 3- or 4-positions, except primary amino, secondary amino, amido having hydrogen on the nitrogen, nitroso and nitro are discussed in this section. Although primary and secondary amino- and amido-3-pyrazolin-5-ones undoubtedly exist as the 3-pyrazolin-5-one tautomer, they are discussed under the heading of the 4-imino-3-pyrazolidinone and 5-imino-3-pyrazolidinone tautomers because of the convention adopted in this discussion regarding compounds having such tautomeric possibilities. These compounds are listed in Table XXIV.

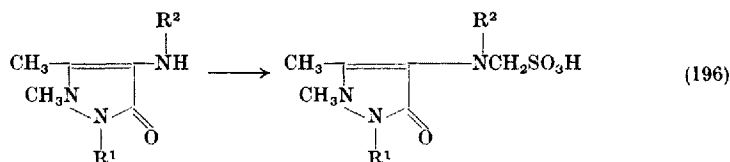
The most important amino-3-pyrazolin-5-one is aminopyrine, which is 4-dimethylamino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one. This compound has been widely used as an antipyretic and analgesic, particularly in Europe, and as a consequence its preparation and chemistry have been studied extensively. Most of the methods used for synthesizing 4-dialkylamino-2-pyrazolin-5-ones have been those used for the 4-dimethylamino compounds.

Most syntheses of tertiary amino-3-pyrazolin-5-ones are based on an alkylation by one means or another of the primary or secondary amino analogs. In some cases simultaneous reduction of a nitroso or nitro compound or of a Schiff base and alkylation of the amine so formed is carried out. 4-Dimethylamino-3-pyrazolin-5-ones (amino-

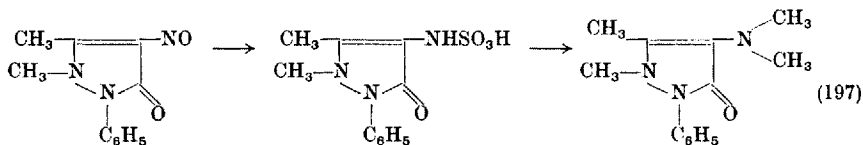
pyrine and analogs) have been synthesized by application of the Eschweiler-Clarke procedure to 4-amino-3-pyrazolin-5-ones (eq. 195).^{548, 860, 941} Other alkylating agents used have been alkyl



halides,^{130, 984} dimethyl sulfate^{984, 992} and methyl-*p*-toluenesulfonate.¹¹⁷⁵ 3-Pyrazolin-5-ones dialkylated at N-4 have frequently been prepared by alkylation of the primary amine by such means as treatment with an aldehyde^{111, 172} and reduction of the Schiff base followed by alkylation. The final alkylation has been achieved by treatment with an alkyl halide,^{524, 1298} by heating with an amine hydrochloride¹¹¹ and by treatment with an aldehyde followed by reduction.⁸⁶⁰ A special type of alkylation of secondary amines is that reported by Boehmühl and Stein.¹⁰⁵ Secondary amines were treated with formaldehyde and sulfur dioxide or an alkali bisulfite to give an aminomethanesulfonic acid (eq. 196). Several patents have reported the synthesis of amino-



pyrine starting with reduction of 4-nitroso-2,3-dimethyl-3-pyrazolin-5-one with sodium bisulfite to give the 4-sulfamino analog (eq. 197). This



is then methylated by various means. The most common method is use of formaldehyde and formic acid.^{150, 661, 781, 860, 1174} Alkylation with dimethyl sulfate^{144, 1256} and electrolysis in the presence of formaldehyde and sulfuric acid⁶⁹¹ have also been used.

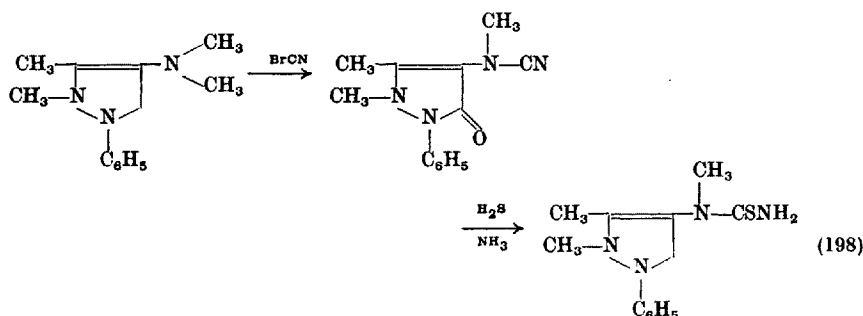
Reduction of 4-nitroso-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one with zinc or iron and acid^{554, 550, 915} or catalytically⁵⁵¹ in the presence of formaldehyde also gives aminopyrine. The analogous 4-nitro compound can also be reduced catalytically in the presence of formaldehyde

to form aminopyrine.^{860,1356} Sonn and Litten¹³²⁰ have replaced the bromine atom in 4-bromo-3-benzyl-2-methyl-1-phenyl-3-pyrazolin-5-one with dimethylamine.

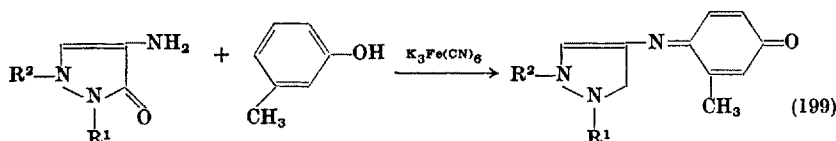
A variety of 4-amino-5-alkoxy- and acyloxy-1,3-disubstituted-pyrazoles have been treated with alkylating agents such as alkyl halides to give 4-dialkylamino-3-pyrazolin-5-ones.⁵²⁵ There is a simultaneous alkylation of ring nitrogen and extranuclear nitrogen.

The reported decomposition of 4-dimethyltriazeno-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one to aminopyrine⁵²⁷ has been shown by Stoltz¹³⁵³ to be incorrect.

Most 4-amido-3-pyrazolin-5-ones have been prepared either by acylation of secondary amines^{537,618,1471} (4-alkylimino-3-pyrazolidinones) or by acylation of the primary amine¹⁴⁷¹ followed by alkylation.⁵³⁷ Shimidzu¹²⁹⁷ has reported the replacement of a methyl group by a cyano group and conversion of this to a thiourea (eq. 198).



4-Amino-3-pyrazolin-5-ones (4-imino-3-pyrazolidinones) react with aldehydes and ketones to form 4-alkylidene- and arylideneamino-3-pyrazolin-5-ones.^{424,984,1001,1365,1592} Formaldehyde,¹⁷² aromatic aldehydes,⁴³⁰ heterocyclic aldehydes^{1184,1186} and aromatic ketones⁹⁹² have been used. Eisenstaedt⁴¹⁷ and Emerson and Kelly⁴²⁶ have prepared somewhat similar compounds by condensation of 4-amino-3-pyrazolin-5-ones with phenols and various amines in the presence of oxidizing agents, such as ferric chloride and potassium ferricyanide (eq. 199).

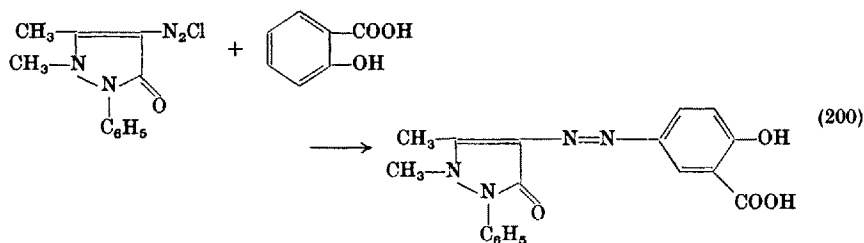


The same type of condensation occurs with 2-pyrazolin-5-ones having no substituent in the 4-position.⁴²⁴ Here, of course, it is unnecessary for

the aromatic ring to assume a quinnooid form, as the 3-pyrazolin-5-one analogs do, since two active hydrogen atoms are present on the C-4. 4-Amino-2-pyrazolin-5-ones react with Schiff bases to form the 4-arylideneamino-3-pyrazolin-5-ones.⁹⁵⁴ Rubtsov¹²¹⁷ reports the condensation of this amine with sodium 1,2-naphthoquinone-4-sulfonate to give a quinoneimine by replacement of the sulfonate group. The 4-arylideneamino substituent has been introduced by condensation of a 4-nitroso-3-pyrazolin-5-one with fluorenes.²⁷⁰ The condensation occurs at the active methylene group of the fluorene. Michaelis and co-workers¹⁰⁰¹ have prepared a compound which they believe to have a sulfur-nitrogen double bond at least formally similar to the $>C=N-$ substituents discussed here. This was prepared by condensation of a 4-amino-3-pyrazolin-5-one with thionyl chloride and supposedly gave a 4-OS=N— substituent. However, it appears unlikely that this type of compound was actually prepared.

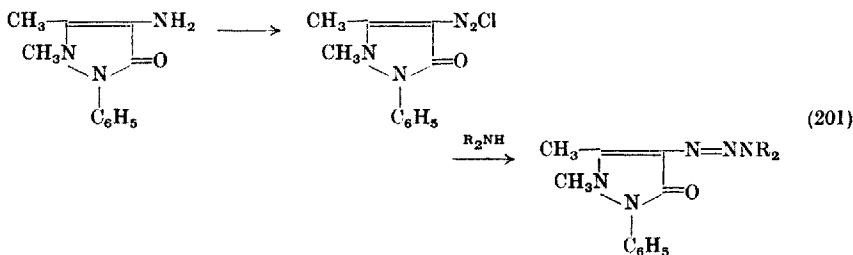
The only amino 4,4'-bis(3-pyrazolin-5-one) reported is *N,N'*-[bis(2,3-dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-yl)]-*N,N'*-dimethylmethylenediamine prepared by acid treatment of the sodium salt of *N*-sulfomethyl-*N*-methylaminoantipyrine with acid.¹⁵⁷²

4-Amino-3-pyrazolin-5-ones (4-imino-3-pyrazolidinones) react with nitrous acid as do ordinary aromatic amines to form diazonium salts.^{426, 984, 1353} These then couple readily with aromatic amines,^{1017, 1018, 1060} phenols^{992, 1323} and aliphatic compounds having active hydrogen atoms,^{426, 1017} such as acetoacetic esters. The products are 4-azo-3-pyrazolin-5-ones (eq. 200). The diazonium salts also couple



with 2-pyrazolin-5-ones in the 4-position.⁴²⁶ Similar compounds can be prepared by the coupling of an aromatic diazonium salt with a 3-pyrazolin-5-one. Coupling occurs in these cases either at the 3- or the 4-position, whichever is unsubstituted.^{972, 1004} Huebner and Link⁶⁷⁰ prepared 4-arylazo-3-pyrazolin-5-ones by reaction of 2,3,4-trioxo-chromane-3,4-bis(phenylhydrazone) and 3-arylhydrazone with phenylhydrazine. The 3-arylhydrazone group becomes the 4-arylazo group in the final product.

The preparation of 1-(2,3-dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-yl)-3,3-dialkyltriazenes has been accomplished by reaction of 2,3-dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-diazonium chloride with dialkylamines (eq. 201).¹³⁵³ The previously reported method of preparation⁵²⁷ was found to be in error.

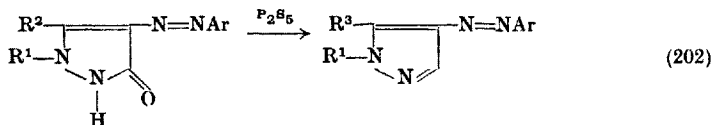


2,3-Dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-diazonium chloride reacts with hydrazoic acid to form the corresponding 4-azide.⁴⁵⁶ This azide decomposed to form 4-(2,3-dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-yl)azo-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one.

Dihlmann³⁷¹ has determined the R_f values of 4-amino- and 4-amido-3-pyrazolin-5-ones by using butanol-acetic acid-water as solvent and ferric chloride or *p*-dimethylaminobenzaldehyde as developer.

The rearrangement of 4-dimethylamino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one to a 2-pyrazolin-5-one has already been mentioned (eq. 169). 4-Benzylideneamino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one reacts with dimethyl sulfate in aqueous media to give the 4-methylamino analog.⁹⁴⁰ Presumably the Schiff base is hydrolyzed and the resulting amino group is methylated. 4-Dimethylamino-3-pyrazolin-5-ones react with phosphorus oxychloride by conversion to the methochloride of a pyrazole.¹⁰⁰⁰

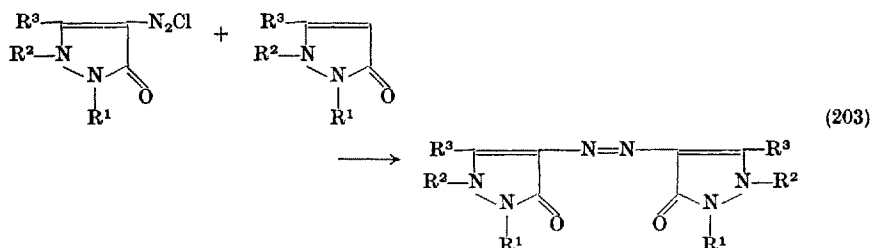
4-Arylazo-3-pyrazolin-5-ones have been used as dyes. They form complexes with chromium which have good dyeing properties.¹⁰⁶⁰ Michaelis, Kotelmann and Drews⁹⁸⁴ report the reduction of 4-aryl-azo-3-pyrazolin-5-ones having no 1-substituent to pyrazoles by use of phosphorus pentasulfide (eq. 202). Reaction of such azo compounds



with phosphorus oxychloride leads to the corresponding 5-chloropyrazole.⁹⁷²

The only 4-dialkylamino-3-pyrazolin-5-thione reported in the literature^{986,1000} was prepared by the action of sodium sulfide or potassium hydrogen sulfide on the methochloride of the corresponding 5-chloropyrazole.

A very few bis(3-pyrazolin-5-ones) in which the two rings are connected by the azo group have been prepared. The preparation of these *via* the 4-azido-3-pyrazolin-5-ones⁴⁵⁶ has already been mentioned. These bispyrazolinones have also been prepared by coupling diazonium salts with 3-pyrazolin-5-ones (eq. 203).^{984,1001} Scott and co-workers¹²⁸⁴

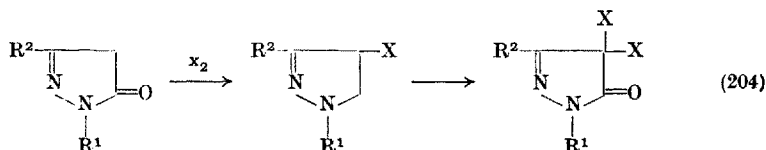


have reported a bis(3-pyrazolin-5-one) having a very extended bridge system prepared by reaction of a 3-pyrazolin-5-one diazonium chloride with *N,N'*-dibenzylidenediaminoguanidine.

5. Halogen Substituted Derivatives

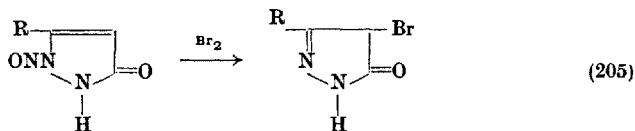
A. 2-Pyrazolin-5-ones

Halogenated 2-pyrazolin-5-ones having halogen at N-1, C-3 and C-4 are known, but by far the largest number of such compounds have the halogen atom at C-4. Such compounds are usually prepared by direct halogenation with elemental halogen. Chlorination or bromination of 2-pyrazolin-5-ones having no 4-substituent with one equivalent of halogen gives the 4-monohalogeno product (eq. 204), but an excess of halogen gives the 4,4-dihalo derivative.^{355,809,1605}



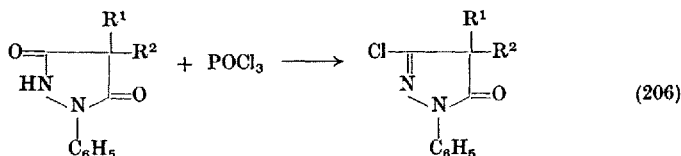
4-Iodo- and 4,4-di-iodo-2-pyrazolin-5-ones can be prepared by treatment of 2-pyrazolin-5-ones with iodine-potassium iodide in an alkaline solution.¹³⁰⁷ Here, again, either the mono or the dihalogeno product is formed, depending upon the amount of halogen used.

Extremely good yields have been reported in these halogenations.¹⁶⁰⁵ 4-Alkyl-2-pyrazolin-5-ones react with halogens readily, but even with an excess only monohalogenated products have been obtained.¹⁶⁰⁵ Smith and co-workers¹³⁰⁹ have found that 1,3-dimethyl-2-pyrazolin-5-one reacts with bromine to give both the expected 4-bromo product and also 1-bromo-3-methyl-2-pyrazolin-5-one. This same compound was obtained by bromination of 3-methyl-2-pyrazolin-5-one with *N*-bromosuccinimide.¹³⁰⁹ 4-Bromo-2-pyrazolin-5-ones have been prepared by bromination of 2-nitroso-3-pyrazolin-5-ones¹²⁰⁹ (eq. 205) with



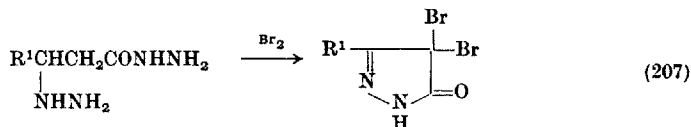
bromine. Treatment of 3-pyrazolidinones with bromine results in oxidation of the pyrazolidinone to a pyrazolinone followed by bromination.^{816,1028} Unless the temperature is controlled this reaction leads to a mixture of mono-, di- and tribromo-2-pyrazolin-5-ones. However, Muckermann¹⁰²⁸ was able to obtain the monobromo derivative at 0° and the dibromo at room temperature.

A number of reagents other than elemental halogen have been used for the introduction of halogen into 2-pyrazolin-5-ones. Treatment of 2-pyrazolin-5-ones with phosphorus pentachloride^{333, 809, 980} or with sodium hypochlorite¹⁰⁰⁴ forms 4,4-dichloro-2-pyrazolin-5-ones. An analogous reaction is the formation of 4,4-dibromo analogs by use of phosphorus tribromide.³³³ The methods already discussed for halogenation of 2-pyrazolin-5-ones lead exclusively to the 4-substituted products, but 3-halogenated-2-pyrazolin-5-ones are known. These have been prepared by Michaelis and co-workers^{994, 998} by reaction of one molar equivalent of phosphorus oxychloride with 1-phenyl-3,5-pyrazolidinediones (eq. 206) or with 3-methoxy-1-phenyl-2-pyrazolin-5-ones.



Some halogenated 2-pyrazolin-5-ones have been prepared by cyclization of various aliphatic compounds. Darapsky, Berger and Neuhaus³⁵³ have treated a β -hydrazino hydrazide with bromine to achieve cyclization, oxidation and halogenation in one step (eq. 207).

The cyclization of a β -phenylazo- α,β -unsaturated ester with hydrochloric acid has been reported by van Alphen^{1513, 1514} to give a 4-chloro-2-pyrazolin-5-one.



These compounds are listed in Table XXV.

The 4,4-dichloro-2-pyrazolin-5-ones are reduced with hydriodic acid to the corresponding monochloro compound.¹⁶⁰⁵ The 4-monohalogenated-2-pyrazolin-5-ones react readily with another mole of the same compound or with unhalogenated 2-pyrazolin-5-ones to give bis(2-pyrazolin-5-ones). In the former case the two rings are linked by a double bond,¹³⁰⁷ and in the latter by a single bond.¹⁵²⁸

Only two halogenated bis(2-pyrazolin-5-ones) have been reported (Table VI). One of these is prepared by bromination of 4,4'-methyldiynbis(3-methyl-1-phenyl-2-pyrazolin-5-one) with bromine to give the 4-bromo analog.¹⁶⁸² In the second case¹¹⁰⁹ bromine is added to a diolefinic system connecting two 2-pyrazolin-5-one rings.

A number of halogenated 5-imino-2-pyrazolines have been reported. These are included in Table XII. They are usually prepared by direct halogenation.^{996, 1655} Another preparative method which has been used is treatment of a 5-imino-3-pyrazolidinone with phosphorus oxychloride.³⁹¹ Michaelis has reported the treatment of a compound, which he believed to have the azipyrazole structure (XXVI, p. 45), with halogen acids to give halogenated 5-imino-2-pyrazolines.⁹⁹⁶ 4-Chloro-3-dichloromethyl-1-phenyl-5-phenylimino-2-pyrazoline has been prepared by treatment of 1,1-bisanilino-2,4,4-trichloro-1-buten-3-one with phenylhydrazine.¹²⁰¹ The reactions of halogenated iminopyrazolinones are essentially the same as of those having no halogen.

B. 3-Pyrazolin-5-ones

These compounds are listed in Table XXVI.

As is the case with 2-pyrazolin-5-ones, direct bromination of 3-pyrazolin-5-ones can be used to prepare the 4-bromo derivatives. This bromination is not complicated by substitution of a second bromine at the same carbon atom, but further bromination occurs to give 3-pyrazolin-5-ones containing two or three atoms of bromine. In spite of considerable investigation of these polybrominated 3-pyrazolin-5-ones, their structures have not been conclusively established and several

very bizarre suggestions as to their nature have been made. Knorr⁸⁰⁹ and other early workers^{978,981} found that reaction of one mole of bromine with one mole of a 3-pyrazolin-5-one gave a compound whose molecular formula was that to be expected from addition of the bromine to the ring double bond to give 4,5-dibromo-3-pyrazolidinones and it was suggested that this was the structure of the products. This view was held for many years¹³²⁰ until Kitamura and Sunagawa^{793,794} suggested that these compounds might be the hydrobromides of 4-bromo-3-pyrazolin-5-ones in the betaine form. The ready conversion of these dibromo-3-pyrazolin-5-ones to the corresponding 4-bromo-3-pyrazolin-5-ones by treatment with base and the reaction of the monobromo compounds with hydrogen bromide to give the dibromo derivatives make the argument of Kitamura and Sunagawa very compelling. Westoo¹⁶⁰⁵ has agreed with this proposal and it seems very likely to be correct. Reaction of excess of bromine with 3-pyrazolin-5-ones leads to the compounds called perbromides, generally considered to be tribromo compounds, although Komada⁸⁴⁴ claimed to have obtained tetrabromo derivatives also. These claims have been discounted by others.⁷⁹⁴ These perbromides have usually been considered as a molecular complex of the halogen and 4-bromo-3-pyrazolin-5-ones. Kitamura and Sunagawa⁷⁹⁴ have proposed more definite structures involving dimerization, with the dimers bound by resonance. However, their suggested structure seems inherently improbable. Whatever may be the structures of these compounds, two of the bromine atoms must be very loosely held, as they are lost by treatment with water,^{794,992} giving a 4-bromo-3-pyrazolin-5-one. Direct chlorination⁹⁸⁸ and iodination^{540,981} with the elemental halogens to give 4-halogeno-3-pyrazolin-5-ones have also been reported. Ledrut and co-workers^{362,899} have found that bromination of 3-pyrazolin-5-ones having hydroxymethyl, formyl and carboxyl groups at C-4 results in replacement of the 4-substituent by bromine. Michaelis⁹⁷⁸ earlier had reported this replacement if a 4-nitro group was present.

A variety of other halogenating agents have been used to prepare 4-halogeno-3-pyrazolin-5-ones. *N*-Bromosuccinimide^{362,899} replaces hydrogen or other substituents in the 4-position with bromine. Hydrobromic acid in the presence of peroxide⁹⁰⁷ and bromocyanogen¹⁴⁹¹ also bring about bromination. 4-Chloro-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one is obtained in excellent yield by chlorination of 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one with sodium hypochlorite.^{795,907,908} 5,5-Dimethyl-1,3-dichlorohydantoin also gives 4-chlorination of 3-pyrazolin-5-ones.³⁶² 4-Iodo-3-pyrazolin-5-ones have been obtained by replacement of a 4-chloromercuri group with iodine.^{1001,1155} 3,4-

Dichloro-2-phenyl-3-pyrazolin-5-one has been prepared by treatment of perchloro-1-penten-3-one with phenylhydrazine.¹²⁰¹

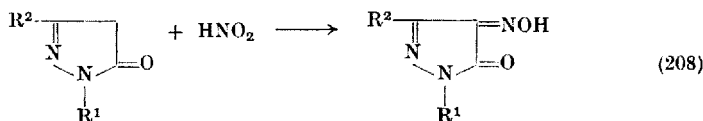
The halogen in these 3-pyrazolin-5-ones is readily replaced with hydrogen by catalytic reduction^{697, 698} or by treatment with acetone.⁷⁹³

A few halogenated 3-pyrazolin-5-thiones are known (Table XVIII). These are prepared from the methyl chlorides of 3- or 4,5-dichloro-pyrazole by reaction with sodium sulfide or potassium hydrogen sulfide.^{795, 981} Michaelis^{988, 992} has reported that 3-pyrazolin-5-selenones form dichlorides and di- and tetrabromides when treated with chlorine or bromine. No specific structures were suggested.

6. Nitroso Substituted Derivatives

A. 2-Pyrazolin-5-ones

Although the compounds obtained by introduction of a nitroso group at C-4 in 2-pyrazolin-5-ones are considered as 4-nitroso-2-pyrazolin-5-ones for purposes of classification in this discussion, they actually exist as the oximino isomers (eq. 208) and are usually so

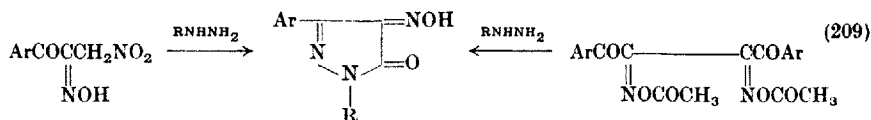


considered in the literature. These compounds are always strongly colored, being light yellow to deep red. Such compounds are listed in Table XXVII.

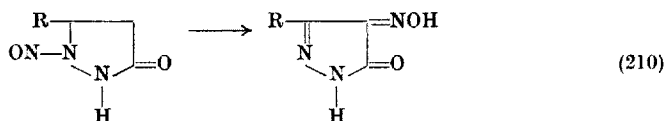
Knorr⁸⁰⁹ first prepared 4-oximino-2-pyrazolin-5-ones by treatment of 2-pyrazolin-5-ones with nitrous acid (eq. 208) and this has remained the standard method of preparation.^{25, 413, 446, 818, 1004, 1549} If an excess of nitrous acid is used, the nitroso substituent introduced is oxidized further to a nitro substituent.⁹⁹² Amyl nitrite⁹ and nitrogen trioxide^{355, 406} have also been used as nitrosating agents, though not extensively.

The standard β -ketoester-hydrazine reaction for preparation of 2-pyrazolin-5-ones has been used for direct synthesis of the 4-oximino derivatives by starting with an α -oximino- β -ketoester.^{269, 1125, 1534, 1536} In a modification of this by Bülow and Bozenhardt²⁵⁸ a hydrazone of the α -oximino- β -ketoester was used. Ponzio and Ruggeri¹¹²⁵ have used α -oximino- β -hydrazonohydroxamic acids and hydrazines, and other oximino compounds, as illustrated in eq. 209.

It has been claimed that 3-pyrazolidinones can be converted to 4-oximino-2-pyrazolin-5-ones by treatment with nitrous acid.^{816, 1550} However, later workers^{911, 1342, 1491} report that this reaction gives

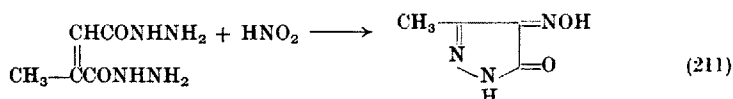


nitrosation at N-1. Since neither Knorr and Duden⁸¹⁶ nor von Rothenburg¹⁵⁵⁰ give sufficient physical data to identify their products, it may well be that they were actually 1-nitroso-3-pyrazolidinones. Curtius and Bleicher³³⁵ have isomerized 1-nitroso-3-pyrazolidinones by boiling with dilute sulfuric acid, thus causing rearrangement of the nitroso group to the 4-position and oxidation to a pyrazolinone (eq. 210). Qvist¹¹⁵³ has



rearranged 3-hydrazino-4-nitroso-5-arylisoxazoles to 4-oximino-2-pyrazolin-5-ones by heating in aqueous sodium hydroxide.

Freri^{478, 480} has reported a very interesting synthesis of 4-oximino-3-methyl-2-pyrazolin-5-one. This consisted in the treatment of citraconic acid hydrazide with nitrous acid (eq. 211). The physical data which



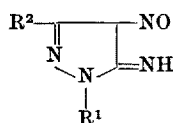
were reported for the product were consistent with those reported by other workers for the same compound. The reaction may go by preferential Curtius rearrangement of one hydrazide to form β -aminocrotonic acid hydrazide which cyclizes and is nitrosated.

Treatment with nitrous acid of a 4-substituted-2-pyrazolin-5-one having no substituent on N-1 gives the 1-nitroso derivative.²⁶²

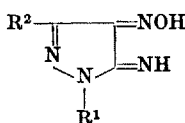
In the section dealing with 4-amino-2-pyrazolin-5-ones the reduction of 4-oximino-2-pyrazolin-5-ones and their reaction with active hydrogen atoms of heterocyclic compounds (eq. 174, p. 68) have been discussed. The oximino group is readily oxidized to the nitro group by ozone^{478, 480} or nitric acid.^{809, 992} The hydrogen of the oximino group can be replaced by silver by use of silver nitrate^{866, 1553} and the silver salt thus formed can be alkylated to form an *O*-alkyl oxime. The oximino group can be replaced by a hydrazino group.¹⁵⁴⁹

Only one oximinobis(2-pyrazolin-5-one) is known.⁴⁵⁹ This is 2,3-bis(4-oximino-3-phenyl-5-oxo-2-pyrazolin-1-yl)naphthalene prepared by nitrosation with nitrous acid.

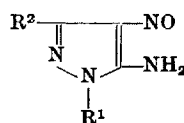
4-Nitroso-5-imino-2-pyrazolines are capable of existing in several tautomeric forms, (XXXII), (XXXIII) and (XXXIV). Although there



(XXXII)



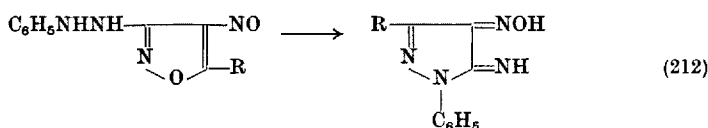
(XXXIII)



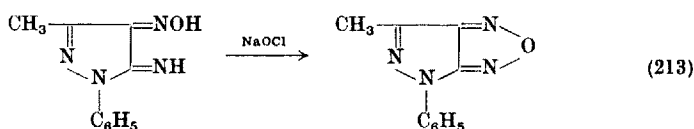
(XXXIV)

is little experimental evidence concerning structures, these compounds have usually been considered to exist in the oximino-imino form (XXXIII).^{996,1002}

Preparation has usually been by the nitrosation of the 5-imino-2-pyrazolines with nitrous acid.^{340,996,1002,1010} Qvist¹¹⁵³ has prepared them by thermal rearrangement of nitrosoisoxazoles (eq. 212). The



4-oximino-5-imino-2-pyrazolines may be reduced to amines or oxidized with potassium permanganate to nitro compounds, similarly to their 5-oxo analogs.¹⁰¹⁰ However, oxidation with sodium hypochlorite forms furoxazans (eq. 213).¹⁰¹⁰



B. 3-Pyrazolin-5-ones

3- and 4-Nitroso-3-pyrazolin-5-ones can only exist as the nitroso compounds. They are green, as would be expected, and somewhat unstable to heat. In many cases they melt with deflagration. They are basic enough to form stable hydrochlorides, which are usually red. This probably means that these hydrochlorides are actually alkyl chloride salts of 4-oximino-2-pyrazolin-5-ones. The 4-nitroso-3-pyrazolin-5-ones have been of great commercial interest because 4-nitroso-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one is an intermediate in the preparation of the

analgesic, aminopyrine. The 4-nitroso-3-pyrazolin-5-ones are listed in Table XXVIII.

The 4-nitroso-3-pyrazolin-5-ones are always prepared by nitrosation of 3-pyrazolin-5-ones with nitrous acid.^{99, 103, 145, 647, 781, 807, 809, 854, 888, 972, 978, 984} Only one 3-nitroso-3-pyrazolin-5-one has been reported.⁹⁷² This was prepared by nitrosation of 3-pyrazolin-5-one having a 4-methyl substituent and no substituent at C-3.

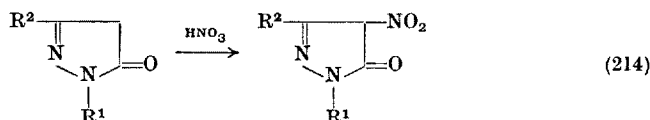
The reduction of 4-nitroso-3-pyrazolin-5-ones has already been discussed in connection with the synthesis of 4-dialkylamino-3-pyrazolin-5-ones. This reduction occurs readily to give the corresponding amine when catalytic hydrogenation or various chemical combinations^{461, 992, 1174, 1175} are used. Oxidation of nitroso to nitro occurs in the presence of excess of nitrous acid or by use of nitric acid.^{984, 992}

7. Nitro Substituted Derivatives

A. 2-Pyrazolin-5-ones

Only a few 4-nitro-2-pyrazolin-5-ones are known. They are listed in Table XXIX. The best-known of these compounds is picrolonic acid, which is 4-nitro-3-methyl-1-(4-nitrophenyl)-2-pyrazolin-5-one. This compound is widely used to form salts of basic compounds for isolation or identification. The hydrogen atom at C-4 is acidic in the 4-nitro-2-pyrazolin-5-ones because of the two adjacent electron-withdrawing groups. This hydrogen is easily replaced by metals when treated with metal alkoxides¹⁶⁴² and reacts with diazomethane.⁴⁷⁸

The usual synthesis of the 4-nitro-2-pyrazolin-5-ones is by nitration of 2-pyrazolin-5-ones under mild conditions (eq. 214).^{61, 672, 690, 1004, 1683}



In the case of picrolonic acid further nitration can be brought about to give the 4,4-dinitro compound.⁶⁹⁰ The oxidation of 4-nitroso-2-pyrazolin-5-ones has already been mentioned in the section dealing with the nitroso compounds. Ajello⁹ has been able to nitrate 3-methyl-2-pyrazolin-5-one using amyl nitrite in acetone or ether for several days. Hill and Black⁶⁵³ have reported the cyclization of *N,N'*-diacetylnitromalondialdimine with base to give 4-nitro-2-pyrazolin-5-one, but such a course for this reaction seems unlikely. The reaction of furlones with sodium nitrite and sulfuric acid to give as one of the products 4-nitro-2-pyrazolin-5-ones¹⁶⁰⁷ has already been illustrated in eq. 62 (p. 33).

The alkylation of 4-nitro-2-pyrazolin-5-ones at C-4 with diazo-methane⁴⁷⁸ has already been mentioned. This hydrogen atom is also replaceable with bromine.¹⁶⁴² Reduction of the nitro group with stannous chloride forms the corresponding amine.^{478, 480} Picrolonic acid condenses with itself to form a bis(2-pyrazolin-5-one) connected by a double bond at the 4,4'-position, with elimination of two moles of nitrous acid.⁶⁹⁰ Condensation also occurs in the presence of phenylhydrazine, but 4,4'-bis[3-methyl-1-(4-nitrophenyl)-2-pyrazolin-5-one] is formed.⁶⁹⁰

Two 4-nitro-5-imino-2-pyrazolines are listed in Table XII. One of these was prepared by permanganate oxidation of the 4-oximino compound¹⁰¹⁰ and the other by direct nitration.¹⁶⁵⁶ These compounds were believed to be aminopyrazoles rather than 5-imino-2-pyrazolines.

B. 3-Pyrazolin-5-ones

The 4-nitro-3-pyrazolin-5-ones are listed in Table XXVIII. They have been prepared most frequently by direct nitration of 3-pyrazolin-5-ones, usually with concentrated nitric acid.^{807, 809, 880, 888, 1001, 1320} The oxidation of 4-nitroso-3-pyrazolin-5-ones to give the 4-nitro compounds has been mentioned in connection with reactions of the 4-nitroso compounds. Nitration of 3-pyrazolin-5-ones with nitrogen tetroxide has been accomplished.¹⁴⁹¹

The nitro group of 4-nitro-3-pyrazolin-5-ones is readily reduced to an amino group by metal-acid combinations.^{984, 1001}

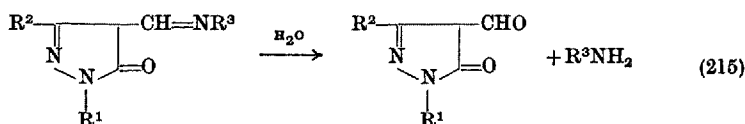
8. Aldehydes and Ketones

A. 2-Pyrazolin-5-ones

A large number of 2-pyrazolin-5-one aldehydes and ketones are known. These are listed in Table XXX. It is possible to have both 3- and 4-formyl and acyl substituents and both are known, although only one 5-oxo-2-pyrazoline-3-carboxaldehyde has been reported. There has been very little study of the effect of 4-acyl substituents on the structure of 2-pyrazolin-5-ones, but it seems probable that such compounds would tend to exist to a large extent as the 5-hydroxypyrazoles since they would be 1,3-dicarbonyl compounds.

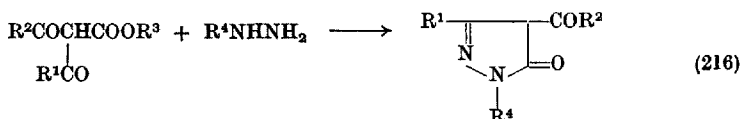
The preparation of the 5-oxo-2-pyrazolinecarboxaldehydes is usually done by procedures which are not applicable to preparation of the acyl homologues. The most extensively used method for preparing the aldehydes is hydrolysis of their Schiff bases,^{824, 1089, 1092, 1186, 1188}

illustrated in eq. 215. R^3 is usually aromatic, although it may be hydrogen.^{586, 1188} This hydrolysis occurs in the presence either of base or of acids. A second method of preparation is treatment of 4-(2,2,2-trichloro-1-hydroxyethyl)-2-pyrazolin-5-ones, obtained by reaction of

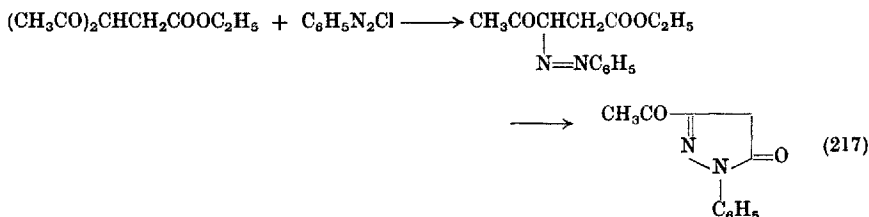


2-pyrazolin-5-ones with chloral, with potassium carbonate.¹⁰⁷ von Rothenburg¹⁵⁴⁶ has reported that heating of the calcium salt of 5-oxo-2-pyrazolin-3-carboxylic acid in the presence of calcium oxide and calcium formate formed 5-oxo-2-pyrazolin-3-carboxaldehyde. However, his product was not well characterized and the work has not been confirmed.

4-Acyl-2-pyrazolin-5-ones have been synthesized by three general methods. These are cyclization of aliphatic compounds, conversion of other 2-pyrazolin-5-ones and conversion of other heterocycles. As might be expected the reaction of β -ketoesters with hydrazines has been utilized.^{124, 1124, 1532, 1533} In this case the β -ketoester has an α -acyl substituent (eq. 216). Both Borsche and Lewinsohn¹²⁴ and Vila¹⁵³³

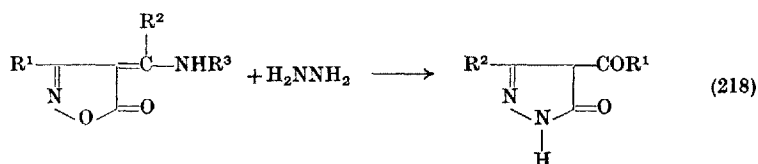


have used α -hydrocinnamoylacetoacetic ester in this reaction. The former workers claim that the 4-acetyl products are obtained, while Vila reported the products were 4-hydrocinnamoyl-2-pyrazolin-5-ones. 4-Acetyl-2-pyrazolin-5-ones have been obtained by cyclization of hydrazones of β -ketoesters with acetic anhydride.¹⁰⁰⁹ Kendall and Fry⁷⁶⁷ have obtained 3-acyl-2-pyrazolin-5-ones by the reaction sequence shown in eq. 217. The reaction of β,γ -diketoesters with hydrazines also forms 3-acyl-2-pyrazolin-5-ones.⁸³⁷

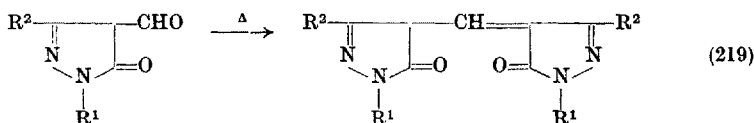


Acylation of 2-pyrazolin-5-ones leads to 4-acyl-2-pyrazolin-5-ones. This has been done by treatment with aromatic acid chlorides¹¹⁰ and with ethyl oxalate in the presence of potassium. A modification of this procedure is acylation of 2-pyrazolin-5-ones to give 4-acyl-5-acyloxy-pyrazoles^{591, 977} or 2,4-diacyl-3-pyrazolin-5-ones¹⁰⁵⁶ followed by hydrolytic removal of the *N*-acyl or *O*-acyl groups. The 4-acyl compounds can also be prepared by hydrolysis of their Schiff bases as shown in eq. 215.

The reaction of hydrazine with appropriately substituted isoxazolones or isoxazolinones also forms 4-acyl-2-pyrazolin-5-ones (eq. 218).^{947, 1295}



5-Oxo-2-pyrazolin-4-carboxaldehydes are oxidized to the corresponding acid by permanganate.¹⁰⁷ These aldehydes under various conditions form 4,4'-methylidynebis(2-pyrazolin-5-ones), and heating alone brings about this reaction (eq. 219).^{1089, 1093, 1188} This same type



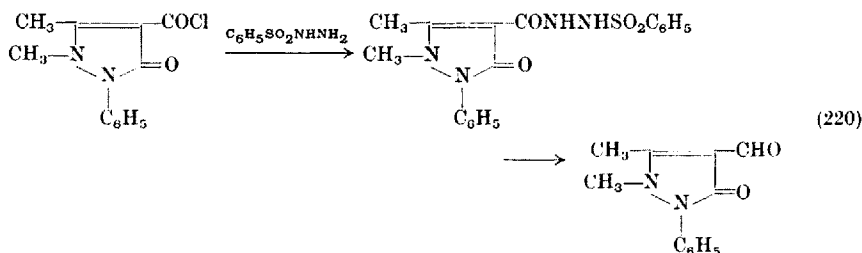
of product is obtained by the reaction of the 2-pyrazolin-5-one aldehydes with 2-pyrazolin-5-ones.¹⁰⁹³ Reaction of these aldehydes with 2-methylindole also gives the bis(2-pyrazolin-5-ones).¹¹⁸⁵ Such aldehydes react normally with amines and hydroxylamines to give Schiff bases and oximes.¹¹⁸⁸ The 4-acyl-2-pyrazolin-5-ones undergo the Mannich reaction.¹⁰⁹⁸ Treatment of acylpyrazolinones with diazonium salts results in replacement of the acyl group by an arylazo group.⁵⁹¹

Kendall and Fry^{768, 770} have prepared 3-acetyl-4-phenylazo-2-pyrazolin-5-one by the reaction of ethyl β -acetyl- δ -oxovalerate with two equivalents of phenyldiazonium chloride.

4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-thione has been prepared by Michaelis and co-workers^{977, 990} by the reaction of sodium and potassium hydrogen sulfide with 4-benzoyl-5-chloro-3-methyl-1-phenylpyrazole. The thiono compound forms a methiodide and gives the characteristic reactions of both ketones and 2-pyrazolin-5-thiones.

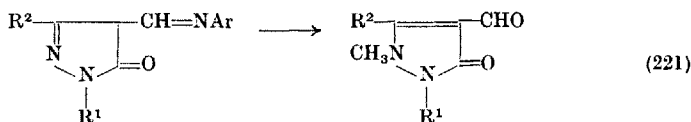
B. 3-Pyrazolin-5-ones

There has been considerable interest in the preparation of 5-oxo-3-pyrazolin-4-carboxaldehydes (listed in Table XXXI) because of their close relationship to antipyrine (2,3-dimethyl-1-phenyl-3-pyrazolin-5-one). The most frequently used preparation of these compounds has already been mentioned (eq. 135, p. 54). This consists of treating the condensation products of 3-pyrazolin-5-ones and chloral with base.^{107, 196, 889, 893, 896, 901, 1190} The McFadyen-Stevens aldehyde synthesis has been applied to the preparation of both 5-oxo-3-pyrazolin-3-carboxaldehydes⁶⁹⁸ and -4-carboxaldehydes.^{204, 892, 1634} This is illustrated in eq. 220. The final step is usually carried out in glycerol at



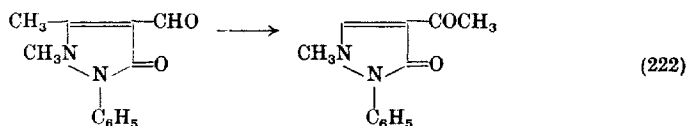
elevated temperatures in the presence of sodium carbonate. The acylsulfonylhydrazide has been prepared alternatively by reaction of the acid chloride with hydrazine followed by treatment of the hydrazide so produced with benzenesulfonyl chloride.

A group of Italian workers has claimed that 1,3-disubstituted-2-methyl-5-oxo-3-pyrazolin-4-carboxaldehydes can be prepared through methylation of the Schiff bases derived from aromatic amines and 1,3-disubstituted-2-pyrazolin-5-ones.¹⁰⁹⁷ The methylation is carried out with methyl iodide which methylates the ring at N-2, and this is followed by hydrolysis of the Schiff bases with alkaline solutions (eq. 221). Passerini and Losco^{1092, 1093, 1097} and Ridi¹¹⁸¹ claimed to have



prepared 2,3-dimethyl-2-phenyl-5-oxo-2-pyrazolin-4-carboxaldehyde in this fashion. Ridi¹¹⁸⁰ has also reported the preparation of similar compounds by the same procedure. However, various other workers^{108, 696, 897, 902} have reported that in the presence of base 2,3-dimethyl-1-phenyl-5-oxo-2-pyrazolin-4-carboxaldehyde isomerized to 4-acetyl-2-methyl-

1-phenyl-3-pyrazolin-5-one (eq. 222), presumably by hydrolytic ring



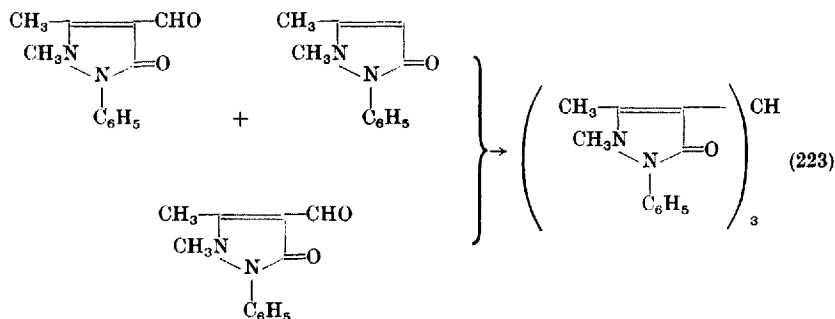
cleavage and reclosure. Ledrut, Combes and Sweikert⁹⁰² have shown that the reaction depicted in eq. 221, in which $\text{R}^1 = \text{C}_6\text{H}_5$ and $\text{R}^2 = \text{CH}_3$, does lead to the acetyl derivative, although other substituents give the expected product. A British patent²⁰¹ has appeared claiming that alkaline hydrolysis of the presumed 2-methyl intermediate in eq. 221 actually can be made to give the aldehyde by using dilute base and mild conditions. In summary it would appear that the various claims of Passerini, Losco and Ridi are largely correct.

A few miscellaneous preparations of 5-oxo-3-pyrazolincarboxaldehydes have been reported. Ito⁶⁹⁸ has prepared 3-carboxaldehydes and 3,4-dicarboxaldehydes by manganese dioxide oxidation of the corresponding alcohols. The 4-carboxaldehydes have also been prepared in this way.¹³⁷⁰ Treatment of antipyrine with dimethylformamide in the presence of phosphorus oxychloride has also been used.⁶⁹⁶ Passerini and Losco¹⁰⁹³ have reported methylation of 3-methyl-1-phenyl-5-oxo-2-pyrazolin-4-carboxaldehyde to the corresponding 3-pyrazolin-4-carboxaldehyde. However, the melting point given for their product is that of 4-acetyl-2-methyl-1-phenyl-3-pyrazolin-5-one, so it is probable that isomerization occurred.

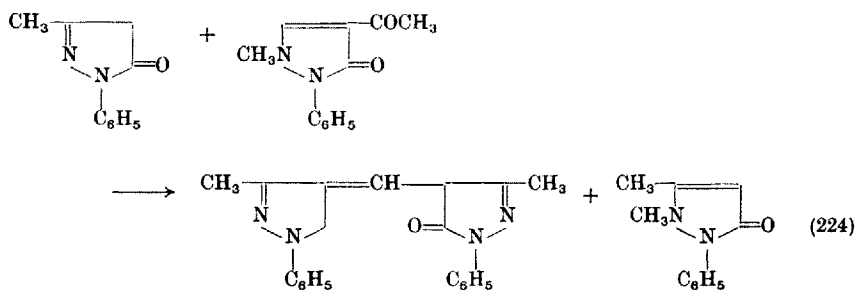
Only 4-acetyl-3-pyrazolin-5-ones are known. Most of those prepared are antipyrine derivatives. The most common method for preparing these is by a Friedel-Crafts reaction on 3-pyrazolin-5-ones with acid chlorides and aluminum chloride,⁸⁸ zinc chloride⁷³⁵ or no condensing agent.⁷³⁷ 2,3-Dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-carboxylic acid and its acid chloride have been condensed with various aromatic compounds to give ketones.⁷⁴⁰ Treatment of 4-benzoyl-5-chloro-3-methyl-1-phenylpyrazole or 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one with dimethyl sulfate gives rise to 4-benzoyl-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one.⁹⁷⁷ Phenylhydrazine reacts with isoxazolidones to give what may be 4-acetyl-2-phenyl-3-pyrazolin-5-one.¹²⁹⁵

The 4-formyl and 4-acyl-3-pyrazolin-5-ones react like normal carbonyl compounds with active methylene groups,^{696, 1190} amines,^{107, 1190} hydroxylamine,¹⁹⁶ hydrazines^{196, 201} and semicarbazide,²⁰¹ although some fail to react with thiosemicarbazide.⁷⁹⁹ They

also form bisulfite addition compounds.¹⁰⁷ Isomerization of 5-oxo-3-pyrazolin-4-carboxaldehydes to 4-acyl-3-pyrazolin-5-ones by base treatment has already been discussed. 4-Acyl-3-pyrazolin-5-ones can be reduced to the corresponding alcohol by sodium-mercury amalgam. Bromination of 5-oxo-3-pyrazolin-4-carboxaldehydes leads to replacement of the formyl group with bromine.³⁶² Bodendorf, Mildner and Lehman¹⁰⁷ have reported the condensation of 2,3-dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-carboxaldehyde with itself and with 2,3-dimethyl-



1-phenyl-3-pyrazolin-5-one (eq. 223) to form a trimeric 3-pyrazolin-5-one. Passerini and co-workers^{1093,1097} have reported that the reaction of 4-acetyl-2-methyl-1-phenyl-3-pyrazolin-5-one with 3-methyl-1-phenyl-2-pyrazolin-5-one gives, in addition to 4,4'-methylidynebis(3-methyl-1-phenyl-2-pyrazolin-5-one), some 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (eq. 224) and this has been confirmed by Curatolo.³³¹



It may be that there is a transfer of the $\text{CH}_3\text{N}-\text{N}-\text{C}_6\text{H}_5$ moiety of the 3-pyrazolin-5-one molecule to the 2-pyrazolin-5-one, or it may be that the N-2 methyl group acts as a methylating agent.

Various bis(3-pyrazolin-5-ones) having acyl substituents are known. In all cases the acyl group is part of a 4,4'-bridge between the 3-

pyrazolin-5-one rings. The condensation of 2,3-dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-carboxaldehyde with 4-acetyl-2-methyl-1-phenyl-3-pyrazolin-5-one gives rise to such a compound.^{108, 696, 902} Antipyrine and its 4-carboxyl derivative condense to form diantipyryl ketone.⁷⁴⁰ Sodium 2,3-dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-carboxylate reacts with 4-chloroacetyl-3-pyrazolin-5-ones to give bis compounds.⁷⁴¹ 4-Acyl-3-pyrazolin-5-ones dimerize by an aldol condensation.⁹⁰¹

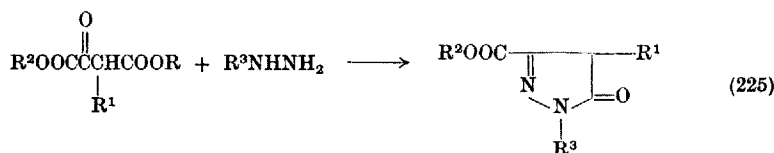
4-Benzoyl-2,3-dimethyl-1-phenyl-5-imino-3-pyrazoline is prepared by treating the methiodide of 4-benzoyl-3-methyl-1-phenyl-5-imino-2-pyrazoline with base.⁹⁷⁷

9. Carboxylic Acids and Derivatives

A. 2-Pyrazolin-5-ones

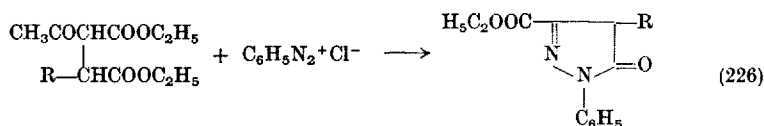
A large number of 5-oxo-2-pyrazolin-3- and 4-carboxylic acids and their derivatives have been prepared. These are listed in Tables XXIII, XXXII and XXXIII. These compounds have been of considerable commercial interest because they are the basis for many azo and azomethine dyes.

The usual procedure for preparing the 5-oxo-2-pyrazolin-3-carboxylic acids is reaction of oxaloacetic acid or esters with hydrazines (eq. 225). Several modifications of this reaction have been used. The

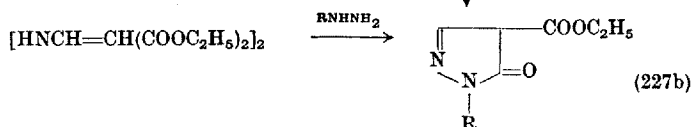
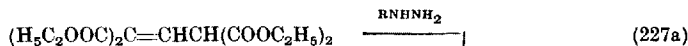


common method is to use the ester in which $\text{R} = \text{R}^2 = \text{CH}_3$ or C_6H_5 and either hydrolyze the ester first obtained ($\text{R}^2 = \text{CH}_3$ or C_2H_5 to $\text{R}^2 = \text{H}$) with base to give the acid^{498, 1544, 1547} or to use base for the cyclization with concomitant hydrolysis of the ester to give acid directly.^{87, 312, 837, 1635} The acid ester in which $\text{R} = \text{H}$ and $\text{R}^2 = \text{C}_2\text{H}_5$ as starting material gives the acid directly.^{347, 624} Oxaloacetic acid has been used and it also gives the acid.⁴³ Of course, hydrolysis of alkyl 5-oxo-2-pyrazolin-3-carboxylates obtained by other means can also be used, as can the hydrolysis of the hydrazide.³³⁷ 5-Oxo-2-pyrazolin-4-carboxylic acids are most frequently prepared by hydrolysis of the corresponding esters.^{306, 1228, 1230} Oxidation of 4-hydroxymethyl-2-pyrazolin-5-ones²⁴ and 5-oxo-2-pyrazolin-4-carboxaldehydes¹⁰⁷ with permanganate also gives the acid.

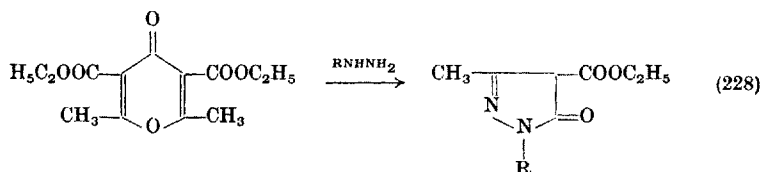
Esters of 5-oxo-2-pyrazolin-3-carboxylic acid are prepared by treatment of the esters of four-carbon dicarboxylic acids with hydrazines or diazonium salts. By far the most frequently used method has been the condensation of oxaloacetic esters (esters of α -oxosuccinic acid) with various hydrazines, as shown in eq. 225.^{358, 1544} This is of course merely a variation of the classical 2-pyrazolin-5-one synthesis. The ester can be substituted⁴³ to give various 4-substituents in the product and various hydrazines^{2, 153, 499} can be used. The reaction mixture can be heated⁵⁹⁴ or mild bases can be used as condensing agents.⁴¹⁴ The hydrazone can first be prepared and then cyclized with acid.⁴³ Usually the 3-carboxylic acid hydrazide is obtained as a by-product.¹⁵⁴⁴ As is the case with other α, β -acetylenic esters, the condensation of diethyl acetylenedicarboxylate with hydrazine forms 2-pyrazolin-5-ones but the dicarboxylic esters give products having 3-carbethoxy substituents.^{1547, 1549} In a very similar type of reaction diethyl chlorofumarate and hydrazines are used.¹²²⁰ Treatment of diethyl α -acetylsuccinate with phenyldiazonium chloride forms ethyl 1-phenyl-5-oxo-2-pyrazolin-3-carboxylates (eq. 226).^{37, 767}



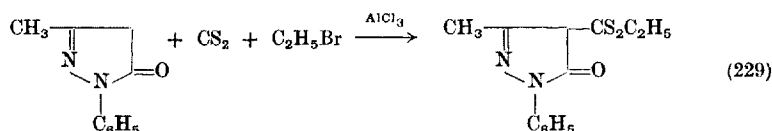
The synthesis of alkyl 5-oxo-2-pyrazolin-4-carboxylates is carried out by reaction of hydrazines with various esters having β -substituents or α, β -unsaturation and also an α -carbalkoxy substituent. These methods are quite analogous to ones used generally for this type of ring formation, being modified only to introduce the carboxylate function at the appropriate place. The reaction of acylmalonic esters^{138, 418, 419, 563, 1222, 1223} and their thiono analogs¹⁰⁰⁸ with hydrazines (eq. 1, p. 9, $\text{R}^2 = \text{COOR}$ and $\text{R}^3 = \text{H}$) gives this type of pyrazolin-one and is the most frequently used synthesis. Ethoxymethylenemalonic esters³⁰⁶ and aminomethylidynemalonic esters^{604, 1231} also react with hydrazines to form alkyl 5-oxo-2-pyrazolin-4-carboxylates. Further syntheses are illustrated in eqs. 227a, 227b and 228. The thio analogs⁸⁹



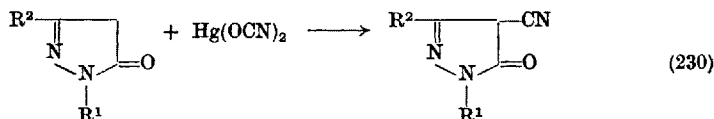
of these esters are synthesized by reaction of 2-pyrazolin-5-ones with carbon disulfide and ethyl bromide (eq. 229).



The usual acid derivatives of 5-oxo-2-pyrazolin-3- and 4-carboxylic acids are known. Amides are prepared by reaction of esters and ammonia,¹³³⁹ by the reaction of urea with 2-pyrazolin-5-ones, and by the reaction of azides with ammonia and amines. Hydrolysis of nitriles



also gives amides.⁹²⁴ The reaction of oxaloacetic esters with excess of hydrazine leads to formation of the hydrazide of 5-oxo-2-pyrazolin-3-carboxylic acid.¹⁵⁴⁴ Fenton and Jones⁴⁴³ have reported the same product obtained from oxaloacetic acid, but their melting point differs from the melting point reported by others for this compound. The 3-hydrazide is also obtained by the reaction of hydrazine with diethyl bromosuccinate.³³⁷ A number of hydrazides have been prepared by standard reactions, such as reaction of esters⁵⁹⁴ and acid chlorides⁴⁹⁸ with hydrazine. Acid chlorides are prepared by reaction of acids with thionyl chlorides.⁴⁹⁸ Azides have been synthesized by treatment of hydrazides with nitrous acid⁴⁹⁸ and by reaction of acid chlorides with sodium azides.⁴⁹⁸ 5-Oxo-2-pyrazolin-4-carbonitriles are prepared by condensation of acylecyanoacetic esters with hydrazine,¹³¹⁰ by dehydration of the 4-carboxaldehyde oxime⁹²⁵ and by direct introduction of a nitrile group. The nitrile group has been introduced by treatment of 2-pyrazolin-5-ones with either cyanogen bromide in the presence of aluminum chloride²⁴ or with mercuric fulminate (eq. 230).^{924, 1186} Ridi



and Checchi¹¹⁹⁰ described a similar reaction but claimed to have obtained the isonitrile.

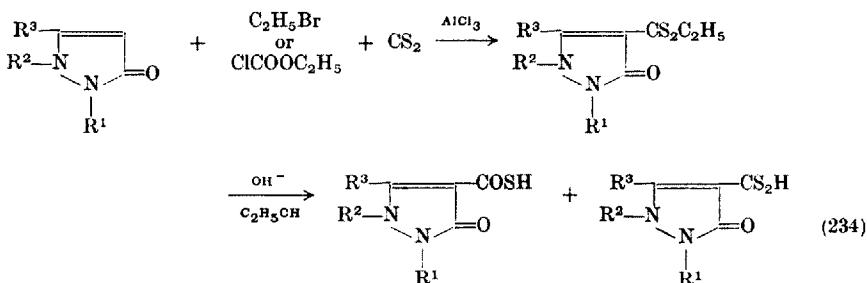
A number of bis(2-pyrazolin-5-ones) having carboxyl groups or carboxyl derivatives as substituents have been prepared. Compounds linked at the 4,4'-positions by a single bond are usually formed by oxidation of a 5-oxo-2-pyrazolin-3-carboxylate with hydrazines (eq. 45).^{1082, 1229} The usual process is to start with a compound, such as an oxaloacetic ester, and treat this with excess of hydrazine. The monomeric pyrazolinone is formed and oxidized to the dimer by the excess of hydrazine present. Another cyclization procedure resulting in dimeric pyrazolinones containing carbethoxy groups is the reaction of hydrazines with α, α' -dicarbethoxy- β, β' -dioxoglutaric esters.¹²²² Dimerization of 5-oxo-2-pyrazolin-3-carboxylic acids or their derivatives has been achieved by reaction with formamide to give 4,4'-methylidyne-bis(5-oxo-2-pyrazolin-3-carboxylic acids).¹²⁶² 5-Oxo-2-pyrazolin-3-carboxylic acids having a 1-(X-aminophenyl)-substituent have been dimerized by reaction with phosgene to give a urea which links the two monomers.^{152, 511} Some 4,4'-bis(2-pyrazolin-5-ones) of the pyrazole blue type, i.e. having an olefin linkage at the 4,4'-positions, have been converted to nitriles by treatment with hydrogen cyanide which adds across the double bond.¹⁶¹² Bis compounds having both carboxyl or carboxyl derivatives and arylazo substituents have been prepared analogously to the mono compounds, except for the use of tetrazonium salts.^{727, 767}

$$\begin{array}{c}
 \text{NCCH}_2\text{COCOOCC}_2\text{H}_5 \xrightarrow{\text{C}_6\text{H}_5\text{N}_2\text{Cl}} \text{NCCHCOCOOCC}_2\text{H}_5 \xrightarrow{\text{C}_6\text{H}_5\text{NNH}_2} \\
 | \\
 \text{N}=\text{NC}_6\text{H}_5 \\
 \\
 \text{NCCH}-\text{COOCC}_2\text{H}_5 \longrightarrow \text{H}_5\text{C}_2\text{OOC}-\text{N}=\text{NC}_6\text{H}_5 \\
 | \qquad \qquad \qquad || \qquad \qquad \qquad / \quad \backslash \\
 \text{N}=\text{NC}_6\text{H}_5 \qquad \text{NNHC}_6\text{H}_5 \qquad \text{N} \qquad \text{N}=\text{NH} \\
 | \\
 \text{C}_6\text{H}_5
 \end{array} \quad (233)$$

B. 3-Pyrazolin-5-ones

A large number of 5-oxo-3-pyrazolin-3- and 4-carboxylic acids, acid derivatives and their sulfur analogs are known and are listed in Tables XXXIV and XXVI. The acids are synthesized by methylation of the N-2 of 5-oxo-2-pyrazolin-3-carboxylic acids¹⁰⁸ or by conversion of 4-substituents to 4-carboxyl groups. These conversions involve oxidation of hydroxyl,^{17,107,697} formyl¹⁰⁷ and carbon chain substituents,¹⁰⁸ hydrolysis of esters^{109,370,993} and hydrolysis of a 4-trichloroacetyl group.⁸⁹⁶ Esters have been prepared by reaction of *N,N'*-diphenylhydrazine with ethyl oxaloacetate³⁷⁰ and with dimethyl acetylenedicarboxylate,³⁷⁰ similarly to the previously mentioned 5-oxo-2-pyrazolin-3-carboxylate analogs. Diethyl ethoxymethylenemalonate and *N*-phenyl-*N'*-acetylhydrazine react to form ethyl 2-phenyl-5-oxo-3-pyrazolin-4-carboxylate.⁹⁹³ Methylation of 2-pyrazolin-5-one esters at N-2, as expected, gives the 3-pyrazoline analogs.^{1228,1230} These esters are also obtained by direct esterification of the acids^{18,697,698} and by reaction of acid chlorides with alcohols.⁷⁴¹ The 5-oxo-2-pyrazolin-3- and 4-carboxamides are synthesized by treatment of the appropriate acid chloride,^{107,741} anhydride²³ or ester^{697,826,1339} with an amine. Partial hydrolysis of nitriles has also given the amides.⁹²⁵ Treatment of 3-pyrazolin-5-ones with ureas or isocyanates gives the 4-carboxamides.⁸²⁶ Hydrazides have been prepared from 5-oxo-3-pyrazolinecarboxylic acid chlorides^{204,892,1634} or esters^{697,698} and hydrazines. Azides are obtained by treatment of hydrazides with nitrous acid.^{167,1387} Various dehydrations of 5-oxo-3-pyrazolin-4-carboxaldehyde oximes have been used to prepare nitriles.^{925,1181,1183} The N-2 methylation of 5-oxo-2-pyrazolin-carbonitriles has also been employed.¹¹⁸³ Acid chlorides,^{18,109} anhydrides⁷⁴¹ and acyl nitriles⁷⁴¹ have been synthesized by the usual procedures.

Sulfur analogs of 5-oxo-3-pyrazolin-4-carboxylic acids, esters and amides are known. The usual synthesis of both thio and dithio acids is by alkaline hydrolysis of the dithioesters,^{109,831} as shown in eq. 234.



Also shown in the same equation is the synthesis of esters by the reaction of 3-pyrazolin-5-ones with carbon disulfide and either ethyl bromide or ethyl chloroformate in the presence of aluminum chloride.^{89, 109} The monothio acids have been synthesized by reaction of acid chlorides with hydrogen sulfide.¹⁰⁹ Kocwa^{826, 829, 830, 831} has studied the preparation of amides and hydrazides of these thio acids and found that two types exist. In one type the compounds are thioamides but in the other they are iminothiolic acids. Treatment



of dithioesters and monothio acids with amines results in a mixture of products. The reaction of 3-pyrazolin-5-ones with *N,N'*-diphenylthiourea or thioisocyanates forms the thioamides.⁸²⁶ Hydrolysis of the iminothiolic acids with base gives amides no longer containing sulfur.⁸²⁶ Mixed anhydrides of sulfonic acids and 5-oxo-3-pyrazolin-4-carboxylic acids have been prepared by the reaction of the sodium salt of the carboxylic acid with benzenesulfonyl chloride.⁷⁴¹

The 5-oxo-3-pyrazolincarboxylic acids react normally. A number of their reactions have already been discussed in connection with the synthesis of analogous aldehydes and ketones. The Curtius rearrangement of the azide will be discussed in more detail in the section concerning 5-imino-3-pyrazolidinones. Both the 3- and 4-carboxylic acids decarboxylate at elevated temperatures.^{107, 108, 370} Hydrolysis of 4-carboxanilides with hydrochloric acid first forms the acid which then loses carbon dioxide.⁸²⁶

A few 5-phenylimino-3-pyrazolin-4-carboxanilides and thioanilides are known (Table XIX). These were prepared by the reaction of phenylisothiocyanates or *N,N*-diphenylthiourea with the corresponding 5-imino-3-pyrazoline⁸²⁶ or by methylation at N-2 of a 5-imino-2-pyrazolin-4-carboxanilide.⁸²⁶

10. Sulfonic Acids and Derivatives

A. 2-Pyrazolin-5-ones

The only compounds of this kind which have been reported are 5-oxo-2-pyrazolin-4-sulfonic acids (Table XXXV). They are prepared by direct sulfonation, usually with fuming sulfuric acid.^{684, 685, 1671, 1672, 1674} Sulfonation occurs at temperatures as low as 10–15°, ⁶⁸⁴ but it takes place much more rapidly at higher temperatures. If an aryl

group is present as a 1-substituent, this too may be sulfonated at higher temperatures.

The sulfonic acid group is readily replaced by a number of reagents, such as nitrous acid⁶⁸⁴ and aryldiazonium salts. It is readily removed by acid hydrolysis.⁶⁸⁴

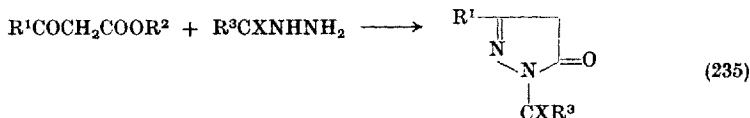
B. 3-Pyrazolin-5-ones

5-Oxo-3-pyrazolin-4-sulfonic acids (Table XXXVI) are prepared by direct sulfonation^{738, 745} with sulfuric acid and acetic anhydride or by chlorosulfonation with chlorosulfonic acid, followed by hydrolysis to the acid.^{1248, 1249} The reaction of 2,3-dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-sulfonyl chloride with urea forms a bis(5-oxo-2-pyrazolin-4-sulfonic acid) derivative,¹²⁴⁹ the only such bis derivative reported. Reduction of the sulfonic acid chlorides with zinc and acid forms the corresponding mercapto compound.¹²⁴⁹

11. Functional Group Substituents on Nitrogen

A. 2-Pyrazolin-5-ones

Functional group substituents on N-1 of 2-pyrazolin-5-ones (Table XXXVII) are acyl, sulfonyl and various carboxyl derivatives, such as carbalkoxy, amides, thioamides, hydrazides, thiohydrazides and amidines. The usual synthesis of these compounds is by the classical 2-pyrazolin-5-one synthesis, reaction of a β -ketoester with a hydrazine. In these cases the hydrazines are special types such as hydrazide, semicarbazide, carbazide or their imino or thio analogs.^{61, 65, 97, 275, 357, 358, 359, 497, 602, 716, 718, 719, 720, 1012, 1013, 1067, 1222, 1345, 1568, 1632} This synthesis is illustrated in eq. 235. Hydrazides of sulfonic acids can also be

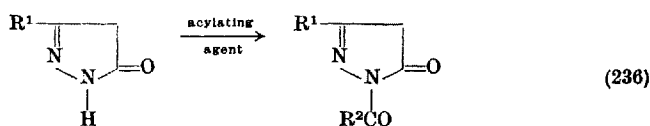


R^3 = alkyl, aralkyl, aryl, NH_2 , NH_2NH , C_6H_5NHNH

X = O, S, NH

used.⁷¹⁶ Sometimes the hydrazone intermediates are isolated and cyclized by heating.^{264, 355, 358} If R^3 is aralkyl or aryl it is necessary to operate at room temperature, otherwise deacylation occurs.⁶ A β -ketoamide can be used instead of a β -ketoester.⁶⁹² 2-Pyrazolin-5-ones having

no N-1 substituent have been acylated by various procedures (eq. 236). Weissberger and Porter¹⁵⁹⁸ have studied such acylations using acetic anhydride and found that a side-product is formed by acylation of both



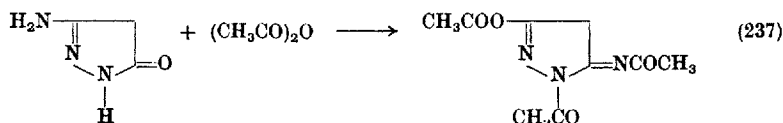
N-1 and O. Other acylating agents used have been arylsulfonyl chlorides¹¹⁹⁹ and alkylchloroformates.⁶¹ Isocyanates react with N-1 of 2-pyrazolin-5-ones having no 1-substituent to form 5-oxo-2-pyrazolin-1-carboxanilides. Treatment of 1-acyl-5-acyloxypyrazoles with piperidine in ethanol removes the O-acyl to give 1-acyl-2-pyrazolin-5-ones.¹⁵⁹⁸

A number of such compounds having a functional group on carbon atoms of the ring are known. Compounds having nitro⁶¹ and carboxyl⁴⁹⁷ substituents are prepared by the above procedures with appropriate substituents in the starting materials. Those compounds having bromine,^{355, 357} nitroso^{355, 357, 1296} and phenylazo^{355, 1499} substituents are prepared by the usual methods for introducing such substituents into the 2-pyrazolin-5-one ring.

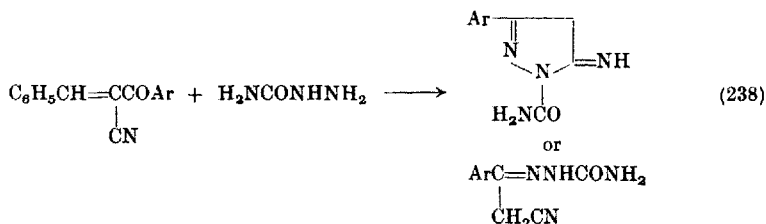
The N-1 acyl substituted 2-pyrazolin-5-ones react as do the other classes of 2-pyrazolin-5-ones since the hydrogen atoms at C-4 are active.^{519, 1296} The N-acyl substituents are readily removed by hydrolysis^{264, 355} or treatment with aniline.⁶ Pyridine and acetic acid cause a rearrangement of N-acetyl groups to the oxygen atom.¹⁵⁹⁸

A few bis(1-acyl-2-pyrazolin-5-ones) are known. Those linked through N-1 have been prepared by reaction of carbazide with two equivalents of a β -ketoester^{1037, 1632} either with²⁵⁵ or without isolation of the intermediate hydrazone. The bis compounds linked at C-3 or C-4 are prepared by reaction of bis(β -ketoesters) with semicarbazide.^{357, 1222}

The 5-imino-2-pyrazolines having no N-1 substituents can be acylated with acetic anhydride to form the 1-acyl derivatives,^{301, 342, 391} as can their 5-oxo analogs. Compounds of this type having a 3-acetoxy substituent have been prepared by reaction of 3-amino-2-pyrazolin-5-ones (5-imino-3-pyrazolidinones) with acetic anhydride (eq. 237).^{594, 1598} Cusmano and Sprio^{343, 344} have treated α -benzylidene- β -ketonitriles



(eq. 238) with semicarbazide to give products which may be 5-imino-



2-pyrazolin-1-carboxamides, although they may be isomeric open-chain compounds.

B. 3-Pyrazolin-5-ones

Many 3-pyrazolin-5-ones having acyl substituents on N-1 or N-2 or on both have been reported and are listed in Table XXXVIII. Most of these compounds have been prepared by acylation of 2-pyrazolin-5-ones with acyl chlorides or anhydrides. Usually it was assumed that acylation occurred on one or the other of the nitrogen atoms and *O*-acylation was not considered. However, Weissberger and Porter¹⁵⁹⁸ have found that acylation occurs quite readily on the oxygen, and have shown that the compound reported by von Rothenburg¹⁵⁵⁷ to be 1,2-diacetyl-3-phenyl-3-pyrazolin-5-one was actually 1-acetyl-3-phenyl-5-acetoxypyrazole. In view of this work it is probable that many of the compounds believed to be 1- or 2-acyl-3-pyrazolin-5-ones are 5-acetoxypyrazoles. Henry and Dehn⁶⁴³ have obtained a product from 3-methyl-1-phenyl-2-pyrazolin-5-one and phenylisocyanate which may be 3-methyl-1-phenyl-2-phenylcarbonyl-3-pyrazolin-5-one but it may be a product of reaction of the enolic hydroxyl group.

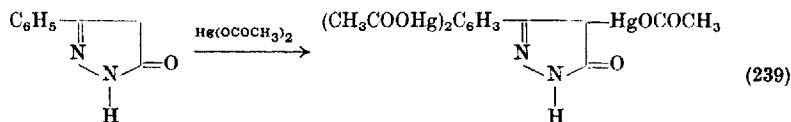
4,4'-Bis(3-methyl-2-benzoyl-1-phenyl-3-pyrazolin-5-one) has been reported as the product obtained from treatment of 4,4'-bis(3-methyl-1-phenyl-2-pyrazolin-5-one) with benzoyl chloride.¹⁰⁵⁶

The reaction of 5-imino-3-pyrazolidinones with acetic anhydride forms 2-acetyl-3-acetoxy-5-acetimido-3-pyrazolin-5-ones as well as the 5-imino-2-pyrazoline derivatives already mentioned.^{594, 1599}

12. Mercury Substituted Derivatives

A. 2-Pyrazolin-5-ones

Only one mercurated 2-pyrazolin-5-one has been reported. This was prepared by Schrauth and Bauerschmidt¹²⁷⁵ and its structure is not completely known (eq. 239).



B. 3-Pyrazolin-5-ones

A few mercurated 3-pyrazolin-5-ones have been prepared by Ragno¹¹⁵⁵ (Table XXXIX). Antipyrine was treated with mercuric acetate or mercuric ammonobasic chloride, giving mercury-containing substituents in the 4-position. The chloromercuri and acetoxymercuri compounds obtained were converted into others by treatment with hydrochloric acid, potassium bromide, potassium iodide, iodine or sodium hydroxide. More vigorous treatment with mercuric acetate introduced a second acetoxymercuri substituent which was in the phenyl ring.

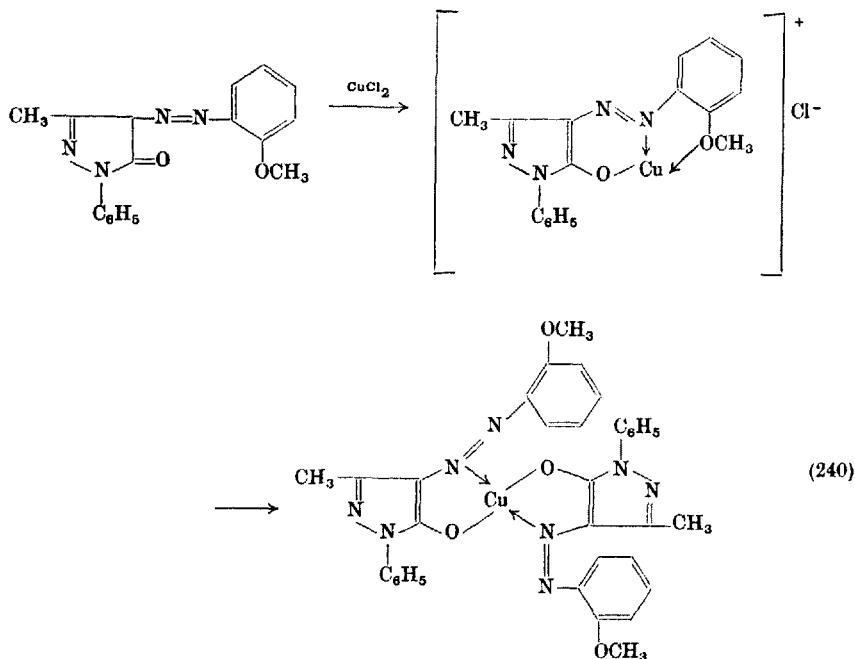
13. Metallic and Non-metallic Complexes

A. 2-Pyrazolin-5-ones

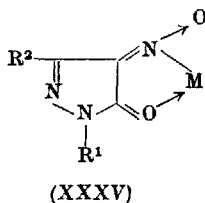
2-Pyrazolin-5-ones react with salts of various metals to form compounds in which the pyrazolinone has reacted in its enolic form with replacement of the enolic hydrogen to give a salt and having semipolar bonds formed by donation of electrons to the metal by the nitrogen atoms^{393, 394} Usually these compounds contain the number of pyrazolinone residues corresponding to the valence of the metal atom. Such salts as cuprous iodide, ferric iodide, cobaltous iodide, silver iodide and silver diiodide participate in such reactions.^{393, 394} In addition, complexes may be formed in which there has been no elimination of a small molecule between the reactants and no formation of ionic bonds.⁴⁸²

Various substituted 2-pyrazolin-5-ones react with metal salts with replacement of hydrogen and formation of semipolar bonds with electron donating atoms. The most important of these compounds are the metal complexes of 4-arylaazo-2-pyrazolin-5-ones. These complexes are widely used in the dye industry to give desired properties to 4-arylaazo-2-pyrazolin-5-one dyes. Although a large number of metal-dye complexes have been used in dyeing, only a few such compounds have been characterized and reported in the literature. Usually a solution of the azo compound and an appropriate salt such as cupric chloride or nickel sulfate are mixed in solution and heated.³²⁶ The reaction is

shown in eq. 240 together with the structure of the final product. In some cases the formation of an intermediate, as shown in eq. 240, has been reported.¹⁰³⁸⁻¹⁰⁴⁰ The structures of complexes with chromium are shown in formulas (XXX) and (XXXI). Brady and Porter¹³⁹ have



reported complexes of 4-oximino-2-pyrazolin-5-ones with lithium, sodium, potassium, rubidium, cesium, thallium and nickel. These complexes have the structure (XXXV) if they are derived from an atom having a valence of one. If the metal has a valence of two, the



complex is a dimer of (XXXV). Giva⁵⁷³ has prepared the thallous salt of picrolonic acid, 4-nitro-3-methyl-1-(4-nitrophenyl)-2-pyrazolin-5-one. This is reported to have a structure similar to (XXXV), with the metal replacing the hydrogen of the pseudo-acid form of the nitro group.

Dains, O'Brien and Johnson³⁵¹ have added bromine to various 4-arylaminomethylidyne-1-aryl-3-alkyl- and 3-aryl-2-pyrazolin-5-ones. Whether this is a complex or an addition to a carbon-nitrogen double bond is uncertain. The bromine is very loosely held and is probably not bound covalently.

The formation of various complexes between 1-methyl-3-phenyl-2-pyrazolin-5-one and organic compounds has been reported.¹¹⁶⁴ These were 1:1 complexes with *m*- and *p*-nitrophenol, *o*-cresol, picric acid, trinitrobenzene, α -naphthol, hydroquinone, hydroxy- and halogeno-aliphatic acids and aromatic acids. It was claimed that these did not behave as salts. Similar complexes of other 2-pyrazolin-5-ones with trinitrobenzene have been reported.¹³⁶⁸

B. 3-Pyrazolin-5-ones

3-Pyrazolin-5-ones form complexes with both inorganic and organic compounds much more readily than do the 2-pyrazolin-5-ones. The most extensive series of complexes is that formed with a variety of metallic salts. Antipyrine (2,3-dimethyl-1-phenyl-3-pyrazolin-5-one) forms a series of complexes with salts of divalent, trivalent and tetravalent metals. Two molecules of antipyrine form a complex with one molecule of copper, cadmium, cobalt and zinc salts.^{266, 868, 1116} Complexes prepared from metallic nitrates are usually hydrated.¹³²² There also exists a series of complexes in which three molecules of antipyrine form a complex with one or two molecules of metallic salts. Such complexes form with two molecules of simple ferric salts²⁷² or with one of complex iron cyanides.⁶⁰⁸ Nitrates of thorium, lanthanum, cerium and samarium also give such complexes.⁸⁴¹ This ratio also occurs in some antipyrine complexes with cadmium and zinc thiocyanate.²⁶⁶ A number of salts of rare earths and iron which have complex anions such as thiosulfate, thiocyanate, dithionic acid and complex iron cyanides form complexes in which six molecules of antipyrine are present.^{405, 408, 608, 841, 950} Stannic chloride forms salts containing three or four molecules of antipyrine and hydrochloric acid.⁴⁶

Aminopyrine (4-dimethylamino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one) forms complexes similar to those of antipyrine, but usually containing fewer molecules of the 3-pyrazolin-5-one. Complexes with mercury, cadmium, antimony, zinc and cobalt salts include only one molecule of aminopyrine. A number of complexes with cobalt, zinc and calcium salts have two molecules of aminopyrine, some also containing acid and water of hydration.^{736, 1322} The complex with cerous nitrate contains three molecules of aminopyrine.¹²³⁸ A few other substituted

antipyrine-metal salt complexes of a similar nature have been reported.^{869, 1158, 1322} These metallic salt complexes are decomposed by sodium hydroxide⁸⁶⁸ or by boiling with water.¹¹⁵⁸

Several complexes of 3-pyrazolin-5-ones with iodine are known.^{321, 429} These contain varying proportions of the pyrazolinones and iodine and always contain hydrogen iodide. The iodine is readily lost by heating or by recrystallization. Iodine complexes with bis(2,3-dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-yl)mercury have been reported.⁴³³

A number of organic compounds form complexes with antipyrine and aminopyrine. Usually these are in a 1:1 ratio, although those with diethylbarbituric acid,¹¹¹² phenylethylbarbituric acid¹⁴⁸⁴ and diphenylhydantoin⁴⁸¹ may contain two molecules of pyrazolinone, and a complex having two molecules of diphenylhydantoin to one of antipyrine has been reported.¹⁰²¹ A series of complexes with phenols, aromatic acids, and hydroxy and halogeno aliphatic acids have been reported.¹¹⁶⁴ These products do not behave like salts. Benzenesulfonyl chloride forms a complex with antipyrine in a 2:1 ratio.¹²⁸¹ Pfeiffer and Seydel¹¹¹⁵ claim that complexes of antipyrine and aminopyrine with 2,2,2-trichloroethyl carbamate and its *N*-phenyl homologue involve bonding at the amide group in the pyrazolinone. Taboury¹⁴⁶⁷ reaches the same conclusion regarding the chloral-antipyrine complex on the basis of Raman spectra.

14. Miscellaneous Derivatives

This section comprises a few 3-pyrazolin-5-ones which do not fit well in other sections and some polymeric 2-pyrazolin-5-ones.

2-Pyrazolin-5-ones have been incorporated into a number of polymers for use in color photography. Many of these are prepared by reaction of a functional group in a polymer with some reactive group in a pyrazolinone. Some are prepared by linking polymers with pyrazolinones through aldehydes, and frequently bifunctional pyrazolinones are made to react with aldehydes to give condensation polymers. In one case a hydrazino group is formed in a copolymer of *p*-aminostyrene and maleic acid and this polymer is condensed with ethyl acetoacetate giving a polymeric pyrazolinone.¹⁶

Several pyrazolinone polymers have been prepared by linking polymers and pyrazolinones by amide linkages. This has been done by treating copolymers containing maleic anhydride with 1-(aminophenyl)-2-pyrazolin-5-ones^{162, 1273} and by treating the acid chloride of 1-(3-carboxyphenyl)-3-methyl-2-pyrazolin-5-one with polymeric

amines.^{483, 484} A similar type of polymer is that obtained from poly-*p*-chlorosulfostyrene and 1-(aminophenyl)-2-pyrazolin-5-one, except that a sulfonamide linkage is obtained.¹⁰⁰⁵

Quite a variety of polymeric pyrazolinones have been prepared by reaction of polymers having amide or hydroxyl groups with aldehydes and pyrazolinones. Some of the pyrazolinones have contained amino groups. The linkages involved are probably acetal for the most part. In one of these cases the aldehyde group is incorporated in the 1-aryl group of the pyrazolinone and the polymer is a polyvinyl alcohol.³⁸⁵ Presumably the polyvinyl alcohol forms an acetal of the formyl group. Woodward^{1647, 1648} has prepared polymers from polyhydroxy compounds such as polyvinyl alcohols and methyl cellulose combined with aldehydes and pyrazolinones. The linkages here are no doubt formed by conversion of the aldehydes to acetals and may be derived from the enolic form of the 2-pyrazolin-5-ones. Jennings⁷⁰⁸ and McQueen⁹⁸⁶ have prepared similar polymers. Condensation of polyvinyl alcohol with 1-(3-aminophenyl)-3-methyl-2-pyrazolin-5-one in the presence of dialdehydes such as glyoxal and terephthalaldehyde has given polymeric pyrazolinones.⁷¹⁰ The linkage is probably a combination of Schiff's base and acetal formation. A polymer has been prepared by reaction of a polyamide with formaldehyde, 3-methyl-1-phenyl-2-pyrazolin-5-one and butanol.⁹⁶⁵ It seems likely that the amide nitrogen of the polymer is connected by a methylene group with C-4 of the pyrazolinone. Jennings, Murray and White⁷¹² have obtained a polymer of uncertain structure from polyvinyl alcohol, *m*-aminobenzaldehyde and 1-phenyl-5-oxo-2-pyrazolin-3-carboxylic acid. There are a number of possibilities for linking groups which may be present in this polymer but, in any case, some must be of acetal or ether type.

Bisamides of amino-2-pyrazolin-5-ones react with aldehydes such as formaldehyde and *p*-hydroxybenzaldehyde to give polymers.^{797, 1041}

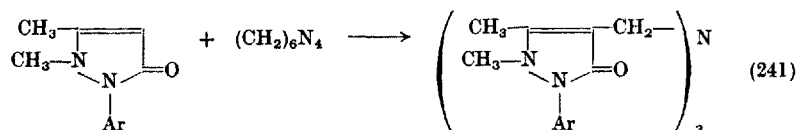
Presumably the linking group is >NCH—N< . Bisamides of 1-(aminophenyl)-2-pyrazolin-5-ones and of 3-amino-2-pyrazolin-5-ones have been used. 1-(3-Aminophenyl)-3-methyl-2-pyrazolin-5-one reacts with many aldehydes and ketones to form polymers.⁹⁶⁴ Probably condensation occurs at C-4 and the amino group. The product of reaction of *p*-cresol with formaldehyde has been found to react with 1-(4-hydroxyphenyl)-3-methyl-2-pyrazolin-5-one to give a polymer that must have the aromatic and pyrazolinone rings connected by ether linkages.¹²⁶⁹

Kirby⁷⁸⁰ has linked a polymer with a pyrazolinone by forming the quaternary salt of 1-(3-bromoacetamidophenyl)-3-methyl-2-pyrazolin-5-one with a polyamine.

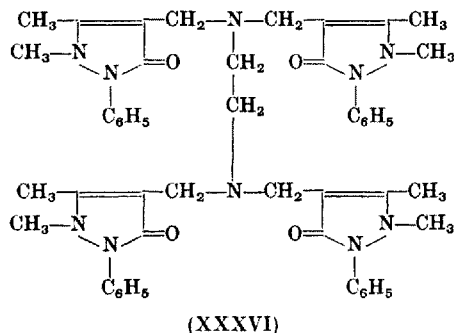
Jennings⁷⁰⁹ has linked pyrazolinones with zein by means of formaldehyde and dimethylolurea. It was suggested that a linkage is formed from amino groups in the zein to C-4 or an amino group in the pyrazolinone.

Verkade and Dhont¹⁵³¹ have treated 3,4-dimethyl-2-pyrazolin-5-one and 4-methyl-3-phenyl-2-pyrazolin-5-one with phenyldiazonium chloride, forming respectively 3,4-dimethyl-2-phenylazo-3-pyrazolin-5-one, m.p. 273°, and 4-methyl-3-phenyl-2-phenylazo-3-pyrazolin-5-one, m.p. 212°. 2,3-Dimethyl-1-phenyl-3-pyrazolin-5-one reacts with thiocyanogen to give its thiocyanate salt and 2,3-dimethyl-1-phenyl-4-thiocyanato-3-pyrazolin-5-one, m.p. 125°. ⁷⁴²

2,3-Dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-carboxaldehyde reacts with 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one to give tris(2,3-dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-yl)methane.¹⁰⁷ Mannich and Krosche⁹⁴⁶ have treated 2,3-dimethyl-1-aryl-2-pyrazolin-5-ones with hexamethylenetetramine to give compounds of the type shown in eq. 241. The aryl groups were phenyl and *p*-tolyl. The reaction of 2,3-



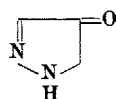
dimethyl-1-phenyl-3-pyrazolin-5-one with ethylene diamine and formaldehyde gives (XXXVI).⁹⁴⁵ 2,3-Dimethyl-1-phenyl-3-pyrazolin-5-one reacts with mercuric oxide to give bis(2,3-dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-yl) mercury, m.p. 180°, ⁴³³ and with selenium or selenium dioxide to give the corresponding selenide, m.p. 240°. ⁵⁴⁵



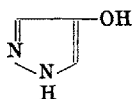
CHAPTER III

2-Pyrazolin-4-ones

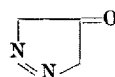
Relatively few 2-pyrazolin-4-ones are known, and most of our knowledge of these compounds has been furnished by Chattaway, Ashworth and co-workers who published an extensive series of papers on this subject in the thirties. These compounds are basic, forming salts with acids and alkyl halides, and they are also acids, giving salts with bases. They form colored complexes with ferric chloride. Four structures are possible for 2-pyrazolin-4-one, (XXXVII), (XXXVIII), (XXXIX) and (XL), but substitution at C-3 and C-5 makes possible



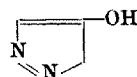
(XXXVII)



(XXXVIII)

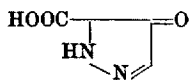


(XXXIX)

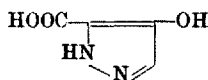


(XL)

several more isomers. If a substituent is present at N-1, only two isomers, (XXXVII) and (XXXVIII), are possible. It has usually been considered that 2-pyrazolin-5-ones have the hydroxypyrazole structure (XXXVIII).²⁸⁶⁻²⁹⁰ Wolff¹⁶⁴⁴ has postulated this structure on the basis of the alcohol derivatives formed by these compounds. However, Emerson and Beegle⁴²⁵ have found that 4-oxo-2-pyrazolin-3-carboxylic acid forms two derivatives by reaction with 4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (2,3-dimethyl-1-phenyl-4-imino-3-pyrazolidinone). This was interpreted to mean that the 2-pyrazolin-4-ones exist in two forms. One of these would be either (XXXVII) or (XXXVIII) with a carboxyl group at C-3, or a mixture of these two forms, and the other would be either (XLI) or (XLII), or a mixture of these. Bertho



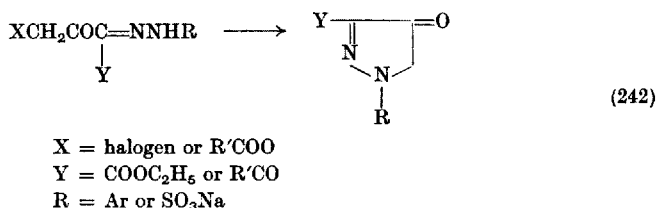
(XLI)



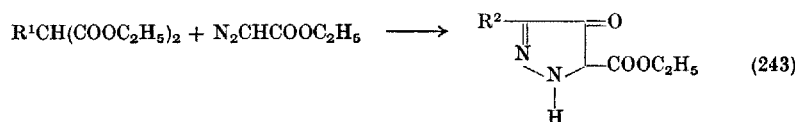
(XLII)

and Nüssel⁹² have argued that 2-pyrazolin-4-ones exist as keto-enol tautomers. 2-Pyrazolin-4-ones having substituents at N-1 and C-3 and disubstituted at C-5 would necessarily exist in the oxo-form (XXXVII). The 2-pyrazolin-4-ones are listed in Table XL.

Only two procedures are known for direct synthesis of the 2-pyrazolin-4-one ring system and one of these has been used very little. The chief method employed has been cyclization of the 1-arylhydrazone of 3-substituted-1,2-dioxo compounds (eq. 242) using basic cyclizing



agents.^{286-290, 295, 1292, 1644} In the case in which R=SO₃Na, the R is lost and in the final product R=H. The only other method of ring formation is that reported by Bertho and Nüssel⁹² in which malonic esters are treated with ethyl diazoacetate (eq. 243). If R¹ is H, the substituent R² in the product is carbethoxyl, but otherwise R¹=R².



Treatment of 2-pyrazolin-4-ones with chlorine results in formation of 5,5-dichloro-2-pyrazolin-4-ones.^{287, 288, 290} Reaction of the 5,5-dichloro compound with hydrogen iodide²⁸⁷ or potassium iodide^{288, 290} removes one chlorine atom to give 5-chloro-2-pyrazolin-4-ones. Bromination does not follow the same course as chlorination, but instead forms 5-bromo-2-pyrazolin-4-ones.^{286, 290, 1292} Carboxyl-containing 2-pyrazolin-4-ones can be obtained by hydrolysis of the esters obtained, as shown in eq. 243, or directly by the cyclization procedure of eq. 242. These acids can then be decarboxylated at elevated temperatures.^{92, 1644} Heating the methiodide of 2-pyrazolin-4-one gives methylation at N-1. 2-Pyrazolin-4-ones couple with diazonium salts to give 5-arylazo substituents.¹⁶⁴⁴

The oxo group in 2-pyrazolin-4-ones reacts as a hydroxyl group, forming acetates,²⁸⁶ benzoates¹⁶⁴⁴ and urethanes.¹⁶⁴⁴ Reaction of 2-pyrazolin-4-ones with phosphorus oxychloride results in replacement

of the oxygen to give 4-chloropyrazoles.¹⁶⁴⁴ Treatment of 2-pyrazolin-4-ones with nitrous acid gives substitution of an oximino group at C-5.

Ethyl 1-aryl-5,5-dichloro-4-oxo-2-pyrazolin-3-carboxylates react with alcohols and alkali by cleavage of the ring and formation of mono-arylhydrazones of diketosuccinic acid and its esters.^{287, 290}

For purposes of classification the 4-aminopyrazoles are considered to be 4-imino-2-pyrazolines and analogs of 2-pyrazolin-4-ones. These compounds are listed in Table XL. Such compounds can be prepared by direct cyclization using ethyl diazoacetate and ethyl cyanoacetate.⁹² This is the same as eq. 243, except that the malonic ester is replaced by ethyl cyanoacetate. Purines can be hydrolyzed to 4-imino-2-pyrazolines by using strong acid.^{1210, 1646} By far the most frequently used preparation is reduction of appropriately substituted pyrazoles, such as 4-nitro,^{368, 812, 819, 1015, 1019, 1049} 4-nitroso¹¹⁶⁵ or 4-aryl-azo.^{671, 974, 995} The hydrolysis of the carbethoxy 4-imino-2-pyrazolines derived from ethyl cyanoacetate and ethyl diazoacetate forms 4-imino-2-pyrazolin-3-carboxylic acid which is readily decarboxylated to the parent compound.⁹²

The 4-imino-2-pyrazolines react as would be expected of 4-amino-pyrazoles. For example, acylation^{368, 1043} and diazotization^{812, 819} occur readily.

Only two bis(4-imino-2-pyrazolines) have been prepared. These were reported by Michaelis and Schäfer.⁹⁹⁵

CHAPTER IV

2-Pyrazolin-4,5-diones

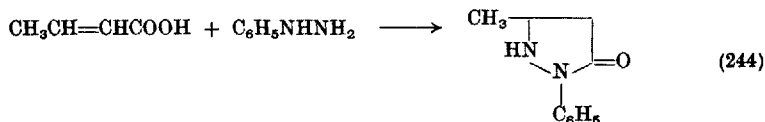
Only half-a-dozen of these compounds are known (Table XLI) and at least this number of methods of preparing them have been reported. Borsche and Manteuffel¹²⁵ have found that 2-pyrazolin-4,5-diones are formed as the by-products when α -ketoesters are treated with aryl-diazonium salts. The principal products are 4-arylaazo-2-pyrazolin-5-ones. Nitric acid oxidation of 3-methyl-1-phenyl-2-pyrazolin-5-one forms the corresponding 4,5-dione.⁸⁰⁹ Wislicenus and Göz¹⁶⁴² heated 4-bromo-4-nitro-1-(4-bromophenyl)-3-methyl-2-pyrazolin-5-one in water and obtained the analogous 4-oxo compound. Acid hydrolysis of rubazonic acids, which are 4-imino-2-pyrazolin-5-ones, leads to 2-pyrazolin-4,5-diones.^{424, 809} Oxidation of 4,4'-bis(2-pyrazolin-5-ones) or of rubazonic acids with nitric acid⁸⁰⁹ forms the 4,5-diones.

CHAPTER V

3-Pyrazolidinones

In recent years there has been extensive work in the field of 3-pyrazolidinones because of their use as photographic developers.^{750, 758, 1176, 1630} This phase of 3-pyrazolidinone chemistry will be considered in more detail in a later section. The 3-pyrazolidinones are monoacidic bases^{911, 1550} forming various salts. They are not acidic,¹⁵⁵⁰ in contrast to the 2-pyrazolin-5-ones. They reduce Fehling's solution and give colors with ferric chloride.¹⁵⁵⁰ Jensen⁷¹³ found that 5-phenyl-3-pyrazolidinone absorbs infrared light in the carbonyl region at 5.83 μ and at 5.91 μ in solution or at 5.97 μ in the solid state. The absorption was markedly different from that of noncyclic hydrazides. These compounds are listed in Table XLII.

As was mentioned previously (eq. 4, p. 10), the principal method used for synthesis of 3-pyrazolidinones is the reaction of hydrazines with α,β -unsaturated acids,^{446, 816, 911, 1342, 1550} α,β -unsaturated esters^{581, 762, 911, 1209, 1569} and α,β -unsaturated amides.⁷⁵⁸ In many cases these reactions do not give 1-substituted-3-pyrazolidinones, as shown in eq. 4, but the isomeric 2-substituted-3-pyrazolidinones, as shown for one particular case in eq. 244. Most frequently aryl hydrazines have

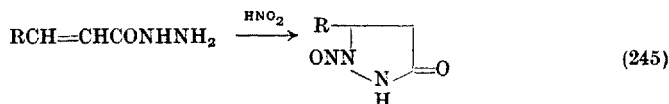


been used in this synthesis, but in a few cases hydrazine has been used.^{911, 1209, 1550} In this situation isomerism is not a problem. Only a few acids have been used in these reactions, but these have all given the 2-isomer (eq. 244).^{446, 816, 1550} Acrylamide, methacrylamide, crotonamide and β,β -dimethylacrylamide and various aryl hydrazines have been condensed in anhydrous solvents in the presence of strong bases. In all cases the 1-isomer (eq. 4) has been obtained.⁷⁵⁸ Kendall, Duffin and

Axford⁷⁶² have found that the reaction of various esters with phenylhydrazine in the presence of sodium ethoxide led to the 1-isomers (eq. 4). Under somewhat similar conditions, but using sodium methoxide as the condensing agent, Vystrčil and Stejskal¹⁵⁶⁹ found that methyl crotonate and phenylhydrazine did not give a 3-pyrazolidinone but rather pyrazolinones. These latter authors studied the condensation of methyl methacrylate and methyl crotonate with phenylhydrazine in the presence of hydroquinone. The chief products were the 2-isomers (eq. 244), but 1-isomers were usually formed in very small yields.

Another widely used procedure for the preparation of 3-pyrazolidinones is one closely related to the preceding one. This method is treatment of a β -substituted acid, lactone, amide or acid chloride with an aryl hydrazine. Substituted β -chloropropionyl chlorides have been used, giving 1-aryl-3-pyrazolidinones.¹⁵ The same kind of product was obtained with a β -bromopropionic acid.¹³²⁷ Condensation of β,β -dimethylglycidamide with phenylhydrazine at 150° gave 5,5-dimethyl-4-hydroxyl-2-phenyl-3-pyrazolidinone.^{156, 1260, 1261} Kendall⁷⁵⁰ has claimed that arylhydrazines react with β -propiolactone to give 1-aryl-3-pyrazolidinones. Reynolds and Tinker¹¹⁷⁷ have stated that this reaction does not occur. However, Gresham and co-workers⁵⁹⁹ have reported that β -propiolactone and phenylhydrazine form the phenylhydrazide of β -hydroxypropionic acid, and Reynolds and Tinker have converted this compound into 1-phenyl-3-pyrazolidinone. Furthermore, the physical constants claimed by Kendall for his products are the same as those reported by others for the same compounds. From these facts it seems likely that Kendall did obtain 3-pyrazolidinones by the procedure claimed.

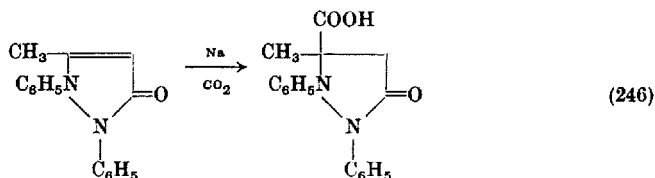
Cyclization of α,β -unsaturated acid hydrazides³¹⁹ or β -hydroxypropionic acid hydrazides^{1177, 1327} forms 3-pyrazolidinones. The β -hydroxy acid derivatives have usually been cyclized with acid at elevated temperatures. If the hydrazides of aryl hydrazines are used, N-1 substitution occurs. It has been reported that α,β -unsaturated acid hydrazines cyclize by treatment of the hydrazide with nitrous acid (eq. 245),^{335, 479, 1028, 1029} leading to formation of 1-nitroso-



pyrazolidinones. However, Godtfredsen and Vangedal⁵⁸¹ have shown that in some cases the starting materials were pyrazolidinones, rather than hydrazides, and this may be true in all cases, so that cyclization by this procedure probably does not occur.

Cyclization of β -hydrazino acids under acid conditions has been used by Lederer⁸⁸⁸ and by Stolz¹³⁵¹ to obtain 3-pyrazolidinones. Treatment of an analogous nitrile with concentrated hydrochloric acid also gives a 3-pyrazolidinone.¹¹²² Vystričil and Stejskal¹⁵⁶⁹ have reported that heating a mixture of methyl α -piperidinobutyrate and phenylhydrazine at 170° gave 4-methyl-2-phenyl-3-pyrazolidinone.

The reaction of 2-phenyl-4-benzylidene-5-oxazolone with hydrazine forms 4-benzamido-5-phenyl-3-pyrazolidinone.^{319, 1342} Both 2-pyrazolin-5-ones and 3-pyrazolin-5-ones have been reduced catalytically to 3-pyrazolidinones.^{1491, 1592} Heymons and Rohland⁶⁴⁷ have treated 3-methyl-1,2-diphenyl-3-pyrazolin-5-one with sodium and carbon dioxide and claimed to have obtained a carboxylic acid, presumably by intermediate addition of sodium to the double bond (eq. 246). A number of

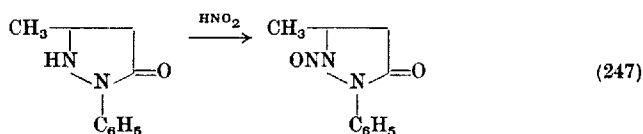


conversions of variously modified ring systems into 3-pyrazolidinones have been reported. 3-Iminopyrazolidines have been hydrolyzed with acid to the analogous oxo compounds. Rondestvedt and Chang¹²⁰⁹ have found that treatment of *N,N*-diethyl-1-pyrazolin-3-sulfonamide with bromine forms 3-pyrazolidinones. The first step is probably the replacement of the sulfonamide portion by bromine; the bromopyrazoline could then go to the pyrazolidinone by hydrolysis. 3-Pyrazolidinone was also obtained by the reaction of ethylenesulfonyl chloride with diazomethane,¹²⁰⁹ which also probably passes through a halogenated pyrazoline stage. Tsumaki¹⁵⁰¹ has claimed that acid hydrolysis of 1,2-diphenyl-3,5-pyrazolidinedione formed 3,4-dihydroxy-1,2-diphenyl-3-pyrazolidinone.

The oxidation of 3-pyrazolidinones to 2-pyrazolin-5-ones has been mentioned (eq. 22). The 3-pyrazolidinones are also oxidized by Fehling's solution¹⁵⁵⁰ and cupric sulfate.⁵⁸¹ The oxidation of 1-aryl-3-pyrazolidinones to 3-pyrazolin-5-ones has been mentioned.^{56, 888}

Substitution in the 3-pyrazolidinone molecule occurs preferentially on one of the nitrogen atoms, if this is possible, although reagents such as bromine may oxidize the 3-pyrazolidinone to a 2-pyrazolin-5-one, and then substitute at C-4. Alkylation of 3-pyrazolidinones with alkyl halides and alkyl sulfates and bases usually occurs at N-2,^{335, 1029} but if substituents are present here, alkylation occurs at N-1.^{888, 1261}

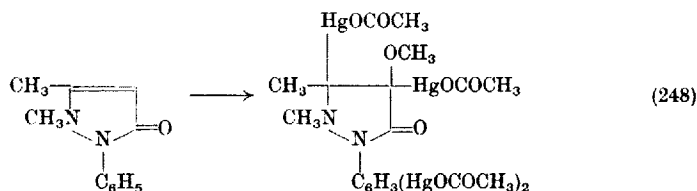
Alkylation of 4-methyl-3-pyrazolidinone with butyl ethylenesulfonate gave alkylation at N-1 with addition of nitrogen at the β -position of the α,β -unsaturated system.¹²⁰⁹ Earlier workers have claimed that nitrosation of 3-pyrazolidinones leads to either substitution at C-4⁴⁴⁶ or oxidation to 2-pyrazolin-5-ones followed by substitution at C-4.^{816,1550} However, later workers uniformly report that nitrosation occurs at N-1 (eq. 247).^{911,1342,1491} Treatment of 3-pyrazolidinones



with bromine results in oxidation to 2-pyrazolin-5-ones followed by substitution of one or two bromine atoms at C-4.^{335,1028} Acetic anhydride reacts with 3-pyrazolidinones to give 1-acetyl derivatives.^{888,1569} Aldehydes react with 3-pyrazolidinones at N-1, giving products which are zwitterions.⁵⁸¹

In the presence of sulfuric acid 1-nitroso-3-pyrazolidinones lose nitrous acid by elimination, giving 2-pyrazolin-5-ones which are then nitrosated at C-4.^{335,1028} The amino group in 4-amino-3-pyrazolidinones is diazotizable and the resulting diazonium salt undergoes coupling.¹²

A number of mercury-containing 3-pyrazolidinones have been prepared by Schrauth and Bauerschmidt.¹²⁷⁵ Treatment of 1-aryl-3-pyrazolin-5-ones having no substituent at C-4 with mercuric acetate in methanol causes addition of acetoxymercuri and methoxy groups at the 3,4-double bond, substitution of acetoxymercuri at C-4 and mercuration in the aryl rings (eq. 248). 2-Pyrazolin-5-ones also undergo

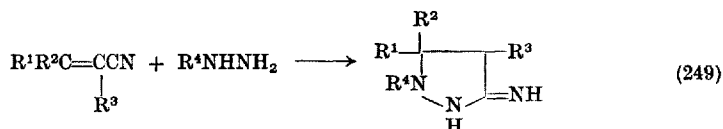


this reaction, behaving as if they were 3-pyrazolin-5-ones. Substituents at C-4 change the course of the reaction. In these cases reaction does not occur at low temperatures but does at 160° to give addition of acetoxymercuri and hydroxyl at the 3,4-double bond. The 4-acetoxymercuri substituents are replaced by hydrogen in the presence of hydrochloric acid, but the same substituents at C-5 are converted to chloromercuri.

Only three bis(3-pyrazolidinones) have been reported in the literature. These are 5,5'-bis(4,4-dimethyl-1-phenyl-3-pyrazolidinone),¹⁵ 4,4'-bis(3-oxopyrazolidin-1-yl)dibenzyl ether¹¹⁷⁷ and 1,4-bis(2-nitroso-3-oxopyrazolidin-5-yl)benzene.¹²²⁶ These are made by procedures already discussed.

A number of 3-iminopyrazolidines have been reported and are listed in Table XLIII. It has generally been believed that these compounds exist as 3-aminopyrazolines, although equilibrium between the two forms has been suggested.⁷⁵⁷ Actually the correct structure of these compounds has not been established and it may well be that they exist primarily as the imino isomer.

The reaction of α,β -unsaturated nitriles^{396, 757, 760} or β -alkoxypropionitriles⁷⁵⁷ with hydrazines gives 3-iminopyrazolidines. If the hydrazine is substituted, the substituent appears at N-1 (eq. 249). The



same type of product is obtained by cyclization of a β -hydrazinopropionitrile.¹¹²² Reduction of 3-arylazopyrazolines also forms 3-iminopyrazolidines.^{396, 757} The imino group of these compounds is readily acylated, and the acyl derivatives can be reduced with lithium aluminum hydride to 3-alkyliminopyrazolidines. The acid hydrolysis of 3-iminopyrazolidines has already been discussed.

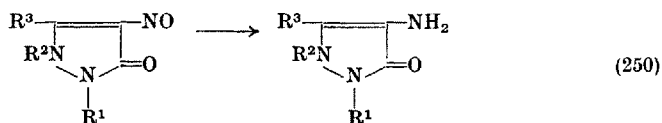
CHAPTER VI

3,4-Pyrazolidinediones

For purposes of classification, 4-hydroxy-, 4-mercapto- and 4-amino-3-pyrazolin-5-ones, except 4-amino having no hydrogen on the nitrogen, have been considered to be 3,4-pyrazolidinediones or derivatives thereof. These compounds could theoretically exist as the 4-oxo, 4-thiono or 4-imino forms but do exist largely, if not exclusively, as the hydroxy, mercapto and amino isomers. The amino compounds will be named as 4-amino-3-pyrazolin-5-ones. They are listed in Table XLIV.

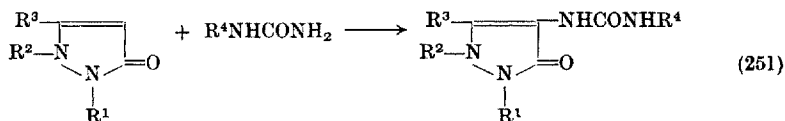
1,5-Dimethyl-2-phenyl-3,4-pyrazolidinedione and its 1,5-diphenyl-2-methyl analog are the only compounds of their class known. The former has been synthesized by treatment of 1-(2,3-dioxobutyl)-1-phenyl-2-methyl-2-nitrosohydrazine hydrate with sodium bisulfite⁹⁹ and by methylation of 4-hydroxy-3-methyl-1-phenyl-2-pyrazolin-5-one.⁸²⁰ The latter compound has been prepared in the same way.¹²⁴³ The dimethyl phenyl compound has also been isolated from urine as a metabolic product of 4-dimethylamino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one⁶¹⁷ and it is formed by treatment of the same compound with sulfuric acid.⁶¹⁸ The 4-thiono analog is also known. Reduction of 2,3-dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-sulfonic acid using zinc in acid gives 1,5-dimethyl-2-phenyl-4-thiono-3-pyrazolidinone.¹²⁴⁹

There has been a great deal of interest in 4-amino-3-pyrazolin-5-ones because of their pharmacological activity. These compounds are closely related to antipyrine and aminopyrine and a great many of them have considerable antipyretic and analgesic activity. By far the most widely used method of preparation of 4-amino-3-pyrazolin-5-ones has been reduction of the corresponding nitroso compounds (eq. 250).



Catalytic hydrogenation,^{145, 1491} zinc-acetic acid,^{992, 1001, 1504} zinc-sodium bisulfite,^{1174, 1175} and a mixture of sodium sulfide, sodium hydrogen sulfide and sodium⁴⁶¹ have been used. Reduction of 4-nitroso-3-pyrazolin-5-ones with sodium bisulfite forms the 4-sulfamino acid or its sodium salt (eq. 197). The reduction of 4-nitro-3-pyrazolin-5-ones with zinc and acetic acid also gives the 4-amino compounds.^{984, 992, 1001} Reduction of 4-arylazo-3-pyrazolin-5-ones with hydrogen⁶⁷⁰ and of iminoquinones in which the imino nitrogen is substituted by a 5-oxo-3-pyrazolin-4-yl⁴¹⁷ are means of obtaining 4-amino-3-pyrazolin-5-ones.

A few other methods of preparing 4-amino-3-pyrazolin-5-ones have been reported but none has been used extensively. Methylation of the N-2 of 2-pyrazolin-5-ones, the classical 3-pyrazolin-5-one synthesis, has been reported only once.⁵³⁶ Emerson and co-workers⁴²⁸ have hydrolyzed iminotoluquinone substituted by antipyrine to give the 4-amino compound. A rather similar reaction, hydrolysis of 4-benzylideneamino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one in the presence of dimethyl sulfate, forms the 4-methylamino analog.⁹⁴⁰ 3-Pyrazolin-5-ones react with urea and acylureas at elevated temperatures, introducing the urea moiety as a substituent at C-4 (eq. 251).^{1300, 1367} 4-Amino-

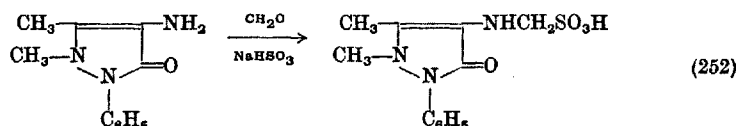


antipyrine has been isolated as one of the metabolic products of antipyrine.^{617, 618}

The amino group of 4-amino-3-pyrazolin-5-ones reacts normally. Acylation occurs readily with a wide variety of acylating agents. Amides are formed by reaction with acid chlorides,^{50, 533, 984, 1414, 1473} acids^{618, 984, 1471} and esters in the presence of phosphorus pentoxide.¹⁴⁷¹ Thioformamides have been prepared by reaction with dithioformic acid and its salts.^{472, 556, 1374} Sulfonyl chlorides react to form sulfonamides.^{98, 489, 984, 1249, 1504} Chlorophosphates react with 4-amino-3-pyrazolin-5-ones to form phosphoramidate derivatives.^{509, 1496}

The alkylation of 4-amino-3-pyrazolin-5-ones has already been discussed to a considerable extent in connection with the preparation of such compounds having two substituents on the extranuclear nitrogen atom (see p. 76). The most straightforward alkylation is that with alkyl halides.^{101, 431} Alkylation by means of formation of the Schiff base with aldehydes or ketones followed by catalytic reduction has frequently been used.^{111, 131, 1303} Treatment of 4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one with formaldehyde and sodium bisulfite in

basic solution forms sulfamipyrine (Melubrin),^{145,164,541} formerly used as an antipyretic and analgesic (eq. 252). The 4-methylamino derivative



gives Dypyrone (Novalgin) used outside the U.S.A. Other aldehydes have also been used in this reaction to give analogous products.⁵⁴² If sulfurous acid and formaldehyde are used in this reaction, the product is the sulfinic acid.¹⁶⁴ The use of formaldehyde and hydrogen cyanide introduces a cyanomethyl substituent on the nitrogen.⁵²⁴ A number of acridine and quinoline substituents have been introduced into the 4-amino group by reaction of 4-amino-3-pyrazolin-5-ones with chlorinated acridines and quinolines.^{69,390,547,717} These compounds were studied for their antimalarial activity.

The amino group of 4-amino-3-pyrazolin-5-ones can be diazotized easily and the resulting diazonium salt couples with the usual reagents. Other diazonium salts couple with 4-amino-3-pyrazolin-5-ones at the amino group. Mercuric halides replace the amino hydrogen in 2,3-dimethyl-1-phenyl-4-sulfamino-3-pyrazolin-5-one.⁵⁴³ The 4-amino groups react normally with isothiocyanates,⁴⁹ epoxides,¹²⁶¹ ureas¹³⁶⁷ and nitrosamines.⁵²⁷

Only a few bis(4-imino-3-pyrazolidinones) are known and most of these are linked through the imino nitrogen atoms. The only exceptions to this are three compounds (Table XLVI) which are linked through arsenic atoms in the *p,p'*-positions of 1,1'-aryl substituents.^{546,1362} These compounds are prepared by way of 1-(4-arsinophenyl)-2,3-dimethyl-4-nitroso-3-pyrazolin-5-one. This compound is reduced, giving 4,4'-amino groups and reducing the arsenic atoms to give the —As=As— linkage connecting the two rings. The amino groups are then alkylated. The type formula and the remaining bis(4-imino-3-pyrazolidinones) are listed in Table XLV. These have been prepared by reaction of 4-amino-3-pyrazolin-5-ones with dihalides such as phosgene,⁵⁸⁹ ethylene dibromide⁹⁹² and β,β' -dichloromethyl ether, with carbon disulfide^{992,1001} and with ketones.⁹⁸⁴

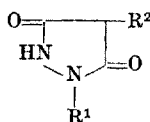
The only 3,4-di-iminopyrazolidine known is the 5-(3-pyridyl) compound prepared by chemical reduction of 3-(3-pyridyl)-4,5-dinitro-pyrazole.⁹³²

CHAPTER VII

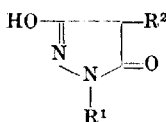
3,5-Pyrazolidinediones

1. Introduction

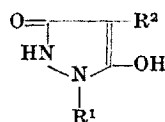
The 3,5-pyrazolidinediones have become of increasing importance in recent years owing to the medical use of 4-butyl-1,2-diphenyl-3,5-pyrazolidinedione which is marketed as Butazolidin (phenylbutazone) and used widely in the treatment of rheumatoid arthritis and various other diseases. A large number of analogs have been prepared for further investigation of their pharmacological and therapeutic properties. 3,5-Pyrazolidinediones have also been of interest as color formers in color photography. The 5-imino-3-pyrazolidinones, contrary to usual practice in this discussion, will be treated separately in the next chapter. This is due to the very large number that are known and the extensive knowledge concerning them and also to the fact that they exist much more as 3-aminopyrazolinones than as 5-imino-3-pyrazolidinones.



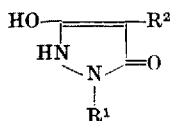
(XLIII)



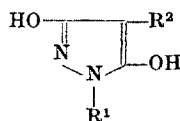
(XLIV)



(XLV)



(XLVI)



(XLVII)

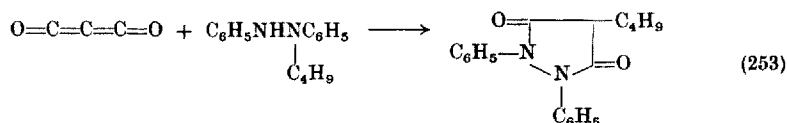
Five isomeric forms of 3,5-pyrazolidinediones are theoretically possible. These are (XLIII), (XLIV), (XLV), (XLVI) and (XLVII)

when R^1 is not hydrogen. When $R^1 = H$ (XLV) and (XLVI) are identical but the fifth isomer, 3,5-dihydroxypyrazole, is still possible. In those instances in which there are substituents on both nitrogen atoms, only forms (XLIII) and (XLV), which would be identical with (XLVI), are possible if both substituents are the same. Different substituents on the nitrogen atoms would then make possible a third form (XLVI). Compounds having four substituents could exist only in form (XLIII). In view of the acidity of 3,5-pyrazolidinediones^{1501,1512} and the ready *O*-alkylation which they undergo, it was suggested by Michaelis and Röhmer⁹⁹⁴ that they must exist in form (XLV). Gagnon and co-workers^{504,506} from a study of their ultraviolet spectra proposed that a mixture of tautomers (XLIV), (XLV) and (XLVI) occurs. The strong absorption of infrared light in the carbonyl regions by 3,5-pyrazolidinediones⁹¹⁹ is indicative of the presence of only a very small amount of form (XLVII) or perhaps of its complete absence. In summary, it would appear that the 3,5-pyrazolidinediones tend to exist as an equilibrium mixture of 2-pyrazolin-5-one forms and 3-pyrazolin-5-one forms if the existence of such forms is possible.

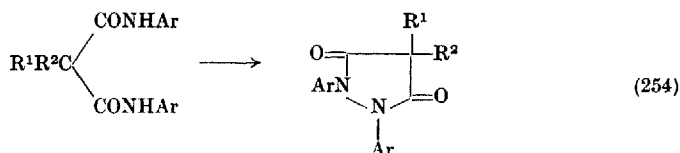
2. Alkyl, Aralkyl, Heterocyclicalkyl and Aryl Substituted Derivatives

By far the most widely used synthesis of 3,5-pyrazolidinediones is the condensation of malonic acids or esters or acid chlorides with hydrazines (eq. 5, p. 10). A large variety of malonic esters have been used. Esters having monoalkyl,^{188,969} monoaryl,²²² aralkyl,⁵⁰⁴ dialkyl,³⁸⁸ diaralkyl,³³⁹ alkyl and aralkyl⁵⁰⁴ and alkyl and aryl³⁸⁸ substituents have been used. The larger the substituents the lower the yields. The hydrazines used have had alkyl,²²² aryl⁵⁰⁶ and diaryl substituents.^{188,1338} Those hydrazines having less bulky substituents react the more readily the smaller the malonic ester substituents. The usual condensing agents have been sodium alkoxides.^{496,1312,1339} Substituted malonic acid chlorides condense with hydrazines under milder conditions than do the esters. The malonic acid chlorides used have had monoalkyl^{252,1032} or monoaryl^{1031,1032} substituents. Only symmetrical diarylhydrazines have been used.^{1032,1338} In most cases involving condensation of malonic acids with hydrazines, *N*-aryl-*N*-acylhydrazines have been used with phosphorus trichloride^{222,997} or phosphorus oxychloride⁹⁹⁸ as the condensing agent. However, a Swiss patent has reported the use of *sym*-diphenylhydrazine.¹⁴⁴⁰ The malonic acid may be unsubstituted,⁹⁹⁷ or monoalkyl,⁹⁹⁸ dialkyl⁹⁹⁷ or monoaryl²²² substituted. A modification of these methods is the use of carbon suboxide instead of the malonic acid derivatives.¹⁵¹² Although Tsumaki¹⁵⁰¹ has

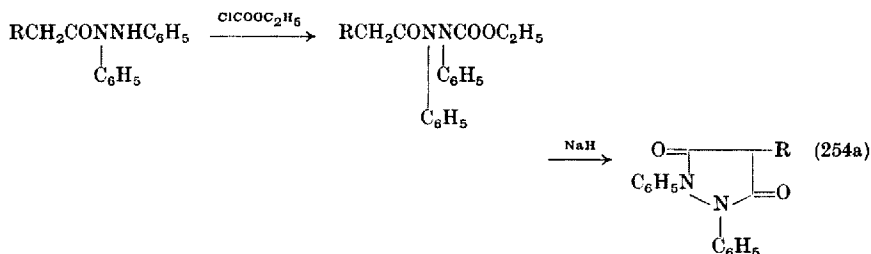
reported poor yields from carbon suboxide, Quintilla¹¹⁵⁰ claimed yields of 80–90 per cent. Phenylhydrazine and *sym*-diphenylhydrazine have been condensed with carbon suboxide. The use of *N,N'*-diphenyl-*N*-butylhydrazine¹¹⁵⁰ led to the formation of 4-butyl-1,2-diphenyl-3,5-pyrazolidinedione (eq. 253).



Three other methods of forming the 3,5-pyrazolidinedione ring system have been reported. One of these involves oxidation of malonic acid amides with potassium hypochlorite⁹⁵² or with sulfur and aluminum chloride (eq. 254).¹³²⁴ The second method is cyclization of



malonic acid half-ester hydrazides with base.⁹⁷⁶ A rather similar method, published recently, is that of Hallman, Ringhardt and Fischer.⁶¹⁹ This involves the sequence of reactions shown in eq. 254a.

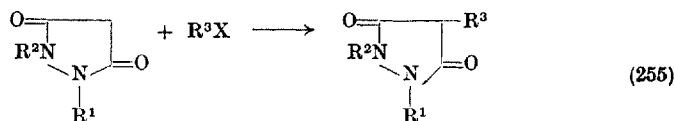


Modification of this synthesis can be achieved by treating the hydrazide with diethyl carbonate or diethyl thiocarbonate. In the latter case the products are 5-thiono-3-pyrazolidinones.

Synthetic methods involving conversion of other, but similar, ring systems to 3,5-pyrazolidinediones have been reduction of 1,2-diphenyl-3,4,5-pyrazolidinetrione with tin and hydrochloric acid⁶³ and hydrolysis of 5-imino-3-pyrazolidinones (3-amino-2-pyrazolin-5-ones) with acid.^{1339, 1596}

A variety of 4-substituted-3,5-pyrazolidinediones has been prepared by alkylation of 3,5-pyrazolidinediones in various ways. The

hydrogen atoms at the 4-position are active and direct alkylation with alkyl halides and a base is possible (eq. 255).²²² Usually the lower alkyl



bromides and benzyl bromide have been used. Sodium ethoxide,⁶³ sodium hydroxide¹⁴³⁷ and sodium³⁰⁴ have been the reagents employed. Either monoalkylation or dialkylation at C-4 can be achieved. In all cases in which this procedure has been used for alkylation, both nitrogen atoms have been substituted. A Wurtz-Fittig reaction on 4-bromo-3,5-pyrazolidinedione using alkyl halides and sodium, zinc or magnesium gives the same type of product.¹³²⁵ Probably the most widely used method for preparing 4-alkyl and 4-aralkyl-3,5-pyrazolidinediones is condensation of the parent 3,5-pyrazolidinedione with aldehydes or ketones¹⁵⁰¹ followed by reduction.¹⁸⁸ The first product is a 4-alkylidene- or 4-arylidene-3,5-pyrazolidinedione. Catalytic reduction using either platinum^{615, 1439} or nickel¹⁴³⁰ as catalyst gives alkyl or aralkyl analogs. A large number of aliphatic aldehydes and ketones, cycloalkanones and such aromatic carbonyl compounds as benzaldehyde, acetophenone and benzophenone^{188, 615, 976, 1439, 1501, 1502} give aldol condensations with 3,5-pyrazolidinediones.

1-Aryl-3,5-pyrazolidinediones having two substituents at C-4 can be alkylated at N-2 with benzyl bromide²⁴⁸ or methyl iodide⁹⁹⁸ and a base. If only one substituent is present at C-4, a second group is introduced at C-4 in addition to the one at N-2.^{222, 998}

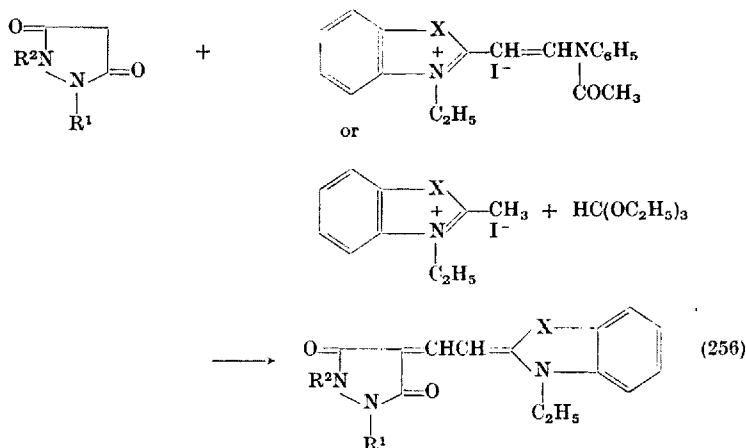
Dyes can be derived from 3,5-pyrazolidinediones by introduction at the 4-position of heterocyclic rings connected through a conjugated unsaturated system to the pyrazolidinediones. This is done in a way very similar to the preparation of the 2-pyrazolin-5-one analogs (eq. 256).^{1330, 1670}

The 3,5-pyrazolidinediones undergo the Mannich reaction⁹¹⁹ and can be readily alkylated in this way.

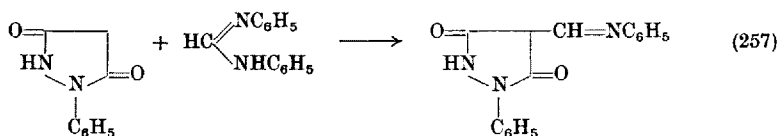
These compounds are listed in Table XLVII.

Owing to the active hydrogen atoms at C-4 in 3,5-pyrazolidinediones various substitutions at C-4 can be accomplished. Reaction with acid chlorides in the presence of aluminum chloride gives 4-acyl-3,5-pyrazolidinediones.^{919, 976} However, if two groups are already present at C-4, the enolic form of the dione is acylated on the oxygen atom to give 3-acyloxy-2-pyrazolin-5-ones.⁹⁹⁸ Treatment of 3,5-pyrazolidinediones with nitrous acid gives nitrosation at C-4.⁹⁷⁶ The nitroso

derivative is thought to exist as the oximino isomer. Reaction with aryldiazonium salts⁹⁷⁶ results in introduction of a 4-aryldazo group.

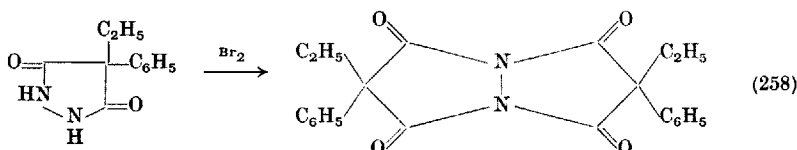


Bromination occurs readily with formation of 4-bromo-3,5-pyrazolidinediones.^{1031, 1032, 1048} A 4-phenyliminomethinyl substituent can be introduced¹¹⁹⁰ by reaction with *N,N'*-diphenylformamidine (eq. 257).



3,5-Pyrazolidinediones having either no substituent at N-2 or at least one hydrogen atom at C-4 form 3-alkoxy-2- or 3-pyrazolin-5-ones by reaction with potassium hydroxide and methyl iodide.⁹⁹⁴ In addition, alkylation occurs at C-4. Arndt, Loewe and Ergener⁴¹ have studied alkylation of 3,5-pyrazolidinediones with diazomethane. 1-Phenyl-3,5-pyrazolidinedione reacted to give 3-methoxy-2-phenyl-3-pyrazolin-5-one. However, if two substituents were present at C-4, the product was a 3-methoxy-2-pyrazolin-5-one in addition to methylation of the unsubstituted nitrogen atom. Similarly, treatment of 4-ethyl-4-phenyl-3,5-pyrazolidinedione with hot acetic anhydride gave 3-acetoxy-4-ethyl-4-phenyl-2-pyrazolin-5-one.¹²³⁴ One or both of the nuclear oxygen atoms in 3,5-pyrazolidinediones are replaced by chlorine upon reaction with phosphorus oxychloride.^{994, 998} Reaction of 1-phenyl-3,5-pyrazolidinedione with one mole of phosphorus oxychloride forms 3-chloro-1-phenyl-2-pyrazolin-5-one. A second mole of phosphorus oxychloride gives 1-phenyl-2,4-dichloropyrazole.

Acid hydrolysis of 3,5-pyrazolidinediones opens the ring, giving under mild conditions a half-hydrazide of malonic acid. Under more vigorous conditions degradation goes further.⁹⁷⁶ 4-Ethyl-4-phenyl-3,5-pyrazolidinedione undergoes an interesting dimerization¹²³⁴ under oxidative conditions to form a bicyclic compound (eq. 258).

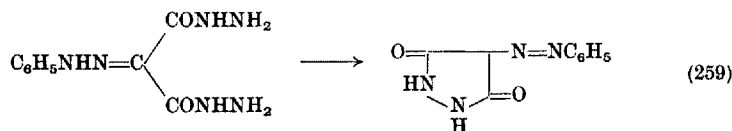


3. Hydroxy and Alkoxy Substituted Derivatives

Only two hydroxy- and alkoxy-3,5-pyrazolidinediones are known (Table XLVIII). 4-Butyl-4-hydroxy-1,2-diphenyl-3,5-pyrazolidinedione is formed as a by-product in the synthesis of 4-butyl-1,2-diphenyl-3,5-pyrazolidinedione by condensation of diethyl butylmalonate with *sym*-diphenylhydrazine in the presence of sodium ethoxide.¹³¹² The reaction of 4-bromo-1,2-diphenyl-3,5-pyrazolidinedione with 2-dimethylaminoethanol forms 4-(2-dimethylaminoethoxy)-1,2-diphenyl 3,5-pyrazolidinedione.¹⁰⁴⁸

4. Amino and Azo Substituted Derivatives

These compounds are listed in Table XLVIII. 4-Amino-3,5-pyrazolidinediones have been prepared by reduction of the corresponding 4-oximino compounds.^{981, 1048, 1339} The preparation of 4-arylo-3,5-pyrazolidinediones by direct introduction of this substituent has already been mentioned in Section 2 of this chapter.^{976, 1048} Bülow and Bozenhardt²⁵⁷ have prepared 4-phenylazo-3,5-pyrazolidinedione by cyclization of the phenylhydrazone of mesoxalic acid hydrazide in acetic acid (eq. 259). Stepanov and Kuzin¹³⁴⁰ have suggested that the



product obtained in the reaction of chloral hydrate with *p*-nitrophenylhydrazine is 1,4-bis(4-nitrophenylazo)-3,5-pyrazolidinedione, but there is very little evidence for this and it seems highly unlikely.

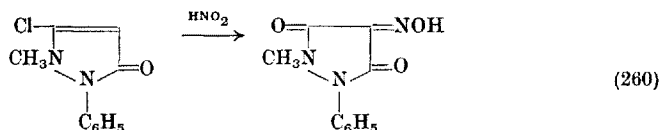
5. Halogen Substituted Derivatives

4-Halogeno-3,5-pyrazolidinediones are listed in Table XLVIII. Preparation by direct halogenation has already been discussed. This has been done with bromine and chlorine^{458, 1031, 1032, 1048} and only mono-halogeno products have been obtained. A number of 4-halogeno-3,5-pyrazolidinediones have been prepared by condensation of halogeno-malonylchloride with *sym*-diphenylhydrazine.¹⁰³³

The replacement of halogen by alkoxy was mentioned in Section 3. The halogen atom is readily replaced by hydrogen upon treatment with *sym*-diphenylhydrazine^{1031, 1032} thus reversing halogenation.

6. Nitroso Substituted Derivatives

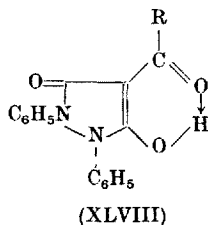
These are listed in Table XLVIII. The nitrosation of 3,5-pyrazolidinediones has already been mentioned (Section 2). A second method of preparation of the 4-nitroso-3,5-pyrazolidinediones (which are usually considered to have the tautomeric oximino form) has been used by Michaelis and Kirstein.⁹⁸¹ This involves treatment of 3-chloro-3-pyrazolin-5-ones with nitrous acid (eq. 260). A third method of syn-



thesis is hydrolysis of 3-amino-4-oximino-2-pyrazolin-5-ones (4-oximino-5-imino-3-pyrazolidinones).¹³³⁹ The reduction of these nitroso compounds has already been discussed (Section 4).

7. C-Acyl Substituted Derivatives

The structure of 4-acyl-3,5-pyrazolidinediones has been studied by use of infrared absorption spectra.⁹¹⁹ These studies indicate that one nuclear oxygen exists in its enolic form and the hydrogen is bonded to acyl oxygen in a chelate ring (XLVIII). These compounds are listed in Tables XLVII and XLVIII.



The preparation of 4-acyl-3,5-pyrazolidinediones by acylation of 3,5-pyrazolidinediones has already been discussed in Section 2.

4-Acetyl-1-methyl-2-phenyl-5-thiono-3-pyrazolidinone^{89,109} has been prepared by hydrolysis of ethyl 2,3-dimethyl-1-phenyl-5-oxo-3-pyrazolin-4-thiocarboxylate with alcoholic potassium hydroxide. This presumably involves ring opening and reclosure.

8. N-Acyl Substituted Derivatives

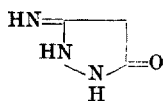
These compounds are listed in Table XLVIII. *N*-Acyl-3,5-pyrazolidinediones are prepared either by acylation with acid chlorides,⁹⁷⁶ in which case acylation at C-4 occurs, or by cyclization.^{506,976} Cyclization involves condensation of semicarbazides with malonic esters or cyclization of 3-acylsemicarbazides.

CHAPTER VIII

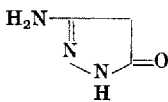
5-Imino-3-pyrazolidinones

1. Introduction

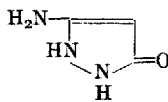
The compounds considered in this section as 5-imino-3-pyrazolidinones can, at least theoretically, have a number of tautomers. Of this number the four structures shown here, (XLIX), (L), (LI) and (LII),



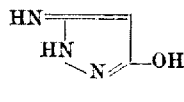
(XLIX)



(L)



(LI)



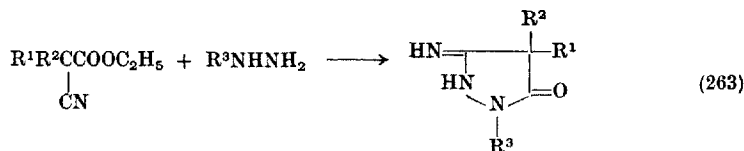
(LII)

are those usually considered to describe adequately the isomers actually occurring. In most cases the structure has not been determined but has been considered to be the 3-amino-2-pyrazolin-5-one form (L). In those cases which have been studied the form (L) and the 3-amino-3-pyrazolin-5-one form (LI) have usually been the ones occurring. Gagnon, Boivin and others,^{120, 497, 499, 507} as a part of their general investigation of the ultraviolet absorption spectra of 2-pyrazolin-5-ones, have studied 5-imino-3-pyrazolidinones. No generalization as to structure can be drawn from their findings, but they show the existence of forms (XLIX), (L) and (LI). Weissberger, Porter and Graham^{594, 1597, 1599} have shown that some 5-imino-3-pyrazolidinones actually exist as the isomeric hydroxyiminopyrazoline form (LII). In some cases¹⁵⁹⁷ the two isomeric forms (L) and (LII) have been isolated. Of course, various combinations of substituents make certain of these tautomeric forms impossible. Four substituents on N-1, N-2 and C-4 would make form (XLIX) the only possible one. Two substituents at N-1 and N-2 would preclude forms (L) and (LII). Two C-4 substituents would likewise eliminate form (LI).

In recent years a great deal of research on 5-imino-3-pyrazolidinones has been done because of their use as color couplers in color

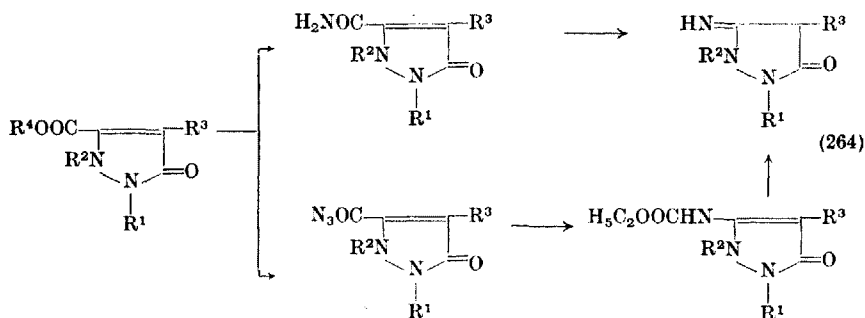
In the preceding methods only compounds having substituents on the nitrogen atoms can be obtained. In order to introduce substituents at C-4, substituted cyanoacetic esters and cyanoacetic hydrazides have been used (eq. 263). Two isomeric products are possible in this reaction,

R^3 being either at N-1 or N-2. Gagnon and co-workers⁴⁹⁸ report that unsubstituted cyanoacetic esters yield the N-2 isomers, while substituted esters give N-1 substituents. Other workers have also found



that unsubstituted cyanoacetic esters give the 2-substituted-5-imino-3-pyrazolidinones.^{870, 1141, 1600} Hydrazine,³⁹¹ arylhydrazines^{498, 872, 1141} and heterocyclic hydrazines^{1142, 1600} have been used. Monoalkyl, monoaryl and dialkyl³⁹¹ cyanoacetic esters undergo this reaction. The usual condensing agents have been sodium alkoxides. A modification of this procedure is isolation of the intermediate cyanoacetic hydrazide and cyclization of this with base^{498, 1138} or acid.⁵⁰⁶ Unsubstituted,^{594, 644} mono-substituted^{120, 500, 508} or disubstituted⁵⁰¹ cyanoacetic esters can be used and either hydrazine⁵⁹⁴ or phenylhydrazine.¹⁵⁹⁶

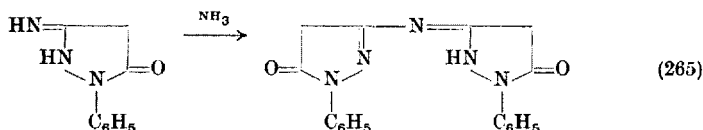
One of the most widely used methods for the preparation of 5-imino-3-pyrazolidinones is from 5-oxo-3-pyrazolin-3-carboxylic acids or their derivatives by use of the Hofmann^{167, 697} or Curtius^{167, 1387, 1395} rearrangements (eq. 264). A similar synthesis is from the analogous



2-pyrazolin-5-ones by way of the Curtius rearrangement.^{497, 499, 594, 1595} The amides and azides are formed by the usual procedures. The usual Hofmann and Curtius conditions are employed and the yields are frequently quite good. The azide rearrangement is usually carried out in ethanol and the carbamate derivatives of 5-imino-3-pyrazolidinones, *N*-(5-oxo-2- or 3-pyrazolin-3-yl) carbamates are prepared as intermediates.^{506, 594, 1387, 1395, 1595} If 3-pyrazolin-5-ones are used as starting materials in this synthesis, the products can have only one substituent

at C-4 and are actually 3-amino-3-pyrazolin-5-ones. Use of 2-pyrazolin-5-ones leads to compounds unsubstituted at N-1. In all cases the products obtained by these syntheses have had substituents at N-2.

A number of 5-substituted imino-3-pyrazolidinones have been prepared by reaction of various reagents with 5-imino-3-pyrazolidinone. For example, 5-alkylimino compounds can be prepared by reduction of 3-benzylideneimino-3-pyrazolin-5-ones.¹⁰⁵² The benzylidene derivatives are prepared by reaction of benzaldehyde with 5-imino-3-pyrazolidinone.¹⁰⁵² The same products can be obtained by direct alkylation of 5-imino-3-pyrazolidinone with benzyl chloride and an analogous reaction has been reported by Jennen^{704,705} with halogenated heterocycles. Various 5-substituted imino-3-pyrazolidinones have been prepared by reaction of the corresponding 5-imino compounds with various amines.^{595,596,1597} This reaction must occur by way of the 5-imino form rather than an amino form and the compounds involved must be at least partially in the 5-imino, rather than the amino, forms. This reaction has been carried out with aniline^{1595,1597} and ethylamine,⁵⁹⁵ although in the latter case a 4,4'-ethyliminobis(2-pyrazolin-5-one) is the chief product. A variation of this is the condensation of 2-phenyl-5-imino-3-pyrazolidinone with ammonia,^{595,596} as shown in eq. 265. The reaction of phenylisocyanate with 2-phenyl-5-imino-3-

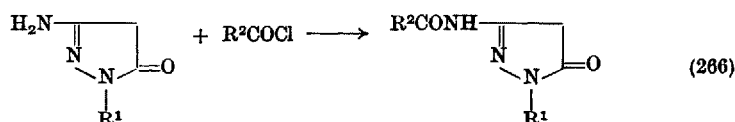


pyrazolidinone leads to the corresponding 5-phenylcarbamyl derivative.¹⁵⁹⁵ Phenylisothiocyanate reacts in the same way but *p*-tolylisothiocyanate in the presence of pyridine has been reported to cyclize to give 2-phenyl-5-[2-(5-methylbenzothiazolyl)imino]-3-pyrazolidinone.⁷⁰⁵

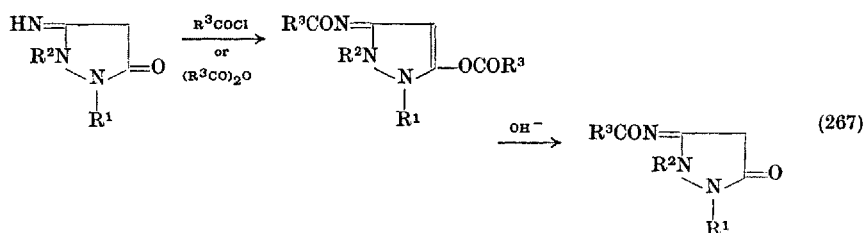
Acylation of 5-imino-3-pyrazolidinone can occur at several places. Most commonly reaction occurs at the 5-imino group and further reaction then may occur by acylation of the enol form of the 5-oxo group.

In compounds which have no substituents at N-1 or N-2 nuclear acylation also occurs and under some conditions acylation occurs at C-4. The use of 2-alkyl- or aryl-5-imino-3-pyrazolidinones, which exist as the 3-amino-2-pyrazolin-5-one isomer, with an equivalent of acid chloride, either aliphatic or aryl, leads to 3-acylamides (eq. 266),^{14,67,594,695,1247,1594,1595} although in some cases a side-reaction gives both *N*- and *O*-acylation.¹⁵⁹⁵ Under the same conditions 3-hydroxy-5-imino-2-pyrazolinones give *O*-acylation.¹⁵⁹⁹ The reaction of

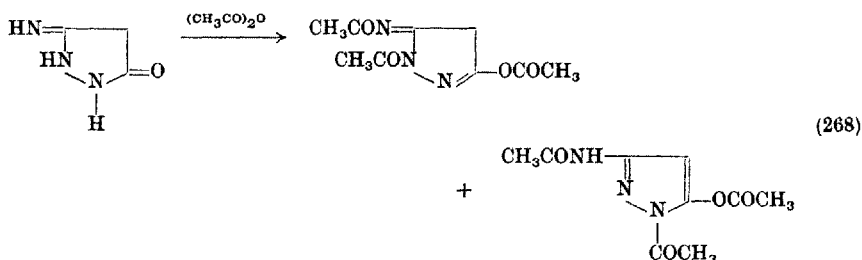
aromatic acid chlorides in excess^{594,1599,1804} or of acetic anhydride^{693,1595} with the same types of compounds leads to both *N*- and



O-acylation. These amide-esters can be hydrolyzed with base to the *N*-acyl derivatives (eq. 267). Hepner and Fajersztejn⁶⁴⁴ have reported



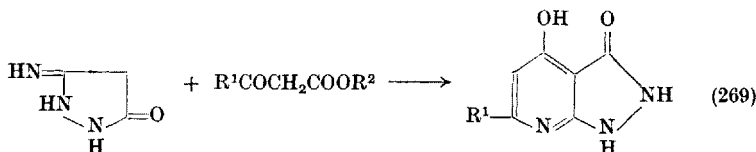
that acetic anhydride and benzoyl chloride react with 5-imino-3-pyrazolidinones to give acylation on nuclear nitrogen and diacylation at C-4. Graham, Porter and Weissberger⁵⁹⁴ have investigated this reaction and have found that acylation does not occur at C-4 but at the 5-imino group and the 5-oxo group (eq. 268). A similar acylation occurs



with 1-phenyl-5-imino-3-pyrazolidinone to give 2-acetyl-3-acetoxy-1-phenyl-5-acetimido-3-pyrazoline if pyridine is present.¹⁵⁹⁹ Otherwise a mixture is obtained, but the chief product is 3-acetoxy-4-acetyl-1-phenyl-5-imino-2-pyrazoline.¹⁵⁹⁹

The reactions undergone by 5-imino-3-pyrazolidinones are in general very similar to those of 2-pyrazolin-5-ones. The hydrogen atoms at C-4 are active and this position is the reactive center in the nucleus of these molecules. Condensation with aldehydes and ketones occurs with formation of benzylidene^{644,1083} or 4,4'-benzylidenebis

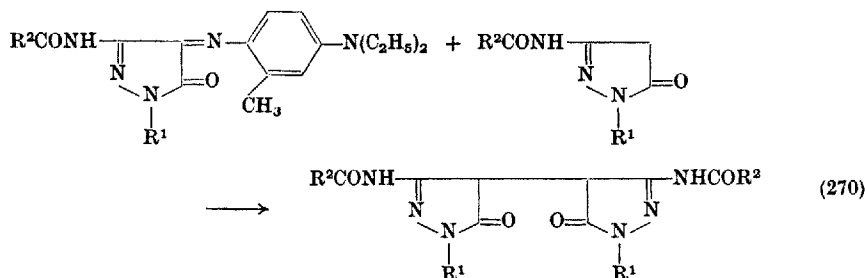
compounds¹⁶⁰³ rather than Schiff bases which are formed with the amino substituent. However, when β -ketoesters or β -ketoacids are used the carbonyl group does react with the amino group and then cyclizes at the C-4 position (eq. 269).¹⁰⁸⁵ Reaction with nitrous acid forms, at



least in compounds having no substituents at C-4, 4-oximino-5-imino-3-pyrazolidinones.⁶⁴⁴ In compounds substituted at C-4 reaction with nitrous acid leads to loss of nitrogen.⁵⁰¹ Coupling occurs with aryl-diazonium salts to give 4-aryloxy-5-imino-3-pyrazolidinones.⁵⁹⁴ Papini and Venturini¹⁰⁸⁵ have found that 5-imino-3-pyrazolidinone reacts with *N,N'*-diphenylformamidine at 150° to introduce at C-4 the phenyl-iminomethylidene group. 5-Imino-3-pyrazolidinones react with sulfur dichloride to give the 4,4'-bis sulfide.^{693, 921} Sulfur monochloride reacts to give the analogous disulfide.⁶⁹³ As is the case with 2-pyrazolin-5-ones, the 5-imino-3-pyrazolidinones undergo condensation at C-4 with *p*-amino-*N,N*-dimethylaniline in the presence of an oxidizing agent to form a magenta dye. Those 5-imino-3-pyrazolidinones which have no N-2 substituent react as enols with phosphorus oxychloride to give 3-chloro-5-imino-2-pyrazolines.³⁹¹ They also give positive color tests with ferric chloride.^{500, 501} They are methylated at N-2 by dimethyl sulfate.³⁹¹ As mentioned previously, the 5-imino group can be hydrolyzed with acid to give 3,5-pyrazolidinediones.^{1339, 1596}

The known bis(5-imino-3-pyrazolidinones) are listed in Tables XLVI and L and are of three types: (1) linked at the 4,4'-positions directly, (2) linked at the 4,4'-positions by a carbon chain, and (3) linked through the nitrogen of the 5-imino group. The compounds of the first type are prepared by reaction of 3-acylamido-1-aryl-4-aryl-imino-2-pyrazolin-5-ones with the corresponding 3-acylamido-1-aryl-2-pyrazolin-5-ones, the 5-imino-3-pyrazolidinones being considered to exist in this case as their 3-amino-2-pyrazolin-5-one tautomers (eq. 270).¹⁵³⁸ The second type is usually synthesized by reaction of a 3-amido-2-pyrazolin-5-one with an aromatic aldehyde to give a 4-arylidene derivative, followed either by addition of a second mole of the original pyrazolinone to give a symmetrical bis compound (eq. 68)^{1255, 1603} or by addition of a different pyrazolinone to give an unsymmetrical bis compound.¹²⁵⁴ Most of those compounds which are

linked through the 5-imino nitrogen are prepared by reaction of 5-imino-3-pyrazolidinones with the acid chloride of a dibasic acid.⁷⁹⁷ However, a bis compound connected only by a carbonyl group has been



obtained as a by-product in the Curtius rearrangement of an azide to give a 5-imino-3-pyrazolidinone.¹³⁸⁷ It would appear that part of the intermediate isocyanate reacts with some of the final product.

3. Functional Group Derivatives

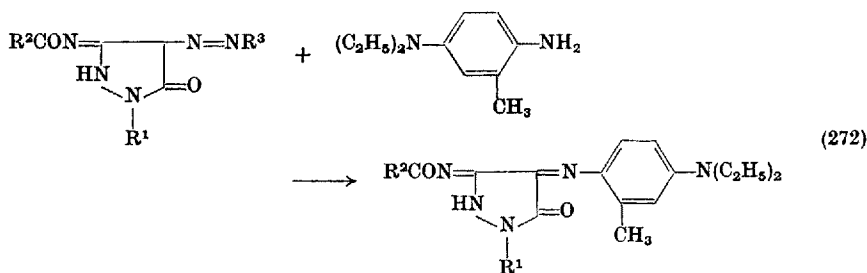
5-Imino-3-pyrazolidinones having functional group substituents are listed in Sections B and C of Table XLIX. These compounds are usually synthesized by procedures which are used for introduction of the same substituents into previously discussed pyrazolinone and pyrazolidinone systems.

4-Bromo-5-imino-3-pyrazolidinones are synthesized by Curtius rearrangement of the azides of 4-bromo-5-oxo-3-pyrazolin-3-carboxylic acids.⁶⁹⁷ 4-Nitroso-5-imino-3-pyrazolidinones are believed to exist as the oximino tautomers.³³⁷ They are usually prepared by direct nitrosation with nitrous acid.^{644, 1339, 1649} A Curtius rearrangement of 4-oximino-5-oxo-2-pyrazolin-3-carboxylic acid azide has also been used.³³⁷

4-Amino-5-imino-3-pyrazolidinones have been synthesized by reduction of the corresponding oximes.^{644, 1339} Such amines form ureas and thioureas by reaction with potassium cyanate in acid solution and with phenyl isothiocyanate.⁶⁴⁴ 4-Arylimino-5-imino-3-pyrazolidinones have been prepared by reaction of the 5-imino-3-pyrazolidinones with *p*-amino-*N,N*-diethylaniline in the presence of silver salts as oxidizing agents (eq. 172).^{244, 519, 1255, 1538} 4-Arylazo-5-imino-3-pyrazolidinones have most frequently been prepared by reaction of 5-imino-3-pyrazolidinones with aryldiazonium chlorides, as is usual for the preparation of similar compounds.^{591, 594, 920, 1087, 1255, 1339, 1539, 1649} One such compound has been prepared by the Curtius rearrangement of the corresponding 4-arylazo azide.⁵⁹⁴

$$\text{RNHCSCCH}(\text{COOC}_2\text{H}_5)_2 + \text{H}_2\text{NNH}_2 \longrightarrow \begin{array}{c} \text{RN}=\text{C}-\text{COOC}_2\text{H}_5 \\ | \quad \quad | \\ \text{HN} \quad \quad \text{C}=\text{O} \\ \quad \quad \quad | \\ \quad \quad \quad \text{N} \\ \quad \quad \quad | \\ \quad \quad \quad \text{H} \end{array} \quad (271)$$

4-Amino-5-imino-3-pyrazolidinones react with formaldehyde at the 4-amino group giving methylol derivatives.⁶⁴⁴ The 4-arylimino derivatives are reduced catalytically to give 4-aryl amino analogs.¹⁵³⁸ An interesting reaction of the 4-arylo-5-imino-3-pyrazolidinones is the replacement of the 4-arylo group by arylimino (eq. 272).^{1255, 1296}



Bis(5-imino-3-pyrazolidinones) linked at the 4,4'-positions by one or two atoms of sulfur are known (Table L) and their preparation was mentioned in the previous section.

CHAPTER IX

Miscellaneous 3,5-Pyrazolidinediones and Analogs

3,4,5-Pyrazolidinetriene has been prepared by oxidation of the anilide of mesoxalic acid with hydrogen peroxide in alkaline solution.⁶³

Six 3,5-di-iminopyrazolidines have been prepared. These compounds are usually considered to exist as diaminopyrazoles, although their structure has not been investigated. The parent compound, 3,5-di-iminopyrazolidine or 3,5-diaminopyrazole, has been reported^{473, 1561} as the product obtained by reaction of malononitrile and hydrazine. However, Taylor¹⁴⁷⁸ has claimed that these same reactants give a different product, derived from dimerization of the malononitrile followed by reaction with hydrazine. Knorr⁸¹⁹ has prepared 3,5-di-iminopyrazolidine by the Curtius rearrangement starting with diethyl pyrazole-3,5-dicarboxylate. Two acyl derivatives and the intermediate carbamates were also prepared. Phenylhydrazine and malononitrile do not give a diaminopyrazole as reported.^{1478, 1561} 2-Methyl-1-phenyl-3,5-bis(phenylimino)pyrazolidine results from the action of aniline on the methiodide of 2,5-dichloro-1-phenylpyrazole.⁹⁸¹

PART 2

APPLICATIONS

CHAPTER I

Medical

Since the synthesis of antipyrine (2,3-dimethyl-1-phenyl-3-pyrazolin-5-one) by Knorr in 1883 pyrazolinones have been widely used in medicine as analgesics and antipyretics. The discovery of this drug led to a widespread search for other pyrazolinones, having the same type of action but more satisfactory properties, and to a very intensive investigation of the biological properties of pyrazolinones. This investigation resulted in the discovery of aminopyrine, which is the 4-dimethylamino analog of antipyrine, and phenylbutazone (4-butyl-1,2-diphenyl-3,5-pyrazolidinedione) and their employment in medicine. Many other pyrazolinones have been synthesized and studied and a number of these have been used as drugs, but these three have been by far the most important and most of this discussion will be concerned with them.

Although antipyrine has been used as an antipyretic and analgesic for many years, it finds very little use today. In part this has been due to the introduction of the more effective aminopyrine, but largely it has been due to replacement by the salicylates. At the present time it is used chiefly in Europe, South America and the Near East where approximately 50,000 lb. per year is consumed. Antipyrine definitely has analgesic activity⁸⁴² but this appears to be of a rather low order.²⁶⁵ It is absorbed rapidly from the gastrointestinal tract and blood plasma levels are at a maximum in 1-2 hours. Metabolism is rather rapid, with disappearance occurring at the rate of 6 per cent per hour. Water solubility is high and distribution in the tissues is in proportion to their water content. This property has been used as a basis for determining the water content of various tissues. About 30-40 per cent of ingested antipyrine is converted to 4-hydroxyantipyrine and excreted in the urine conjugated with glucuronic acid.⁵⁸⁷

At present aminopyrine is little used in the United States but is still widely used in Europe, South America and the Near East. World

production is 250,000–300,000 lb. per year. It is somewhat more effective than antipyrine and is administered in doses of 0.3 or 0.6 g. every four hours. Absorption occurs from the gastrointestinal tract and blood levels reach a maximum in 1–2 hours and then the drug disappears at the rate of 10–30 per cent per hour. A large proportion of it is demethylated in the liver to 4-aminoantipyrine^{230, 617, 618} and this is acetylated and excreted in the urine.^{617, 618} A small amount, about 9 per cent, is excreted as 4-aminopyrine and about 5 per cent as 4-hydroxyantipyrine.^{617, 618} As is the case with antipyrine the fate of about half of the aminopyrine ingested is unknown. Its primary effect is on the autonomic nervous system which it depresses^{1235, 1495} and its analgesic action is exerted through this system.¹⁴⁷⁹ The mechanism of action of aminopyrine is not known. It does not appear to act through its metabolite, 4-aminoantipyrine,⁵⁸⁷ but it may act through some as yet unknown metabolite. The action of aminopyrine in rheumatic fever is equal to that of the salicylates⁵⁸⁷ and it is effective in reduction of inflammation due to edema and necrosis.¹⁶²⁵ The chief toxic manifestation of aminopyrine is agranulocytosis. This occurs only in a small minority of those taking the drug, but it may be extremely severe and there is a high death rate among those in whom agranulocytosis occurs. In some individuals there seems to be a hypersensitivity to this drug. Other toxic effects are central nervous system involvement, rash and hemoglobin alterations.

Aminopyrine forms complexes with barbiturates containing one or two molecules of aminopyrine for each molecule of barbiturate. These complexes have a synergistic action on the analgesic activity of the pyrazolinone.²⁶⁵ Two of these complexes have been marketed as analgesics under the names Allonal and Veramon. The former is a 1:1 complex with phenylisopropylbarbituric acid and the latter is a 2:1 complex with diethylbarbituric acid. A complex of aminopyrine with trichloroethylurethan has been sold as an analgesic under the trade name Compral.

A tremendous number of 3-pyrazolin-5-ones have been tested for activity as antipyretics and analgesics. Of these many have been found to have such activity, most of them being rather closely related to antipyrine.^{58, 249, 490, 530, 532, 859, 1337, 1476} Many of these have been claimed to be superior to antipyrine and aminopyrine, but only a few have been used to any extent. Dypyrone (Novalgin) is perhaps the most widely used of these, although on a small scale and almost exclusively outside the U.S.A. This compound has the antipyrine nucleus, but the 4-substituent is $\text{NaO}_3\text{SCH}_2(\text{CH}_3)\text{N}$. Sulphamipyrine (Melubrin) is similar to this but lacks the methyl group attached to the side-chain

nitrogen atom and is very little used at present. A pyrazolinone which has enjoyed some use as an analgesic is 2,3-dimethyl-4-isopropyl-1-phenyl-3-pyrazolin-5-one. This compound is very closely analogous to aminopyrine and is of the same order of activity.⁸⁴²

The most interesting of the pyrazolinones and pyrazolidinones from the medical standpoint at the present time is phenylbutazone. This was synthesized by H. Stenzl in the laboratories of J. R. Geigy, S.A. in 1946 and was shortly found to have activity in various rheumatoid and arthritic conditions. Phenylbutazone was then marketed as the sodium salt under the trade name of Butazolidin. It has also been marketed as a mixture with aminopyrine under the name Irgapyrine. Since then practically every aspect of the biological activity of phenylbutazone has been investigated and a large number of analogs have been synthesized. Hemming and Kuzell⁶³⁹ have published an excellent review of the biological properties and medical uses of phenylbutazone and most of the material reported here is drawn from that publication.

After oral administration phenylbutazone is completely absorbed in a short time and high plasma concentrations are reached in about two hours. Intramuscular injection gives a much slower peak concentration in the plasma, requiring six to eight hours. The usual dose is about 800 mg. per day and under this regime a stable plasma concentration is reached in three or four days. A considerable amount of phenylbutazone is bound by plasma protein and this acts as a reservoir. The drug is metabolized at a rate of 15–25 per cent per day in the human but dogs and rats metabolize it much more rapidly. The metabolic products are 4-(3-hydroxybutyl)-1,2-diphenyl-3,5-pyrazolidinedione and 4-butyl-1-(4-hydroxyphenyl)-2-phenyl-3,5-pyrazolidinedione.²⁶⁷ It has been suggested that the former metabolite is responsible for the effect of phenylbutazone on uric acid excretion and the latter metabolite has the antirheumatic effect and causes sodium chloride retention.¹⁶⁶³ Some phenylbutazone is excreted in the urine.¹³³⁵

Several workers have found that phenylbutazone has a pronounced effect upon electrolyte balance.^{435, 597, 1626} A decrease in urine volume occurs with retention of sodium and chloride ions. This is apparently caused by increased reabsorption in the renal tubules.¹⁶²⁶ After discontinuance of the drug diuresis occurs and the edema disappears.

Phenylbutazone brings about a number of changes in the blood. In rabbits it decreases total protein albumin, but increases globulin.¹⁵⁰⁰ There is frequently a drop in the platelet count, mild anemia, occasionally hemorrhage from the gastrointestinal tract and sometimes granulocytopenia. The most serious blood reaction is the occurrence of

agranulocytosis.^{779, 906} This occurs infrequently but may result from moderately low doses and therefore must be kept constantly in mind. It has been reported that concurrent administration of ferrous iron reverses the agranulocytosis.³⁹² Some physicians have regarded this toxic manifestation as being so serious that they recommend the complete discontinuance of the use of phenylbutazone.

The principal action of phenylbutazone is its inhibition of inflammatory action, although it is also a mild analgesic and antipyretic. It has a very striking clinical effect in many arthritic cases, giving rapid and complete relief from pain. There is also significant improvement of joint function and objective remission of the arthritic condition. Its field of usefulness is very similar to that of the corticosteroids, and as a consequence it has been suggested that it may be a stimulant of the pituitary-adrenal system. However, its failure to affect urinary ketosteroid excretion, eosinophil count and the erythrocyte sedimentation rate make this action unlikely. It may be that it acts by a cortisone-sparing mechanism. Korns and others⁸⁵² have suggested this because of their finding that phenylbutazone prevents the inactivation of cortisone by rat liver slices. Wallenfels and Sund¹⁵⁸⁷ believe that phenylbutazone may be transported to inflamed tissue as a complex with the zinc attached to dehydrogenase systems. In these tissues the complex may be broken down owing to the relatively acid conditions and phenylbutazone enter the intracellular space where it inhibits dehydrogenases.

Phenylbutazone has been found to be clinically useful in several forms of arthritis. It is particularly effective in acute gouty arthritis, in which it is superior to any other drug. In several series of patients it has been claimed that nearly all patients are improved by phenylbutazone treatment. This is probably a result of its ability to increase urate clearances.¹⁶⁶⁴ In such diseases as rheumatoid arthritis, osteoarthritis and rheumatoid spondylitis phenylbutazone affords prompt relief of pain in something like 75 per cent of cases in which it is used. Although there is considerable disagreement as to the incidence of measurable objective improvement, it is probable that this occurs in at least 50 per cent of patients using phenylbutazone. The objective improvement is reduction in swelling and increased mobility. Some have claimed that improvement is due to analgesic effect, but the beneficial effect is too pronounced for mere analgesia and must be due to a specific antirheumatic effect of phenylbutazone. An amazing number of other conditions, usually arthritic, have been reported to be improved by phenylbutazone, although its use is as yet not completely established in many of these. Some of these diseases are psoriatic

arthritis, osteoporosis of the spine, acute peritendonitis, acute myofibrillitis, degenerative diseases of the hip, bursitis, fibrositis, postmenopausal arthralgia, scleroderma with arthropathy and lumbrosacral sprain. Phenylbutazone has also been used in arthritic conditions in veterinary medicine.

The clinical efficacy of phenylbutazone has been well established but the high percentage of side-effects resulting from it has severely curtailed its usefulness. In many of the arthritic conditions for which it is used treatment for long periods of time is necessary and drug toxicity is particularly disadvantageous. It has been found that 25 per cent of patients taking phenylbutazone are subject to toxic reaction, many so severe as to prevent further use of the drug. The most common of these are gastrointestinal upset, edema and drug rash. Of other side-effects, as already mentioned, the most dangerous is agranulocytosis. A number of phenylbutazone analogs have been studied in attempts to decrease side-effects and retain potency,^{233, 1624} and it is to be hoped that these studies will be successful. In the case of phenylbutazone it seems that the drug can be used effectively, but only with great care and conservatively. Its tendency to reactivate peptic ulcers contraindicates its use in patients who have ulcers. Periodic blood counts should be made, and the patient should be under close supervision of a physician. In order to overcome some of these side-effects phenylbutazone has been marketed mixed with aluminum hydroxide, magnesium trisilicate and homatropine methyl bromide.

Various publications have appeared in which pyrazolinones, either alone or as mixtures with other materials, have been claimed to be effective as germicides,²⁶ in influenza,³⁷⁷ as antimicrobial agents,⁵⁷¹ as fungicides,⁶⁷⁶ as antiactinics,¹¹⁵¹ and as antidiuretics.^{663, 1078} At present it appears that none of these claims have led to clinical use.

CHAPTER II

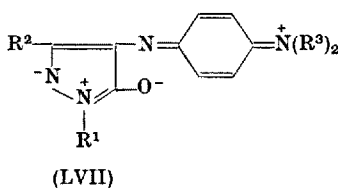
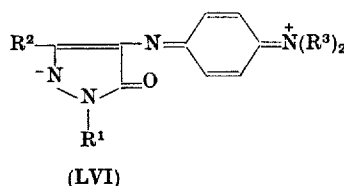
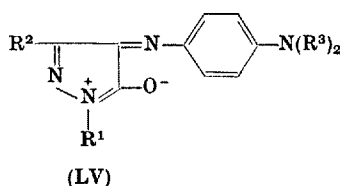
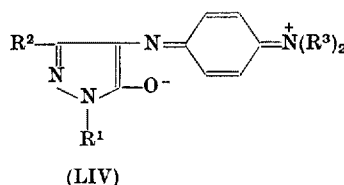
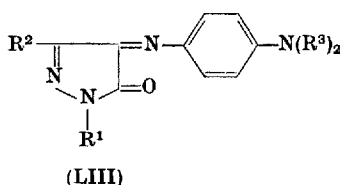
Color Photography

The pyrazolinones and pyrazolidinones are extensively employed in photography as color couplers, sensitizers, supersensitizers, developers and antihalation agents. A number of pyrazolinones which have been prepared for use as sensitizers are listed in Tables LI and LII.

The most important use of pyrazolinones in photography is their utilization as color couplers. The reaction of *p*-phenylenediamines with 2-pyrazolin-5-ones in the presence of oxidizing agents, in this case silver ions, forms magenta azomethine dyes (eq. 172, p. 67). These magenta dyes are then used to reproduce the green component in pictures. Two processes have been devised to form the magenta dye at the appropriate place on the developed film. In one process one coating of a three-coated film contains a substance sensitizing that coating to green light. After the film has been exposed it is developed in a solution containing a *p*-phenylenediamine developer, usually a *p*-amino-*N,N*-diethylaniline, and a 2-pyrazolin-5-one. The silver halide which has been affected by light acts as an oxidizing agent to couple the two compounds, hence the name color coupler, and a magenta color appears at those points where green light has been absorbed. This can then be reprinted as green. In the second method, which is now much more extensively used, a three-layer film is used. The middle layer contains a green-sensitized emulsion and a 2-pyrazolin-5-one. Upon exposure to a developer an azomethine magenta dye is formed.

The chemistry involved in the formation of these azomethine dyes has been extensively investigated by Vittum and others.^{244, 1538, 1539a} The present interpretation of the reactions involved is that the primary amino group of the developer is oxidized to give a quinonediimine cation which then reacts with the anion of the coupler to form a leuco dye. Subsequent oxidation converts the leuco dye to a colored form (LIII). This may be done by silver ion or by the oxidized form of the developer. The over-all reaction requires the reduction of four silver ions.

The azomethine dyes have two absorption bands in the visible region.^{244, 519} One, of much higher intensity, is in the green region at wave lengths of 510–560 m μ . A lower intensity band occurs in the blue region at 420–450 m μ . The second band is undesirable in photographic applications and can be suppressed to a certain extent by modifications in the group at C-3. Amide substitutions at this position are effective for this purpose. The structures contributing to the resonance hybrid responsible for the absorption of the dyes are considered to be (LIII)–(LVII). The forms (LIII) and (LV) represent the ground state. Transitions of these to the forms (LVI) and (LVII) are responsible for absorption at the longer wave lengths, while transitions to form (LIV) give rise to the shorter wave length, less intense band. Electropositive and electronegative substituents at C-3 have considerable effect upon the electron density at N-2 and thus alter the light absorption of the 2-pyrazolin-5-ones.



A very large number of compounds have been claimed to be useful as color couplers.^{492, 493, 634, 705, 766, 769, 797, 870, 921, 922, 965, 966, 1041, 1138 – 1140, 1142, 1247, 1684} Weissberger and Edens¹⁵⁹³ have reported very complex amides which are useful as color couplers, but are so complex that they are listed in none of the tables. In the color photography process employing the 2-pyrazolin-5-one in solution in the developer, low

molecular weight compounds were used. These, being acidic, are soluble in the alkaline developer solution. When the 2-pyrazolin-5-one is incorporated in one layer of the film, diffusion from layer to layer is a serious problem. In order to prevent this, large groups are introduced in the molecule, usually at N-1 or at C-3. The substituent at N-1 is always aromatic and may have very complex substituents. Frequently it has a carboxyl or sulfonic acid group to assist in dispersion in the gelatin. One of the most successful approaches to the problem of diffusion is that developed by Weissberger and co-workers. Their solution to the problem was use of 1-aryl-3-amino-2-pyrazolin-5-ones (2-aryl-5-imino-3-pyrazolidinones). In order to increase the bulk of the molecule the amino group was acylated^{592, 870, 921, 922} or carried a heterocyclic substituent.⁷⁰⁴ 2-Pyrazolin-5-ones having a carboxyl substituent as an amide at C-3 are also satisfactory. Kendall and Fry^{768, 769} have suggested the use of 3,5-pyrazolidinediones as color couplers.

Although by far the majority of 2-pyrazolin-5-ones used as color couplers have no substituent at C-4, this is not a necessary condition. 4,4'-Bis(2-pyrazolin-5-ones) can be used for this purpose since the 4-substituents can be eliminated and an azomethine dye formed. Such couplers may offer certain advantages. It is claimed that they are more stable and also they make it possible to form two azomethine dyes if the two portions of the molecule are different. Weissberger, Vittum and Porter^{1540, 1603} have patented a number of 4,4'-arylidenebis(2-pyrazolin-5-ones) for use as color couplers. Gluck⁵⁸⁰ has suggested 4,4'-bis(2-pyrazolin-5-ones) linked by sulfur which he prepared.

Another approach to prevention of diffusion of color couplers has been the incorporation of 2-pyrazolin-5-ones into some type of polymer.

The pyrazolone can be incorporated directly in the polymer by utilizing a polymer-forming derivative such as a 1-(amino or hydroxyphenyl)pyrazolone in a phenol (or aniline)-formaldehyde polymerization. Alternatively, the pyrazolone nucleus can be combined with a synthetic or natural polymer by reaction of a functional group in the pyrazolone with the polymer. Thus, a 1-formylphenyl type is used to form a polyvinyl acetal. A compilation of such reactions is given in Part 1, Chapter II, Section 14, pp. 108-110.

In many photographic processes it has been found advantageous to use a colored coupler. In these processes a 4-arylazo-2-pyrazolin-5-one is the coupler and it reacts with a developer as shown in eq. 272 (p. 138).¹⁵³⁹ This results in the formation of an azomethine dye which counteracts the overlapping absorption of the negative image dyes present and leads to improved color reproduction. These compounds usually have a negative substituent at N-1^{1058, 1305} as this enhances the

rate of reaction.¹⁵³⁹ Amide substituents at C-3 have the same effect.

Another important use for pyrazolinones in photography is as sensitizers and supersensitizers. Addition of certain dyes to silver halide gelatin emulsions increases the sensitivity of the silver halide to the green or red regions of the spectrum and a number of methine dyes derived from pyrazolinones have been used for this purpose. These compounds sensitize at 475–700 m μ , although their maximum absorption is at somewhat shorter wave lengths. Both 2-pyrazolin-5-ones^{488,707,747,749,765,771,772,1069,1195} and 3-pyrazolin-5-ones^{765,1516,1517} have been used. These nuclei are connected through one or more unsaturated groups to heterocyclic rings such as benzoxazoline, benzimidazoline or benzothiazoline rings.^{747,749,771} Frequently the pyrazolinone is a substituent on the unsaturated chain of a cyanine dye (Table LIII).^{765,1516} The more extended the unsaturated chain is the longer are the wave lengths at which sensitization occurs. A variety of substituents have been used at C-3. Among these are methyl,^{488,747} carbethoxy,⁷⁷² amino¹³³⁰ and hydroxyl.¹³³⁰ Supersensitization occurs in some cases by addition of a second dye which is synergistic with the first. Brooker and White have patented a number of azomethine 2-pyrazolin-5-ones for this purpose.²⁴⁰

There has been a great deal of interest in Great Britain in 1-phenyl-3-pyrazolidinone (phenidone) and some of its analogs as photographic developers. In combination with various weak developers, pyrazolinones greatly enhance their developing powers. Such compounds as ascorbic acid, gallic acid, glucose, dihydropyrogallol and various reductones show this property.^{57,640,641,1630} Reynolds¹¹⁷⁶ in the United States has also reported such a phenomenon with iminoascorbic acid. A number of 3-pyrazolidinones having various aryl substituents at N-1 and hydrogen or alkyl groups at C-4 have been reported to be effective.^{701,750,758,758,1176,1630,1631} It has been claimed by Kendall^{57,751} that in the course of development 1-phenyl-3-pyrazolidinone is oxidized to 2-phenyl-3-pyrazolin-5-one. A number of compounds having two alkyl substituents at C-4^{701,1176,1630} or at C-5⁷⁵⁸ have been reported to be photographic developers and these could not undergo such an oxidation.

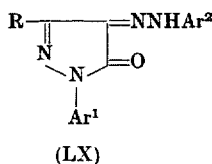
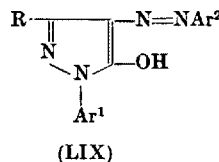
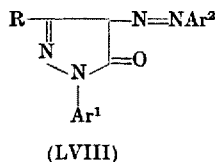
A number of 2-pyrazolin-5-ones have been reported in patents to be useful as color filters and for antihalation. Most of these are colored compounds, in two cases merocyanine dyes¹³⁰¹ and in others various methine dyes having heterocyclic rings at the end of unsaturated chains.⁷⁷⁶ van Dormael and van der Aurwa¹⁵¹⁸ have reported that a mixture of the product of reaction between aromatic amines and furfural with 3-methyl-1-phenyl-2-pyrazolin-5-one is useful for antihalation.

CHAPTER III

Textile and Fabric Dyes

The most important commercial use for pyrazolinones is as dyes. They have been extensively employed for this purpose since tartrazine (Table LIV) was synthesized by Ziegler and Locher in 1884^{1681a} and this dye is still widely used today as an approved coloring for foodstuffs. Almost all pyrazoline dyes are azo dyes having an arylazo group substituted at the 4-position of a 2-pyrazolin-5-one and frequently having two, three or four azo groups in the entire molecule. The preparation of these compounds has already been discussed in the section dealing with 4-arylazo-2-pyrazolin-5-ones. A tremendous variety of 1-aryl-2-pyrazolin-5-ones have been used to prepare azo dyes, although most of the commercially important dyes have been derived from 1-aryl-2-pyrazolin-5-ones having methyl, carboxyl groups or carboxyl derivatives substituted at C-3. The 1-aryl substituents have been so greatly varied that no generalizations can be made. Most dyes contain at N-1 substituted phenyl groups which frequently have sulfonic groups as substituents. The arylazo groups also have been extremely varied and in many cases are very complex. The majority of pyrazolinone azo dyes are either acid dyes or dyes which are complexed with metals. The acid dyes are compounds having carboxylic and/or sulfonic acid functions and can be used to dye fabrics directly, while the metal complexes are formed with various metals either before or after deposition on the material to be dyed. The outstanding feature of the pyrazolinone dyes is their excellent fastness to light and to severe wet treatments. A number of pyrazolinone dyes are produced in very large quantities. In the U.S.A. the production of tartrazine in 1960 was 437,000 lb. and the production of many more is in the tens of thousands of pounds. In Table LIV are listed the trade names and structures of a number of representative commercially important dyes. It is generally considered that pyrazolinone azo dyes have one or more of the structures (LVIII),

(LIX) and (LX) but other structures are theoretically possible. Little research has been published to indicate which of these structures is the correct one, although the usual methods of preparation would allow



any of the three. In the case of dyes complexed with various metals it is believed that (LIX) is the usual structure. In these cases it is probable that the metal reacts with the enol form of the pyrazolinone and with a hydroxyl group at the *ortho*-position in the arylazo group—formulas (XXX) and (XXXI).¹²⁵⁹ This is then stabilized by electron donation by the nitrogen atoms of the azo group.³²⁶ However, in most uncomplexed dyes it has not been established which form is the correct one. A few 4-aryldazo-3-pyrazolin-5-ones have been patented for use as dyes.¹⁰⁶⁰

The earlier pyrazolinone azo dyes were used to dye wool yellow,^{81, 214, 217, 312, 582, 1384, 1424} but this situation has changed so that by use of suitable complexes almost any color can be obtained with almost any material it is desired to dye. A very large variety of orange dyes are available^{199, 207, 475, 622, 840, 1449, 1459, 1617} as well as brown,^{169, 576, 856, 1446} red,^{312, 803, 839, 1119} green,^{630, 1060, 1291} violet,^{186, 189} gray²⁰⁵ and intermediate shades.^{190, 208, 221, 577} In addition to wool other materials which can be dyed with pyrazolinone azo dyes are cotton and its derivatives such as rayon,^{169, 177, 205, 215, 453, 877, 963, 1326, 1449, 1451} synthetic polyamides,^{216, 865, 1117} silk,^{453, 582, 1117, 1457} leather^{39, 1117, 1457} and rubber.^{476, 577} Complexed metal dyes are not suitable for polyesters and polyacrylonitriles.

As already mentioned, numerous pyrazolinone azo dyes form complexes with metals. This can be done either before or after deposition but is usually done after the azo dye has been used to treat the fabric. In those dyes which are applied to wool the usual metal employed is chromium.^{77, 177, 213, 441, 935, 1061, 1259, 1421, 1448} For cotton dyes it is more common to use copper.^{38, 177, 276, 622, 879, 1429, 1619} Cobalt,^{207, 276} lead,²¹³

nickel^{213, 276} and iron^{177, 276} have also been used. Many metal salts and oxides can be used for the metallizing operation. In the case of chromium, various salts of chromosalicylic acid have been widely used^{186, 207, 1384, 1426} as well as sulfates, fluorides and others.

The polymethine dyes derived from pyrazolinones have not been of importance in dyeing fabrics because of their lack of fastness to light. However, methyldiyne bispyrazolinones are suitable for dyeing polyester fabrics.

The following list of references is made up of those reporting azo dyes having structures so complex that it was considered inadvisable to include them in the tables:

168, 174, 177, 179, 182, 203, 205, 209, 215, 218, 220, 221, 224, 227, 477, 486, 487, 635, 657, 782, 839, 840, 853, 886, 904, 958, 1020, 1062, 1121, 1267, 1326, 1358, 1361, 1366, 1381, 1394, 1398, 1403, 1408, 1412, 1415, 1416, 1419, 1420, 1429, 1449, 1451, 1465.

CHAPTER IV

Analytical Reagents

The use of various pyrazolinones as reagents in qualitative and quantitative analysis has been proposed, although these procedures have not been widely applied. Calcium ions form an insoluble precipitate with picrolonic acid. They can therefore be determined by using excess of the acid and back titration.³¹³ Sodium, potassium, ammonium, copper, zinc and strontium ions form crystalline salts with picrolonic acid and these salts can be used for identification of the ions.^{415, 416} Trivalent and tetravalent plutonium ions form insoluble salts of picrolonic acid and can be isolated as such.¹⁰⁹⁹ Hovorka and Šykora^{665, 666} have studied the use of various 4-nitroso-2-pyrazolin-5-ones in the gravimetric determination of a number of metal ions. It was found that the 3-methyl, 3-phenyl and 1,3-diphenyl compounds give precipitates with silver, mercuric, cuprous, cupric, plumbous, cadmium, ferrous, ferric, manganous, nickel and cobalt ions. However, only silver was precipitated quantitatively. The cupric ion could also be precipitated quantitatively by use of 3-methyl- or 3-phenyl-4-nitroso-1-(2-phenethyl)-2-pyrazolin-5-one. In the presence of ammonium thiocyanate cobalt gives a blue color with antipyrine¹³⁶⁹ or 4,4'-methylenebis(2,3-dimethyl-1-phenyl-3-pyrazolin-5-one)¹⁶⁷⁸ which can then be used to determine the cobalt colorimetrically. It is claimed that cobalt can be determined in concentrations of one part per million,¹³⁶⁹ but iron, copper and bismuth interfere. 4,4'-Methylenebis(2,3-dimethyl-1-phenyl-3-pyrazolin-5-one) also forms insoluble complexes with various ions and this can be used to determine the ions gravimetrically. Cadmium forms such a complex in the presence of bromide ion^{1306, 1678} and cobalt, copper, zinc, ferric, cadmium and mercury ions form such complexes in the presence of ammonium thiocyanate.¹⁶⁷⁹

Cyanides and cyanogen halides in the presence of pyridine and 3-methyl-1-phenyl-2-pyrazolin-5-one give a color which can be used for

their determination.⁴³⁶ The cyanides must be converted to cyanogen halides. The determination depends on conversion of pyridine to glutaconaldehyde which reacts with the pyrazolinone to form a colored compound.

The ferricyanide ion forms an insoluble complex with 4,4'-benzylidene-bis(2,3-dimethyl-1-phenyl-3-pyrazolin-5-one). This complex can be used to determine the ion gravimetrically if other complex ions are not present.⁶⁰⁹ A green color is formed by the ferricyanide ion in the presence of aminopyrine and can be used for determination because of its fluorescence.¹²¹² The ferrocyanide ion does not interfere.

Emerson, Kelly, Beegle and Beacham^{423, 425, 427} have studied the coupling of various phenols with 4-aminoantipyrine and suggest the use of this reaction as a volumetric test for phenols. Phenols having no *para*-substituent or such *para*-substituents as carboxyl, sulfo, hydroxy or methoxy groups couple, in the presence of mild oxidizing agents such as potassium ferricyanide, with the pyrazolinone to give a color which can be used as the basis for determination of the phenol.

CHAPTER V

Miscellaneous

Various pyrazolinones have been reported in patents and publications to have a variety of applications and activities. For example, both 2-pyrazolin-5-ones and 3-pyrazolin-5-ones have been reported to cause abnormal mitosis in plants and to inhibit their growth.^{1489, 1565} Howland⁶⁶⁷ has reported that a number of 2-pyrazolin-5-ones are effective antioxidants for rubber and linseed oil. The same property is probably responsible for their inhibition of odor formation in synthetic detergents.⁴⁵⁴ The perchlorate of antipyrine has been patented for use as an explosive.⁹³³ Matsumoto⁹⁵³ has found that aminoantipyrine (probably the 4-amino) is an effective catalyst for decarboxylation.

5-Methyl-2-(3-sulfophenyl- and 2-chloro-3-sulfophenyl)-3-pyrazolidinone forms complexes with choromethylcumene to give surface-active textile assistants.¹³⁸⁸

The use of antipyrine as an agent for the concentration of tannin in tannin extracts has been proposed.⁶⁶ Antipyrine forms a water-insoluble complex with tannin and the complex is easily decomposed by treating an aqueous suspension with organic solvents. These properties can be utilized for tannin concentration.

APPENDIX

SYSTEMATIC TABLES OF PYRAZOLONES
AND THEIR DERIVATIVES

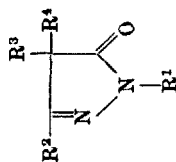


TABLE II. 2-Pyrazolin-5-ones

Section A. Alkyl and Alicyclic Substituents

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	H	H	H	165°	457, 813, 1228, 1232, 1522, 1544, 1546, 1547, 1548, 1550, 1553, 1556
H	CH ₃	H	H	215°	6, 54, 61, 338, 354, 359, 479, 480, 1047, 1075, 1085, 1199, 1485, 1553, 1622
H	H	CH ₃	H	226°	51, 457
H	C ₃ H ₇	H	H	207°	360, 1012
H	iso-C ₃ H ₇	H	H	183°	1012
H	i-C ₄ H ₉	H	H	210°	354, 1522
H	C ₅ H ₁₁	H	H	198°	1024
H	C ₆ H ₁₃	H	H	201°	1024
H	C ₆ H ₁₅	H	H	187°	855

(Table continued)

TABLE II, Section A (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	C ₁₁ H ₂₃	H	H	67°	135
H	C ₁₆ H ₃₃	H	H	108°	1480
H	C ₂ H ₅ OOC(CH ₂) ₃	H	H	149°	96
H	F ₃ C	H	H	208°	564
H	(CH ₃) ₃ SiCH ₂ CH ₂	H	H	203°	1317
H	C ₂ H ₅ OOCCH ₂	H	H	189°	866
H	H	C ₂ H ₅ OOCCH ₂	H	167°	962
H	H ₂ NNHCOCH ₂	H	H	180°	866
H	C ₆ H ₅ CH=NNHCOCH ₂	H	H	>190°	866
H	2-HOC ₆ H ₄ CH=NNHCOCH ₂	H	H	>200°	866
H	3-NO ₂ C ₆ H ₄ CH=NNHCOCH ₂	H	H	>145°	866
H	C ₆ H ₅ CH=CHCH=NNHCOCH ₂	H	H	>145°	866
H	HOOCCH ₂ CH ₂	H	H	222°	1221
H	CH ₃ OOCCH ₂ CH ₂	H	H	168°	1221
H	H ₂ NHNOCCH ₂ CH ₂	H	H	178°	1221
CH ₃	CH ₃	H	H	117°	788, 985, 1622
C ₂ H ₅	CH ₃	H	H	250	250
C ₃ H ₇	CH ₃	H	H	115°	250
iso-C ₃ H ₇	CH ₃	H	H	99°	250
C ₄ H ₉	CH ₃	H	H	56°, 86°	206, 250, 1681
iso-C ₄ H ₉	CH ₃	H	H	120°	250
C ₆ H ₁₇	CH ₃	H	H	59°	206
C ₁₀ H ₂₁	CH ₃	H	H	65°	206
HOOCCH ₂ CH	CH ₃	H	H	209°	1118, 1119
HOOCCH ₂ CH ₂	CH ₃	H	H	164°	1119
H	CH ₃	C ₂ H ₅ OOCCH ₂	H	166°	962
C ₄ H ₉ OOCCH ₂ CH ₂	CH ₃	H	H	52°	1118, 1119
C ₂ H ₅ OOCCH ₂ CH ₂	CH ₃	H	H	106°	1118, 1119
NOCCH ₂ CH ₂	CH ₃	H	H	—	1119
NH ₂ COCH ₂ CH ₂	CH ₃	H	H	167°	1119

NCCHCH_3	CH_3	H	H	146°	1119
$\text{iso-C}_6\text{H}_{17}\text{OOCCH}_2\text{CH}_3$	CH_3	H	H	liquid	1119
$\text{HO}_3\text{SCH}_2\text{CH}_3$	CH_3	H	H	—	1684
$\text{HO}_3\text{SCH}_2\text{CH}_3$	$\text{C}_{17}\text{H}_{35}$	H	H	—	1684
$\text{HO}_3\text{SCH}_2\text{CHCH}_2$	CH_3	H	H	—	1684
$\text{HO}_3\text{SCH}_2\text{CHCH}_2$	$\text{C}_{17}\text{H}_{35}$	H	H	—	1684
H	CH_3	CH_3	H	272°	61, 358, 359, 692, 1012, 1531, 1645
H	CH_3	C_2H_5	H	229°	61, 358, 359, 660, 729, 1012, 1645
H	C_6H_5	CH_3	H	232°	730
H	CH_3	C_3H_7	H	211°	359, 720, 1522, 1645
H	CH_3	$\text{iso-C}_3\text{H}_7$	H	182°	250
H	CH_3	C_3H_5	H	193°	883, 1522, 1546
H	CH_3	C_4H_9	H	197°	1526
H	CH_3	$\text{n-C}_4\text{H}_9$	H	158°	917
H	CH_3	C_3H_{11}	H	198°	1012
H	CH_3	$\text{C}_{12}\text{H}_{25}$	H	178°	1505
H	CH_3	HOCH_2CH_2	H	182°	60, 1171
H	CH_3	CH_3CH	H	273°	513, 514, 515
H	CH_3	HOOCCH_2	H	240°	349
H	CH_3	$\text{C}_2\text{H}_5\text{OOCCH}=\text{C}$	H	188°	1288

(Table continued)

TABLE II, Section A (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	CH ₃	NH ₂ NHCOCH CH ₃ CH ₃	H	212°	1277
H	CH ₃	NO ₂ CH ₂ C CH ₃	H	—	64
H	CH ₃	CH ₃ -N=CH-N(CH ₃) CH ₃	H	285°	1169
CH ₃ CH ₃ CH ₃ CH ₃ C ₂ H ₅ C ₃ H ₇ C ₂ H ₅ C ₄ H ₉ iso-C ₄ H ₉ H	CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ CH ₃	CH ₃ C ₂ H ₅ C ₃ H ₇ C ₃ H ₆ iso-C ₃ H ₇ iso-C ₃ H ₇ iso-C ₃ H ₇ iso-C ₃ H ₇ CH ₃	H H H H H H H H H CH ₃	133° 94° 84° 71° 113° 85° 84° 83° 74° 109°, 268°	51, 1531 1522 1522 1522 250 250 250 250 250 61, 358, 359, 759, 1012, 1531, 1560 61 61, 759, 1522
H H	CH ₃ CH ₃	CH ₃ C ₂ H ₅	C ₂ H ₅ C ₂ H ₅	76° 105°	
H		H	H	224°	1579

	CH ₃	H	H	152°	101
	CH ₃	H	H	139°	101, 103, 161, 859, 1280
H	CH ₃		H	255°	1526
H	CH ₃	—CH ₂ CH ₂ —		195°	1546

TABLE II (continued)

Section B. Monoaryl, Alkyl, and Alicyclic Substituents

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	H	H	H	118°	306, 810, 858, 1002, 1230, 1350, 1351, 1554, 1559
H	C ₆ H ₅	H	H	244°	181, 610, 982, 1023, 1024, 1085, 1205, 1431, 1522, 1549, 1552, 1553, 1578

(Table continued)

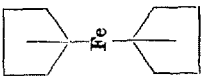
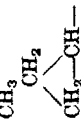
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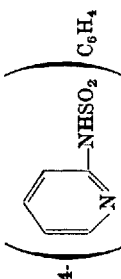
R ¹	R ²	R ³	R ⁴	M.p.	Reference
2-CH ₃ C ₆ H ₄	H	H	H	177°	1004
4-IC ₆ H ₄	H	H	H	126°	446
H	4-NO ₂ C ₆ H ₄	H	H	217°	798
H	3-(4-CH ₃ C ₆ H ₄ SO ₂ NH)C ₆ H ₄	H	H	210°	467
H	3-NO ₂ -4-CH ₃ OC ₆ H ₃	H	H	225°	181
2,4,6-(CH ₃) ₃ C ₆ H ₂	H	H	H	290° (dec.)	835
H	1-C ₁₀ H ₇	H	H	233°	1577
H	3-CH ₃ O-2-C ₁₀ H ₆	H	H	205°	1575
6-HO ₂ S-8-HO-2-C ₁₀ H ₅	H	H	H	—	522
C ₆ H ₅	CH ₃	H	H	127°	68, 95, 629, 723, 788, 805, 806, 809, 811, 816, 838
C ₆ H ₅	H	CH ₃	H	142°	1569
CH ₃	C ₆ H ₅	H	H	207°	54, 992, 1560
H	C ₆ H ₅	CH ₃	H	127°, 213°	54, 1531, 1560
C ₆ H ₅	CF ₃	H	H	—	564
C ₆ H ₅	C ₂ H ₅	H	H	100°	1686
C ₆ H ₅	H	C ₂ H ₆	H	99°	303
H	C ₆ H ₅	C ₂ H ₅	H	165°	505
C ₆ H ₅	C ₃ H ₇	H	H	110.5°	1686
H	C ₆ H ₅	C ₃ H ₇	H	186°	505
C ₆ H ₅	iso-C ₃ H ₇	H	H	81°	1588
H	C ₆ H ₅	C ₆ H ₅	H	182°	1294
H	iso-C ₃ H ₇	C ₆ H ₅	H	191°	1640
C ₆ H ₅	C ₄ H ₉	H	H	83°	1686
H	C ₆ H ₅	C ₄ H ₉	H	180°	505
C ₆ H ₅	iso-C ₄ H ₉	H	H	79°, 107°	97, 448, 1589, 1590
C ₆ H ₅	<i>t</i> -C ₄ H ₉	H	H	110°	1582, 1589, 1590

C_6H_5	C_6H_{11}	H	H	95°	1023, 1589, 1590, 1686
H	C_6H_5	C_6H_{11}	H	139°	505
C_6H_5	$CH_3-\overset{\overset{CH_3}{ }}{C}-CH_2$ $ $ CH_3	H	H	138°	1588, 1589, 1590
C_6H_5	C_6H_{13}	H	H	84°	1023, 1024, 1589, 1590
H	C_6H_5	C_6H_{13}	H	116°	505
C_6H_5	C_7H_{15}	H	H	82°	143
H	C_6H_5	C_7H_{15}	H	108°	505
C_6H_5	C_8H_{17}	H	H	65°	143
H	C_6H_5	C_8H_{17}	H	110°	505
C_6H_5	C_9H_{19}	H	H	—	143
H	C_6H_5	C_9H_{19}	H	100°	505
C_6H_5	$C_{10}H_{21}$	H	H	67°	143
H	C_6H_5	$C_{10}H_{21}$	H	95°	505
C_6H_5	$C_{11}H_{23}$	H	H	240°	42
C_6H_5	$C_{12}H_{25}$	H	H	76°	636
$HOOCCH_2CH_2$	C_6H_5	H	H	185°	1118
C_6H_5	$CH_3OOCCH_2CH_2$	H	H	79.5°	1221
C_6H_5	$C_2H_5OOCCH_2CH_2$	H	H	107.5°	1341
C_6H_5	$H_2NOCCH_2CH_2$	H	H	172°	1221
C_6H_5	$\begin{array}{c} CH_2 \\ \diagup \quad \diagdown \\ CH_2-CH- \end{array}$	H	H	115°	274, 1477
C_6H_5		H	H	126°	778

(Table continued)

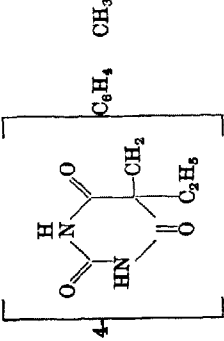
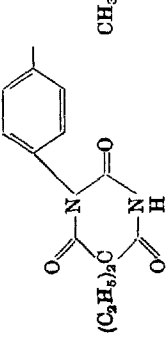
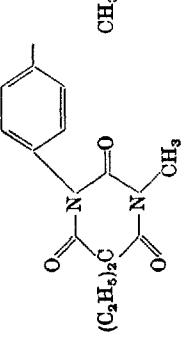
TABLE II, Section B (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅		H	H	186°	628
2-CH ₃ C ₆ H ₄	CH ₃	H	H	143°, 183°	806, 838, 1524, 1584
3-CH ₃ C ₆ H ₄	CH ₃	H	H	104°	723, 838
3-CH ₃ C ₆ H ₄		H	H	103°	1477
4-CH ₃ C ₆ H ₄	CH ₃	H	H	91.5°, 140°	68, 723, 806, 838
4-CH ₃ C ₆ H ₄		H	H	104°	1477
4-CH ₃ OC ₆ H ₄	CH ₃	H	H	122°	838
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	H	H	—	902
4-C ₃ H ₇ OC ₆ H ₄	CH ₃	H	H	132°	1149
3-NH ₂ C ₆ H ₄	CH ₃	H	H	—	197
4-NH ₂ C ₆ H ₄	CH ₃	H	H	—	192
3-[3,5-(HO) ₂ C ₆ H ₃ NH]C ₆ H ₄	CH ₃	H	H	—	470
4-HSCH ₂ CONHC ₆ H ₄	CH ₃	H	H	—	492
4-[2,3-(HO) ₂ -1-C ₁₀ H ₇ CONH]C ₆ H ₄	CH ₃	H	H	260°	863
2-ClC ₆ H ₄	CH ₃	H	H	182°, 199°	192, 296, 838, 1494
3-ClC ₆ H ₄	CH ₃	H	H	131°	296, 838
4-ClC ₆ H ₄	CH ₃	H	H	172°	296, 838, 1002

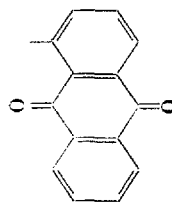
3-BrC ₆ H ₄	CH ₃	H	H	134°	1683
4-BrC ₆ H ₄	H	CH ₃	H	233°	1569
4-BrC ₆ H ₄	H	C ₂ H ₅	H	170°	303
4-IC ₆ H ₄	CH ₃	H	H	196°	446
3-NO ₂ C ₆ H ₄	CH ₃	H	H	185°	837
4-NO ₂ C ₆ H ₄	CH ₃	H	H	220°	777, 838, 1282, 1372
4-NO ₂ C ₆ H ₄	H	C ₂ H ₅	H	212°	303
HO ₃ SCH ₂ CH ₂	4-NO ₂ C ₆ H ₄	H	H	—	1684
HO ₃ SCH ₂ CH(OH)CH ₂	4-NO ₂ C ₆ H ₄	H	H	—	1684
4-(4-C ₆ H ₄ CO)C ₆ H ₄	CH ₃	H	H	170°	1497
2-HOCC ₆ H ₄	CH ₃	H	H	189°	1004, 1520
3-HOCC ₆ H ₄	C ₁₇ H ₃₅	H	H	—	165, 1270
4-HOCC ₆ H ₄	CH ₃	H	H	278°	356
4-C ₂ H ₅ OCC ₆ H ₄	CH ₃	H	H	145°	1490
4-(3-HOCC-4-HOC ₂ H ₅ NHCO)C ₆ H ₄	CH ₃	H	H	—	1361
2-HO ₃ SC ₆ H ₄	CH ₃	H	H	—	1305
3-HO ₃ SC ₆ H ₄	C ₆ H ₁₇	H	H	265°	583
3-HO ₃ SC ₆ H ₄	C ₁₇ H ₃₅	H	H	—	1348
4-HO ₃ SC ₆ H ₄	CH ₃	H	H	306°	191, 356, 684, 1163
4-HO ₃ SC ₆ H ₄	C ₁₅ H ₃₁	H	H	> 300°	694
4-NaO ₃ SC ₆ H ₄	C ₁₆ H ₃₃	H	H	—	1481
4-H ₂ NO ₂ SC ₆ H ₄	CH ₃	H	H	237°	324, 328, 356, 695, 1475, 1476, 1628
4-()C ₆ H ₄	CH ₃	H	H	248°	25

(Table continued)

TABLE II, Section B (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
4-HO ₂ AsC ₆ H ₄	CH ₃	H	H	—	546
4-(3-CH ₃ C ₆ H ₁₀)C ₆ H ₄	CH ₃	H	H	150°	141
4-(3-H ₂ NC ₆ H ₄)C ₆ H ₄	CH ₃	H	H	—	197
4-(4-H ₂ NC ₆ H ₄)C ₆ H ₄	CH ₃	H	H	194°	163, 1377
4-(4-CH ₃ CONHC ₆ H ₄)C ₆ H ₄	CH ₃	H	H	—	163
					
	CH ₃	H	H	—	1160
					
	CH ₃	H	H	190°	517
					
	CH ₃	H	H	198°	517

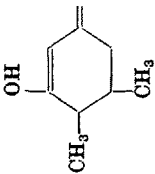
2,5(CH ₃) ₂ C ₆ H ₃	CH ₃	H	H	164°	679
2-CH ₃ -4-IC ₆ H ₃	CH ₃	H	H	194°	446
2-C ₂ H ₅ -4-HOC ₆ H ₃	CH ₃	H	H	—	1389
2-HO-5-HO ₃ SC ₆ H ₃	CH ₃	H	H	—	539
2-HO ₃ S-4-CH ₃ OC ₆ H ₃	CH ₃	H	H	—	1162
2-C ₂ H ₅ O-5-NO ₂ C ₆ H ₃	CH ₃	H	H	—	364
3-HO ₃ S-4-C ₆ H ₅ OC ₆ H ₃	C ₁₅ H ₃₁	H	H	> 300°	694
3-HO ₃ S-4-C ₃ H ₇ OC ₆ H ₄	C ₁₇ H ₃₅	H	H	—	1348
2,4-Cl ₂ C ₆ H ₃	CH ₃	H	H	178°	296, 885
3,4-Cl ₂ C ₆ H ₃	CH ₃	H	H	164°	80
3-HO ₃ S-4-ClC ₆ H ₃	C ₁₇ H ₃₅	H	H	—	1348
2,4-I ₂ C ₆ H ₃	CH ₃	H	H	153°	446
2,4-(NO ₂) ₂ C ₆ H ₃	CH ₃	H	H	144°, 126°	723, 777, 1207
4-(2-H ₃ OS-4-NH ₂ C ₆ H ₃ CH=CH)-3-HO ₃ SC ₆ H ₃	CH ₃	H	H	—	197
4-CH ₃ -3-NO ₂ -5-HO ₃ SC ₆ H ₃	CH ₃	H	H	—	123
2,4,6-Cl ₃ C ₆ H ₂	CH ₃	H	H	—	312
2,5-Cl ₂ -4-HO ₃ SC ₆ H ₂	CH ₃	H	H	—	1393
2,4,6-(NO ₂) ₃ C ₆ H ₂	CH ₃	H	H	211°	777
1-C ₁₀ H ₇	CH ₃	H	H	190°	806
2-C ₁₀ H ₇	CH ₃	H	H	190°	806
4-HO ₃ S-1-C ₁₀ H ₇	CH ₃	H	H	—	238, 239
X,Y-(HO ₃ S) ₂ -2-C ₁₀ H ₅	CH ₃	H	H	—	534
X-HO ₃ S-Y-HO-2-C ₁₀ H ₅	CH ₃	H	H	—	534
5-HO-7-HO ₃ S-2-C ₁₀ H ₅	CH ₃	H	H	—	71
	CH ₃	H	H	—	1251



(Table continued)

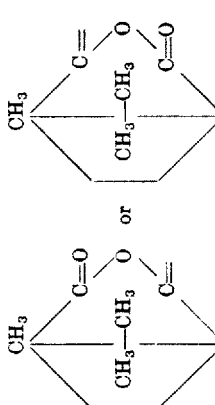
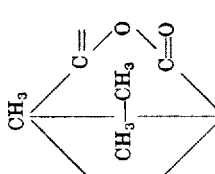
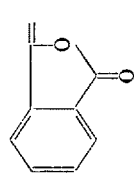
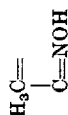
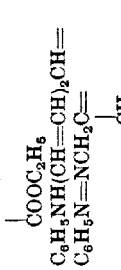
TABLE II, Section B (continued)

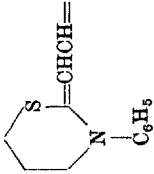
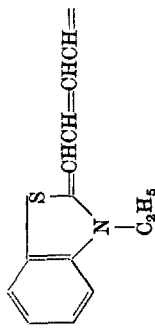
R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃	H	127°	95, 809, 811, 814, 1056, 1299
C ₆ H ₅	CH ₃	C ₂ H ₅	H	107°	95, 814, 1007, 1522, 1524
C ₆ H ₅	C ₂ H ₅	CH ₃	H	111.5°	1277, 1589, 1590
C ₆ H ₅	CH ₃	C ₆ H ₇	H	101°	53, 1522
C ₆ H ₅	CH ₃	iso-C ₃ H ₇	H	116°	53, 249, 1336
C ₆ H ₅	CH ₃	iso-C ₃ H ₇	H	—	1477
C ₆ H ₅		CH ₂ =CHCH ₂	H	b _{0.008} 148–151°	1477
C ₆ H ₅	CH ₃	C ₄ H ₉	H	95°	53, 560
C ₆ H ₅	CH ₃	iso-C ₄ H ₉	H	118°	560, 1336
C ₆ H ₅	CH ₃	s-C ₄ H ₉	H	92°	1336
C ₆ H ₅	CH ₃	CH ₃	H	114.5°	1582
C ₆ H ₅	CH ₃	CH ₃	H	80.4°	277
C ₆ H ₅	CH ₃		H	133°	1239
C ₆ H ₅	CH ₃		H	130°	1336
C ₆ H ₅	CH ₃	HOCH ₂ CH ₂	H	94°	1171
C ₆ H ₅	CH ₃	BrCH ₂ CH ₂ CH ₂	H	190°	563

C_6H_5 C_6H_5	CH_3 CH_3	$(C_2H_5)_2NCH_2CH_2$ CH_3COCH_2	H H	145° 114°	574 113
C_6H_5	CH_3	$\begin{array}{c} NOH \\ \\ CH_3CCH_2 \end{array}$	H	105°	113
C_6H_5	CH_3	$\begin{array}{c} O \\ \\ CH_3CCH_2C \\ \\ CH_3 \end{array}$	H	142°	686
C_6H_5 C_6H_5 C_6H_5 C_6H_5 C_6H_5	CH_3 CH_3 CH_3 CH_3 CH_3	$\begin{array}{c} O \\ \\ CH_3CCH=CH \\ \\ HOOCCH_2 \\ C_2H_5OOCCH_2 \\ C_2H_5OOCCH_2CH_2 \\ C_2H_5OOCCH=CH \\ \\ CH_3 \end{array}$	H H H H	181° 178° 138° $b_p 215^\circ$ 246°	721 814 309 814 1298
C_6H_5 C_6H_5	CH_3 CH_3	$\begin{array}{c} (CH_3)_2C= \\ \\ -CH_2CH_2- \end{array}$		117° 94°, 138° (2 forms)	809 872
C_6H_5	CH_3			110°	753
C_6H_5	CH_3	$\begin{array}{c} CH_3C= \\ \\ CH_2COOC_2H_5 \end{array}$		98°	1347

(Table continued)

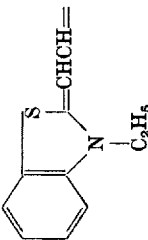
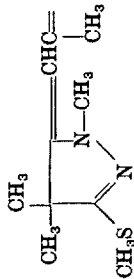
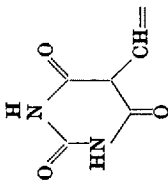
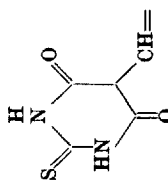
TABLE II, Section B (continued)

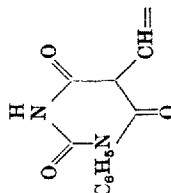
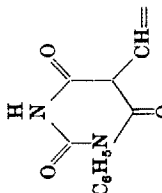
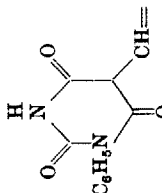
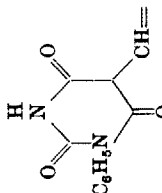
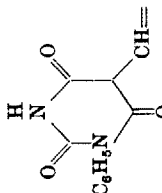
R ¹	R ²	R ³	R ⁴	M.P.	Reference
C ₆ H ₆	CH ₃			195°	1237
C ₆ H ₅	CH ₃			212°	1279
C ₆ H ₅	CH ₃	4-(CH ₃) ₂ NC ₆ H ₄ N=CHC=		184°	1131
C ₆ H ₅	CH ₃			198°	1347
C ₆ H ₅ C ₆ H ₅	CH ₃ CH ₃			182° 173°	1070 1130, 1131
C ₆ H ₅	CH ₃	4-NO ₂ C ₆ H ₄ N=NCH ₂ C=		234°	1130
C ₆ H ₅	CH ₃	2,5-Cl ₂ C ₆ H ₃ N=NCH ₂ C=		194°	1130

C_6H_5	CH_3	$3-HOOC-C_6H_4-N=N-CH_2-C(=CH_3)-$	235°	1130
C_6H_5	CH_3	$2,5-Cl_2-C_6H_3-N=N-CH_2-C(=C_6H_5)-$	185°	1130
C_6H_5	CH_3	$4-NO_2-C_6H_4-N=N-CH_2-C(=C_6H_5)-$	235°	1130, 1131
C_6H_5	CH_3	$2-NO_2-4-Cl-C_6H_3-N=N-CH_2-C(=C_6H_5)-$	226°	1130
C_6H_5	CH_3	$C_6H_5-N=N-CH_2-C(=C_6H_5)-$	118°	1130, 1131
C_6H_5	CH_3	$2-HOOC-C_6H_4-N=N-CH_2-C(=C_6H_5)-$	214°	1130
C_6H_5	CH_3	$4-NO_2-C_6H_4-N=N-CH_2-C(=3-NO_2-C_6H_5)-$	231°	1130, 1131
C_6H_5	CH_3		177°	389
C_6H_5	CH_3		—	166

(Table continued)

TABLE II, Section B (*continued*)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃			218°	675
C ₆ H ₅	CH ₃			146°	759
C ₆ H ₅	CH ₃			297°	1191
C ₆ H ₅	CH ₃			305°	1187

7 + C ₆ H ₅ + C ₆ H ₅ .C. 20		CH ₃	308°	1188
2-CH ₃ C ₆ H ₄ 2-CH ₃ C ₆ H ₄		CH ₃ C ₂ H ₅	179° 82.5°	1004 1524
4-C ₂ H ₅ OC ₆ H ₄		CH ₃	> 300°	1188
4-NH ₂ C ₆ H ₄ 4-FC ₆ H ₅ 4-NO ₂ C ₆ H ₄ 4-NO ₂ C ₆ H ₄ 2-HOOC ₆ H ₄ 1-C ₁₀ H ₇ 2-C ₁₀ H ₇ C ₆ H ₅		CH ₃ CH ₃ C ₂ H ₅ HOCH ₂ CH ₂ C ₂ H ₅ iso-C ₃ H ₇ iso-C ₃ H ₇ CH ₃	(CH ₃) ₂ C=	535 1263 532 136 1171 1520 849 849 95, 785, 809, 1056
C ₆ H ₅ C ₆ H ₅ C ₆ H ₅ C ₆ H ₅ C ₆ H ₅ C ₆ H ₅		CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ C ₂ H ₅	C ₃ H ₅ C ₃ H ₇ iso-C ₃ H ₇ C ₃ H ₅ C ₃ H ₅ C ₃ H ₅ CH ₃	53 53 53 53 53 53 53

(Table continued)

TABLE II, Section B (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	C ₂ H ₅	C ₂ H ₅	39°, 61°	53, 95
C ₆ H ₅	CH ₃	C ₂ H ₅	C ₃ H ₇	b ₁₂ 181°	53
C ₆ H ₅	CH ₃	C ₂ H ₅	C ₃ H ₇	b ₁₂ 184°	53
C ₆ H ₅	CH ₃	C ₃ H ₅	C ₃ H ₅	b ₁₁ 192°	53, 1321
C ₆ H ₅	C ₂ H ₅	C ₂ H ₅	C ₃ H ₇	b ₃₀ 203°	53
1-(4-NH ₂ C ₆ H ₅)	CH ₃	CH ₃	CH ₃	—	538
1-[4-(CH ₃) ₂ NC ₆ H ₅]	CH ₃	CH ₃	CH ₃	—	538

TABLE II (continued)

Section C. Aalkyl, Heterocycalkyl, Aryl, and Alkyl Substituents

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	C ₆ H ₅ CH ₂	H	H	197°	1320
H	H	H	H	180°	813
C ₆ H ₅ CH=CH	H	H	H	216°	181
C ₆ H ₅ CH ₂	CH ₃	H	H	174°	54, 250, 333
C ₆ H ₅ CH ₂ CH ₂	CH ₃	H	H	134°	1566
2-CH ₃ OC ₆ H ₄ CH ₂	CH ₃	H	H	82°	334
3,4-(OCH ₂ O)C ₆ H ₄ CH ₂	CH ₃	H	H	155°	334
H	CH ₃	C ₆ H ₅ CH ₂	H	213°, 218°, 230°	302, 660, 729
H	CH ₃	C ₆ H ₅ CH=CH	H	214°	883
H	CH ₃	C ₆ H ₅ CH ₂ CH ₂ CH ₂	H	176°	883

H	CH ₃	C ₆ H ₅ CH CH=CH ₂	H	184°	882
H	CH ₃	C ₆ H ₅ CH C ₂ H ₅ CH—CH NO ₂ C ₆ H ₅	H	193°	882, 883
H	CH ₃	C ₆ H ₅ CH C ₂ H ₅ CH—CH NO ₂ C ₆ H ₅	H	235°	383
C ₂ H ₅	CH ₃	C ₆ H ₅ CH ₂	H	177°	302
C ₆ H ₅ CH ₂	CH ₃	iso-C ₃ H ₇	H	74°	250
C ₆ H ₅ CH ₂	CH ₃	C ₆ H ₅ CH=	H	111°	333
C ₆ H ₅	C ₆ H ₅ CH ₂		H	—	1320
C ₆ H ₅	H	C ₆ H ₅ CH ₂	H	146°	1236, 1320
C ₆ H ₅ CH ₂	C ₆ H ₅	H	H	204°	333
H	C ₆ H ₅	C ₆ H ₅ CH ₂	H	184°	505
H	C ₆ H ₅ CH ₂	C ₆ H ₅	H	172°	1200
C ₆ H ₅	H	C ₆ H ₅ CH=	H	170°	306
H	C ₆ H ₅	C ₆ H ₅ CH=		> 250°	1552, 1560
C ₆ H ₅	C ₆ H ₅ CH ₂ CH ₂		H	133°	1534
C ₆ H ₅ CH ₂ CH ₂	C ₆ H ₅	H	H	145.5°	1567
C ₆ H ₅ CH=CH	C ₆ H ₅ CH=CH		H	148°	124, 1334
C ₆ H ₅ O(CH ₂) ₃	C ₆ H ₅ O(CH ₂) ₃	H	H	115°	246
C ₆ H ₅ O(CH ₂) ₄	C ₆ H ₅ O(CH ₂) ₄	H	H	118.5°	246
H	H	C ₆ H ₅ CH C ₆ H ₅	H	220°	1639
H	C ₆ H ₅	HOCC=C C ₆ H ₅	H	145°	1050
2,4-(CH ₃) ₂ C ₆ H ₃ CH ₂	C ₆ H ₅	H	H	162°	334
3,4-(OCH ₂ O)C ₆ H ₃ CH ₂	C ₆ H ₅	H	H	144.5°	334
4-NO ₂ C ₆ H ₄	H	C ₆ H ₅ CH ₂	H	176°	1236
2,4-(NO ₂)C ₆ H ₃	C ₆ H ₅ CH=CH	H	H	171°	1334
H	2,4,6-(CH ₃) ₃ C ₆ H ₂	C ₆ H ₅ CH=	H	280°	835

(Table continued)

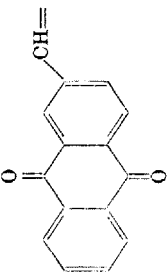
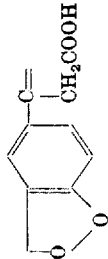
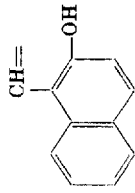
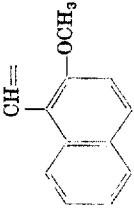
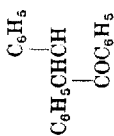
TABLE II, Section C (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	2,4,6-(CH ₃) ₃ -3-HO-5-CH ₃ COOC ₆ H ₄ (CH ₃) ₂ C=		208°	1308
C ₆ H ₅	CH ₃			116°	1128
C ₆ H ₅	CH ₃	C ₆ H ₅ CH ₂	H	140°	1321, 1584
C ₆ H ₅	CH ₃	2-CH ₃ -5-iso-C ₃ H ₇ -C ₆ H ₃ CH ₃	H	143°	1148
C ₆ H ₅	CH ₃	C ₆ H ₅ CH=		106°	686, 809, 1250
C ₆ H ₅	CH ₃	C ₆ H ₅ CH=CHCH=		139°	809
C ₆ H ₅	CH ₃	C ₆ H ₅ CH=C— C ₆ H ₅	H	220°	1522
C ₆ H ₅	CH ₃	HON=CHC=		208°	1131
C ₆ H ₅	CH ₃	HON=CHC=		235°	1131
C ₆ H ₅	CH ₃	H ₂ NCONHN=CHC=		227°	1131
C ₆ H ₅	CH ₃	4-(CH ₃) ₂ NC ₆ H ₄ N=CHC=		181°	1131
C ₆ H ₅	CH ₃	4-(CH ₃) ₂ NC ₆ H ₄ N=CHC=		185°	1131
C ₆ H ₅	CH ₃	3-NO ₂ C ₆ H ₄ C=		150°	1128
C ₆ H ₅	C ₆ H ₅ CH ₂	C ₆ H ₅ CH ₂	H	139°	1320
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ CH=	H	147°	818
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ CH ₂	H	178°	505
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ CH=	H	229°	1200
C ₆ H ₅	C ₆ H ₅	4-CH ₃ OC ₆ H ₄ CH=	H	163°	1227
C ₆ H ₅	CH ₃			127°	1254, 1255

CH_3	$4\text{-H}_2\text{NC}_6\text{H}_4\text{CH}_2$	H	oil	110
CH_3	$4\text{-CH}_3\text{CONHC}_6\text{H}_4\text{CH}_2$	H	185°	110
CH_3	$3\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{CH=}$		117°	311
CH_3	$4\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{CH=}$		196°	376
CH_3	$4\text{-(CH}_3\text{N)C}_6\text{H}_4\text{CH=}$		154°	34
	$\text{CH}_3\text{CH}_2\text{Cl}$			
CH_3	$4\text{-(C}_2\text{H}_5\text{N)C}_6\text{H}_4\text{CH=}$		117°	34
	$\text{CH}_2\text{CH}_2\text{Cl}$			
CH_3	$4\text{-(ClCH}_2\text{CH}_2)_2\text{NC}_6\text{H}_4\text{CH=}$		167°	34
CH_3	$2\text{-NO}_2\text{C}_6\text{H}_4\text{CH=}$		—	633
CH_3	$3\text{-NO}_2\text{C}_6\text{H}_4\text{CH=}$		162°	633
CH_3	$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH=}$		180°, 209°	110, 376, 633
CH_3	$2\text{-H}_5\text{C}_7\text{OOCCH}_2\text{OC}_6\text{H}_4\text{CH=}$		122°	832
CH_3	$3\text{-CH}_3\text{O-4-HOC}_6\text{H}_3\text{CH=}$		169°	22
CH_3	$3\text{-CH}_3\text{O-4-HOC}_6\text{H}_3\text{CH}_2$	H	240°	24
CH_3	$3,4\text{-(CH}_3\text{O)}_2\text{C}_6\text{H}_3\text{CH=}$		157°	22
CH_3	$2,4\text{-[(CH}_3)_2\text{N]}_2\text{C}_6\text{H}_3\text{CH=}$		181°	1241
CH_3	$3\text{-NO}_2\text{-4-(CH}_3)_2\text{CHC}_6\text{H}_3\text{CH=}$		205°	1123
CH_3	$3,5\text{-(CH}_3\text{O)}_2\text{-4-HOC}_6\text{H}_2\text{CH=}$		208°	956
CH_3	$3,4,5\text{-(CH}_3\text{O)}_3\text{C}_6\text{H}_2\text{CH=}$		141°	955
CH_3	$2\text{-NO}_2\text{-3-CH}_3\text{O-4-HOC}_6\text{H}_2\text{CH=}$		192°	702
CH_3	$[4\text{-(CH}_3)_2\text{NC}_6\text{H}_4]_2\text{C=}$		265°	1073
CH_3	$4\text{-(CH}_3)_2\text{NC}_6\text{H}_4]_2\text{CH}$	H	185°	836
CH_3	$2,4\text{-(NO}_2)_2\text{C}_6\text{H}_4\text{N=CHCH=CHCH=CH}$	H	247°	1114
CH_3	$(\text{C}_6\text{H}_5)_3\text{C}$	H	209°	567
CH_3	$4\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{C}$	H	179°	570
	$(\text{C}_6\text{H}_5)_2$			
CH_3	$[4\text{-(CH}_3)_2\text{NC}_6\text{H}_4]_2\text{C}$	H	162°	570
	C_6H_5			
CH_3	$[4\text{-(CH}_3)_3\text{NC}_6\text{H}_4]_2\text{CH}$	H	193°	570

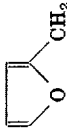
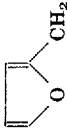
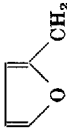
TABLE II, Section C (continued)

R ¹	R ²	R ³	R ⁴	M.P.	Reference
C ₆ H ₅	CH ₃	[4-(CH ₃) ₂ NC ₆ H ₄] ₃ C 	H	154°	567
C ₆ H ₅	CH ₃		H	188°	567
C ₆ H ₅	CH ₃		H	161°	686
C ₆ H ₅	CH ₃		H	220°	686
C ₆ H ₅	CH ₃		—	—	1202
C ₆ H ₅	CH ₃		—	272°	1204

C_6H_5	CH_3		243°	1219
C_6H_5	CH_3		145°	957
C_6H_5	CH_3		—	948
C_6H_5	CH_3		219°	1036
C_6H_5	CH_3		212°	689
C_6H_5	CH_3		200°	689

(Table continued)

TABLE II, Section C (continued)

R ¹	R ²	R ³	R ⁴	M.P.	Reference
C ₆ H ₅	CH ₃	$ \begin{array}{c} \text{C}_6\text{H}_5 \\ \\ 3,4\text{-(CH}_2\text{O}_2\text{)C}_6\text{H}_3\text{CHCH} \\ \\ \text{COC}_6\text{H}_5 \\ \\ \text{C}_6\text{H}_5 \end{array} $	H	206°	689
C ₆ H ₅	CH ₃	$ \begin{array}{c} \text{COC}_6\text{H}_5 \\ \\ 4\text{-(CH}_3\text{)}_2\text{NC}_6\text{H}_4\text{CHCH} \\ \\ \text{C}_6\text{H}_5 \end{array} $	H	201°	689
2-CH ₃ C ₆ H ₄	CH ₃	4-(CH ₃) ₂ NC ₆ H ₄ CH=		140°	702
2-CH ₃ C ₆ H ₄	CH ₃	2-NO ₂ C ₆ H ₄ CH=		183°	702
2-CH ₃ C ₆ H ₄	CH ₃	3-NO ₂ C ₆ H ₄ CH=		176°	702
2-CH ₃ C ₆ H ₄	CH ₃	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH=		222°	702
4-CH ₃ C ₆ H ₄	CH ₃	4-(CH ₃) ₂ NC ₆ H ₄ CH=		142°	702
4-CH ₃ C ₆ H ₄	CH ₃	4-HO-3-CH ₃ OC ₆ H ₃ CH=		183°	702
4-CH ₃ C ₆ H ₄	CH ₃	4-HO-3-CH ₃ O-2-NO ₂ C ₆ H ₃ CH=		209°	702
4-C ₂ H ₅ OC ₆ H ₄	CH ₃		H	—	378
4-H ₂ NC ₆ H ₄	CH ₃		H	—	378
4-CH ₃ CONHC ₆ H ₄	CH ₃		H	244°	378
2-ClC ₆ H ₄	CH ₃	C ₆ H ₅ CH=		159°	296, 1494
3-ClC ₆ H ₄	CH ₃	C ₆ H ₅ CH=		128°	296
4-ClC ₆ H ₄	CH ₃	C ₆ H ₅ CH=		156°	296

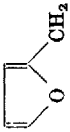
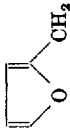
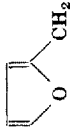
4-BrC ₆ H ₄	CH ₃		H	—	378
4-NO ₂ C ₆ H ₄	CH ₃		H	—	378
2-HOOCCH ₃	CH ₃	C ₆ H ₅ CH=	—	243°	1004
3-HOOCCH ₃	CH ₃			251°	980
4-HOOCCH ₃	CH ₃			281°	980
4-HO ₃ SC ₆ H ₄	CH ₃		H	—	378
2,4-Cl ₂ C ₆ H ₃	CH ₃	C ₆ H ₅ CH=	—	131°	296
1-C ₁₀ H ₇	CH ₃			168°	849
2-C ₁₀ H ₇	CH ₃			153°	849
C ₆ H ₅	C ₆ H ₅ CH ₂			160°	1313
C ₆ H ₅	CH ₃			81°	53
C ₆ H ₅	CH ₃			91°	1321

TABLE II (continued)

Section D. Polyaryl Substituents

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	C ₆ H ₅	H	H	136°	777, 818, 1023, 1522, 1524, 1552

(Table continued)

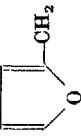
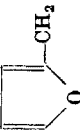
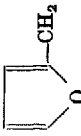
TABLE II, Section D (*continued*)

R ¹	R ²	R ³	R ⁴	M.P.	Reference
C ₆ H ₅	H	C ₆ H ₅	H	195°	506, 1636
C ₆ H ₅	4-F ₃ CC ₆ H ₄	H	H	140°	673
C ₆ H ₅	4-C ₂ H ₅ OC ₆ H ₄	H	H	152°	1588, 1589, 1590
C ₆ H ₅	2-ClC ₆ H ₄	H	H	113°	1580
C ₆ H ₅	3-ClC ₆ H ₄	H	H	144°	1580
C ₆ H ₅	4-ClC ₆ H ₄	H	H	140°, 161°	1580, 1589
C ₆ H ₅	4-NO ₂ C ₆ H ₄	H	H	209°	340
C ₆ H ₅	4-HOOC ₆ H ₄	H	H	—	857
C ₆ H ₅	H	2-HSC ₆ H ₄	H	195°	578
C ₆ H ₅	H	2-HS-4-C ₂ H ₅ OC ₆ H ₃	H	243°	578
C ₆ H ₅	1-C ₁₀ H ₇	H	H	199°	1577
C ₆ H ₅	2-C ₁₀ H ₇	H	H	127.5°	1577
C ₆ H ₅	H	2-C ₁₀ H ₇	H	219°	1640
C ₆ H ₅	3-CH ₃ O-2-C ₁₀ H ₆	H	H	235°	1575
C ₆ H ₅	4-(4-CH ₃ COOC ₆ H ₄ O)C ₆ H ₄	H	H	128°	1585
	NNHC ₆ H ₅				
C ₆ H ₅	3-CH ₃ CC ₆ H ₄	H	H	230°	1225
C ₆ H ₅	4-CH ₃ SO ₂ C ₆ H ₄	H	H	215°	455
2-CH ₃ C ₆ H ₄	C ₆ H ₅	H	H	191°	1004, 1524
3-CH ₃ OC ₆ H ₄	C ₆ H ₅	H	H	124°	1581
4-CH ₃ OC ₆ H ₄	C ₆ H ₅	H	H	137°	1581
4-BrC ₆ H ₄	C ₆ H ₅	H	H	164°	351
3-NO ₂ C ₆ H ₄	C ₆ H ₅	H	H	174°	777, 1003
4-NO ₂ C ₆ H ₄	C ₆ H ₅	H	H	207.5°	777
2-HOOC ₆ H ₄	C ₆ H ₅	H	H	196°	1520
4-HOOC ₆ H ₄	C ₆ H ₅	H	H	—	857
2-HO ₃ SC ₆ H ₄	C ₆ H ₅	H	H	—	469, 857
3-HO ₃ SC ₆ H ₄	C ₆ H ₅	H	H	—	857
4-HO ₃ SC ₆ H ₄	C ₆ H ₅	H	H	—	857
4-H ₂ NO ₂ SC ₆ H ₄	C ₆ H ₅	H	H	236°	695

4-(4-CH ₃ CONHC ₆ H ₄)C ₆ H ₄	H	—	163
2-CH ₃ -4-HO ₃ SC ₆ H ₃	H	—	857
2-Cl-4-HO ₃ SC ₆ H ₃	H	—	857
2-Cl-5-HO ₃ SC ₆ H ₃	H	—	857
2,4-(NO ₂) ₂ C ₆ H ₃	H	160°	777
4-NO ₂ -2-HO ₃ SC ₆ H ₃	H	—	469, 857
2-NO ₂ -4-HO ₃ SC ₆ H ₃	H	—	857
2,5-(HO ₃ S) ₂ C ₆ H ₃	H	—	857
2-HO-3-HOOC-5-HO ₃ SC ₆ H ₂	H	—	857
3-CH ₃ -4-Cl-6-HO ₃ SC ₆ H ₂	H	—	857
2,5-Cl ₂ -4-HO ₃ SC ₆ H ₂	H	—	857
2,4,6-(NO ₂) ₃ C ₆ H ₂	H	223°	777
2-(4-HO-3-HOOC-5-HO ₃ SC ₆ H ₂) ₂ C ₆ H ₂	H	—	857
2-CH ₃ -4,5-(HO ₃ S) ₂ C ₆ H ₂	H	—	857
4-CH ₃ OC ₆ H ₄	H	204°	1581
4-NO ₂ C ₆ H ₄	H	203°	1580
4-NO ₂ C ₆ H ₄	H	189°	1580
4-NO ₂ C ₆ H ₄	H	200°	1580
4-NO ₂ C ₆ H ₄	H	—	857
4-NO ₂ C ₆ H ₄	H	228°	1577
4-NO ₂ C ₆ H ₄	H	235°	1577
4-NO ₂ C ₆ H ₄	H	235°	1575
3-HOOC ₆ H ₄	H	—	694
3-HOOC ₆ H ₄	H	—	694
3-HOOC ₆ H ₄	H	256°	694
3-HOOC ₆ H ₄	H	—	857
3-HOOC ₆ H ₄	H	256°	694
2-HO ₃ SC ₆ H ₄	H	—	857
3-HO ₃ SC ₆ H ₄	H	—	469
4-HO ₃ SC ₆ H ₄	H	—	857
2-Cl-5-HO ₃ SC ₆ H ₃	H	—	469, 857
2,4-(NO ₂) ₂ C ₆ H ₃	H	243°	229

(Table continued)

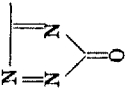
TABLE II, Section D (*continued*)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
2-HO-3-HOOC-5-HO ₂ SC ₆ H ₅	4-HO ₂ CC ₆ H ₄	H	H	—	857
1-HO ₂ 3,2-C ₁₀ H ₈	4-HO ₂ CC ₆ H ₄	H	H	—	857
C ₆ H ₅	C ₆ H ₅	CH ₃	H	204°	505
C ₆ H ₅	CH ₃	C ₆ H ₅	H	199°	1522
C ₆ H ₅	H	C ₆ H ₅	CH ₃	57°	1643
C ₆ H ₅	C ₆ H ₅	C ₂ H ₅	H	213°	505
C ₆ H ₅	C ₆ H ₅	C ₃ H ₇	H	198°	505
C ₆ H ₅	C ₃ H ₇	C ₆ H ₅	H	151°	1276
C ₆ H ₅	iso-C ₃ H ₇	C ₆ H ₅	H	192°	1640
C ₆ H ₅	C ₆ H ₅	C ₄ H ₉	H	192°	505
C ₆ H ₅	iso-C ₄ H ₉	C ₆ H ₅	H	170°	1276
C ₆ H ₅	C ₆ H ₅	C ₆ H ₁₁	H	174°	505
C ₆ H ₅	C ₆ H ₅	C ₆ H ₁₃	H	158°	505
C ₆ H ₅	C ₆ H ₅	C ₇ H ₁₅	H	134°	505
C ₆ H ₅	C ₆ H ₅	C ₈ H ₁₇	H	144°	505
C ₆ H ₅	C ₆ H ₅	C ₉ H ₁₉	H	133°	505
C ₆ H ₅	C ₆ H ₅	C ₁₀ H ₂₁	H	116°	505
C ₆ H ₅	C ₆ H ₅		H	130°	378
4-CH ₃ C ₆ H ₅	C ₆ H ₅		H	135°	378
4-NO ₂ C ₆ H ₅	C ₆ H ₅		H	203°	378

3-HOOC-4-HOC ₆ H ₃	CH ₃	2-HO ₃ S-4-(4-NO ₂ C ₆ H ₄ CONH)C ₆ H ₅	H	—	1361
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	H	204°	3, 1640
C ₆ H ₅	C ₆ H ₅	CH ₃	CH ₃	45	1343
4-Br-C ₆ H ₄	C ₆ H ₅	C ₆ H ₅ CH=		>265	351
2-HOOC-C ₆ H ₄	C ₆ H ₅	C ₆ H ₅ CH=		241°	1004
4-HO ₃ SC ₆ H ₄	4-HO ₃ SC ₆ H ₄	4-(4-HO ₃ SC ₆ H ₄ CH ₂ NH)-3-CH ₃ C ₆ H ₃ CH=		—	1371

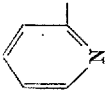
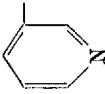
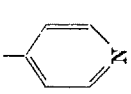
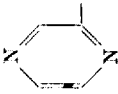
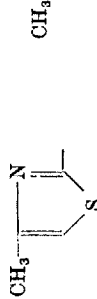
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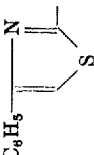
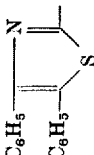
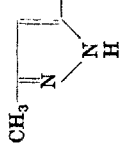
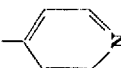
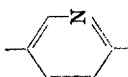
Section E. Heterocyclic, Alkyl, and Aryl Substituents

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H		H	H	223°	1498, 1499
H		H	H	205°	662
H		H	H	265°	358

(Table continued)

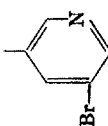
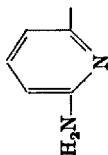
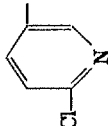
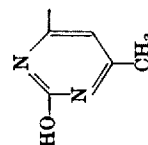
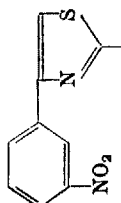
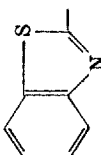
TABLE II, Section E (*continued*)

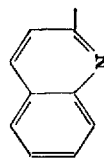
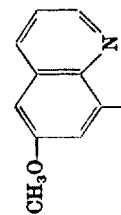
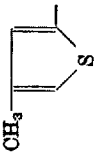
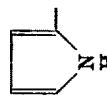
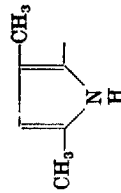
R ¹	R ²	R ³	R ⁴	M.p.	Reference
H		H	H	219°	308
H		H	H	268°	307
H		H	H	286°	1659
H		H	H	245°	437
		H	H	180°	1296
		H	H	190°	94

	CH ₃	H	H	196°	94
	CH ₃	H	H	198°	94
	CH ₃	CH ₃	H	260°	1347
	CH ₃	H	H	110°	438
	CH ₃	H	H	198°	833
	CH ₃	H	H	128°	1687

(Table continued)

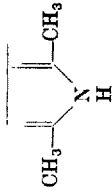
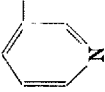
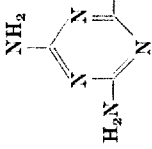
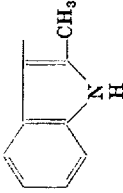
TABLE II, Section E (*continued*)

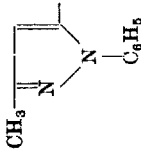
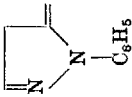
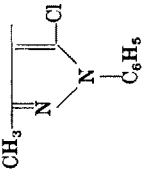
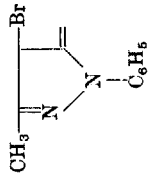
R ¹	R ²	R ³	R ⁴	M.P.	Reference
	CH ₃	H	H	191°	1687
	CH ₃	H	H	188°	91
	CH ₃	H	H	175°	1120
	CH ₃	H	H	205°	1570
	CH ₃	H	H	235°	421
	CH ₃	H	H	231°	74, 413

	CH_3	H	H	140°	438
	CH_3	H	H	135°	1053
	C_6H_5	H	H	178°	912, 1215, 1499
	C_6H_5	H	H	137°	662, 909
	C_6H_5	H	H	136°	662
	C_6H_5	H	H	193°	1067
	C_6H_5	H	H	141°	682

(Table continued)

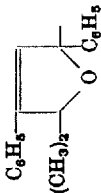
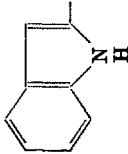
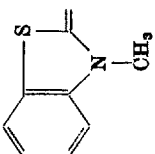
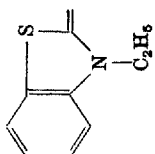
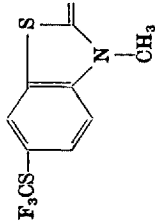
TABLE II, Section E (*continued*)

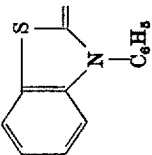
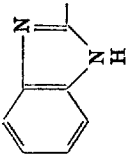
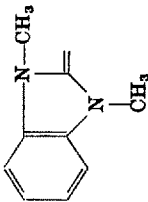
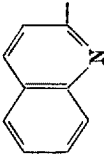
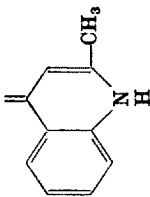
R ¹	R ²	R ³	R ⁴	M.P.	Reference
C ₆ H ₅		H	H	225°	1068
C ₆ H ₅		H	H	188°	307
C ₆ H ₅		H	H	261°	1492
C ₆ H ₅		H	H	258°	10
4-BrC ₆ H ₄		H	H	160°	1499
3-NO ₂ C ₆ H ₄		H	H	174°	1499

4-HO ₃ SC ₆ H ₄		H	H	> 295°	1499
H		CH ₃	CH ₃	118°	662
C ₆ H ₅	CH ₃		H	260°	1347
C ₆ H ₅	CH ₃			258°	323, 688
C ₆ H ₅	CH ₃		H	240°	991
C ₆ H ₅	CH ₃			214°	323

(Table continued)

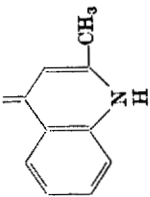
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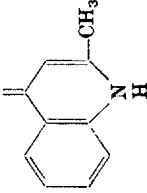
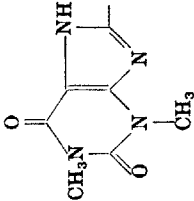
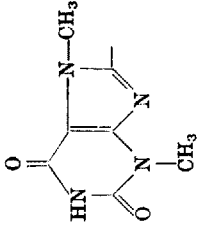
R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃		H	137°	1530
C ₆ H ₅	CH ₃		H	238°	559
C ₆ H ₅	CH ₃			177°	1072
C ₆ H ₅	CH ₃			143°	1072
C ₆ H ₅	CH ₃			175°	1658

C_6H_5	CH_3		280°	1072
C_6H_5	CH_3		172°	558
C_6H_5	CH_3		153°	1195
C_6H_5	CH_3		159°	796
C_6H_5	CH_3		320°	971
C_6H_5		$C_6H_5CH=$	210°	1499

(Table continued)

TABLE II, Section E (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
4-CH ₃ C ₆ H ₄	CH ₃			302°	971
4-C ₂ H ₅ OC ₆ H ₄	CH ₃		H	—	378
4-NH ₂ C ₆ H ₄	CH ₃		H	—	378
4-CH ₃ CONHC ₆ H ₄	CH ₃		H	244°	378
4-BrC ₆ H ₅	CH ₃		H	—	378
4-NO ₂ C ₆ H ₄	CH ₃		H	—	378

4-HU ₃ NC ₆ H ₄	C ₁₁ H ₃		H	—	310°
C ₆ H ₅	C ₆ H ₅		H	136°	378
C ₆ H ₅	C ₆ H ₅			207°	971
4-CH ₃ C ₆ H ₄	C ₆ H ₅		H	203°	378
	CH ₃	H	H	310°	1147
	CH ₃	H	H	267°	1147

(Table continued)

TABLE II, Section E (continued)

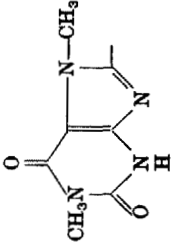
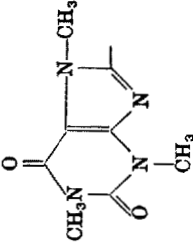
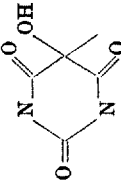
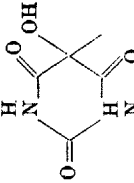
R ¹	R ²	R ³	R ⁴	M.p.	Reference
	CH ₃	H	H	292°	1147
	CH ₃	H	H	216°	1147

TABLE II (continued)

Section F. α -Hydroxy- and α -Alkoxyalkyl, Alkyl, Aryl, Aromatic, and Heterocyclic Substituents

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	C ₂ H ₅ OCH ₂	H	H	148°	1315
H	C ₂ H ₅ OCH ₂	H	CH ₃	135°	1314
H	C ₂ H ₅ OCH ₂	H	C ₂ H ₅	99°	1314

H	$C_2H_5OCH_2$	H		$C_6H_5CH_2$	—	1315
H	C_6H_5			H	254°	1194
C_6H_5 4- $NO_2C_6H_5$	$C_2H_5OCH_2$			H	82°	1316
C_6H_5	$HOCH_2$	H		H	—	532
C_6H_5	CH_3	$HOCH_2$		H	158°	24
C_6H_5	CH_3	Cl_3CCH		H	189°	895
CH_3	C_6H_5	OH				
		Cl_3CCH		H	184°	1190
		OH				
4- $CH_3C_6H_4$	CH_3	Cl_3CCH		H	191°	107
C_6H_5	CH_3	OH				
C_6H_5	CH_3	$C_2H_5OC=$ CH_3			129°	764
C_6H_5	CH_3	$C_2H_5OC=$ C_2H_5			120°	764
C_6H_5	CH_3	$C_2H_5OC=$ C_2H_5			130°	764
C_6H_5	CH_3	$C_2H_5OC=$ C_6H_5				
C_6H_5	CH_3			H	196°, 243°	1194, 1253

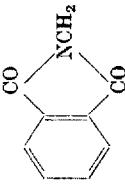
(Table continued)

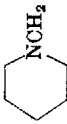
TABLE II, Section F (continued)

R ¹	R ²	R ³	R ⁴	M.P.	Reference
C ₆ H ₅		C ₂ H ₅ OC(=CH ₃)		90°	764
C ₆ H ₅	C ₆ H ₅ OCH ₂	C ₆ H ₅	H	145°	1562
C ₆ H ₅	C ₆ H ₅ OCH ₂	4-ClC ₆ H ₅	H	166°	1562

TABLE II (continued)

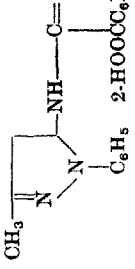
Section G. α -Amino- and α -Iminoalkyl Alkyl, and Aryl Substituents

R ¹	R ²	R ³	R ⁴	M.P.	Reference
H	CH ₃	CH ₃ C(=NH)	H	280°	1193
H	CH ₃	C ₆ H ₅ C(=NH)	H	> 300°	1193
H	CH ₃	C ₆ H ₅ C(=NH)	H	230°	1193
C ₆ H ₅	2-HOOCCH ₂ CH ₂ CONHCH ₂	CH ₃ C(=NNHC ₆ H ₅)	H	164°	138
C ₆ H ₅		H	H	192°	138

H	C ₆ H ₅	HN=CH	H	283°	1188, 1189
H	C ₆ H ₅	C ₆ H ₅ N=CH	H	263°	1188
H	C ₆ H ₅	4-C ₂ H ₅ OC ₆ H ₄ N=CH	H	240°	1188
H	C ₆ H ₅	NH ₂ CONHNHCH COOCH ₃	H	172°	1179
H	C ₆ H ₅	NH ₂ CONHNHCH COOC ₂ H ₅	H	171°	1179
C ₆ H ₅	CH ₃	ONCH ₃	H	170°	925
C ₆ H ₅	CH ₃	HN=CH	H	155°	1189
CH ₃	C ₆ H ₅	HN=CH	H	210°	1189
C ₆ H ₅	CH ₃	(CH ₃) ₂ NCH ₂	H	221°	1098
C ₆ H ₅	CH ₃	(C ₂ H ₅) ₂ NCH ₂	H	221°	1098
C ₆ H ₅	CH ₃		H	224°	1098
C ₆ H ₅	CH ₃	CH ₃ C NH	H	172°	1192, 1193
C ₆ H ₅	CH ₃	C ₂ H ₅ C NH	H	68°	1193
C ₆ H ₅	CH ₃	C ₃ H ₇ C NH	H	137°	1193
C ₆ H ₅	CH ₃	H ₂ NN=CH	H	201°	1206
C ₆ H ₅	CH ₃	C ₆ H ₅ N=CH	H	184°	348, 823, 824, 923, 1070, 1088, 1089, 1090
CH ₃	C ₆ H ₅	C ₆ H ₅ N=CH	H	110°	1189

(Table continued)

TABLE II, Section G (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	C ₆ H ₅ N=C CH ₃	H	183°	947, 1192
C ₆ H ₅	CH ₃	2,4,5-(CH ₃) ₃ C ₆ H ₄ N=CH	H	162°	348
C ₆ H ₅	CH ₃	3,4-(NH ₂) ₂ C ₆ H ₃ N=CH	H	173°	351
C ₆ H ₅	CH ₃	2-C ₂ H ₅ OC ₆ H ₄ N=CH	H	170°	351
C ₆ H ₅	CH ₃	4-C ₃ H ₇ OC ₆ H ₄ N=CH	H	144°	1092
C ₆ H ₅	CH ₃	2-NH ₂ C ₆ H ₄ N=CH	H	—	1190
C ₆ H ₅	CH ₃	4-BrC ₆ H ₄ N=CH	H	164°	348
C ₆ H ₅	CH ₃	3-NO ₂ C ₆ H ₄ N=CH	H	175°	351
C ₆ H ₅	CH ₃	4-NO ₂ C ₆ H ₄ N=CH	H	170°	351
C ₆ H ₅	CH ₃	4-C ₆ H ₅ CH ₂ OC ₆ H ₄ N=CH	H	181°	350
C ₆ H ₅	CH ₃	4-C ₆ H ₅ N=NC ₆ H ₄ N=CH	H	203°	923
C ₆ H ₅	CH ₃	1-C ₁₀ H ₇ N=CH	H	122°	348
C ₆ H ₅	CH ₃	2-C ₁₀ H ₇ N=CH	H	171°	348
C ₆ H ₅	CH ₃	C ₆ H ₅ NHC=	H	161°	947
		C ₆ H ₅			
C ₆ H ₅	CH ₃			242°	1202
		C ₆ H ₅ 2-HOOC-C ₆ H ₄			
C ₆ H ₅	CH ₃	C ₆ H ₅ NHN=C	H	197°, 210°	559, 1192
		CH ₃			
C ₆ H ₅	CH ₃	C ₆ H ₅ NHN=C	H	168°	1193
		CH ₃			
C ₆ H ₅	CH ₃	C ₆ H ₅ NHN=C	H	185°	1193
		C ₂ H ₅			
		C ₃ H ₇			

C_6H_5	CH_3	$C_6H_5NHN=C$ C_6H_5	H	204°	1193
C_6H_5	CH_3	$C_6H_5NHN=C$ $COOC_2H_5$	H	182°	1641
C_6H_5	CH_3	$C_6H_5NHN=C$ COOH	H	205°	1641
C_6H_5	CH_3	$4-BrC_6H_4NHN=C$ $COOC_2H_5$	H	213°	1641
C_6H_5	CH_3	$(C_6H_5)_2NNHC=$ $COOC_2H_5$		137°	1641
$2-CH_3C_6H_4$	CH_3	$C_6H_5N=CH$	H	140°	351
$2-CH_3C_6H_4$	CH_3	$3-CH_3C_6H_4N=CH$	H	232°	351
$2-CH_3C_6H_4$	CH_3	$4-C_2H_5OC_6H_4N=CH$	H	160°	351
$4-CH_3C_6H_4$	CH_3	$3-CH_3C_6H_4N=CH$	H	122°	351
$4-CH_3C_6H_4$	CH_3	$2,5-(CH_3)_2C_6H_3N=CH$	H	249°	349
$4-CH_3C_6H_4$	CH_3	$2-C_2H_5OC_6H_4N=CH$	H	133°	351
$4-CH_3C_6H_4$	CH_3	$4-BrC_6H_4N=CH$	H	196°	351
$4-CH_3C_6H_4$	CH_3	$C_6H_5NHN=C$ COOH	H	217°	1641
$4-CH_3C_6H_4$	CH_3	$C_6H_5NHN=C$ $COOC_2H_5$	H	195°	1641
$4-CH_3C_6H_4$	CH_3	$C_6H_5NHNHC=$ $COOC_2H_5$		209°	1641
$4-C_2H_5OC_6H_4$	CH_3	$HON=CH$	H	182°	1186
$4-C_2H_5OC_6H_4$	CH_3	$C_6H_5N=CH$	H	155°	902

(Table continued)

TABLE II, Section G (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	4-C ₂ H ₅ OC ₆ H ₄ N=CH	H	132°	1186
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	CH ₃ C(=NH)	H	235°	1193
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	C ₆ H ₅ C(=NH)	H	177°	1193
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	2-NH ₂ C ₆ H ₄ N=CH	H	190°	1190
C ₆ H ₅	C ₆ H ₅	NH ₂ C(=NH) H		175°	1189
C ₆ H ₅	C ₆ H ₅	HON=CH	H	254°	902
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ N=CH	H	195°, 140°	348, 902
C ₆ H ₅	C ₆ H ₅	2-CH ₃ C ₆ H ₄ N=CH	H	146°	348
C ₆ H ₅	C ₆ H ₅	2-NH ₂ C ₆ H ₄ N=CH	H	215°	1190
C ₆ H ₅	C ₆ H ₅	4-BrC ₆ H ₄ N=CH	H	184°	600
C ₆ H ₅	C ₆ H ₅	2-C ₁₀ H ₇ N=CH	H	192°	348
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ NHN=C	H	208°	1641
		 COOC ₂ H ₅			
2-CH ₃ C ₆ H ₄	C ₆ H ₅	C ₆ H ₅ N=CH	H	169°	351
2-CH ₃ C ₆ H ₄	C ₆ H ₅	2,4-(CH ₃) ₂ C ₆ H ₃ N=CH	H	142°	351
2-CH ₃ C ₆ H ₄	C ₆ H ₅	4-ClC ₆ H ₄ N=CH	H	181°	351
2-CH ₃ C ₆ H ₄	C ₆ H ₅	3-BrC ₆ H ₄ N=CH	H	148°	351
2-CH ₃ C ₆ H ₄	C ₆ H ₅	4-BrC ₆ H ₄ N=CH	H	142°	351
4-BrC ₆ H ₄	C ₆ H ₅	C ₆ H ₅ N=CH	H	188°	351
C ₆ H ₅	C ₆ H ₅	CH ₃	CH ₃	77°	512
		 C ₂ H ₅			

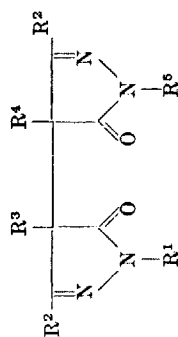


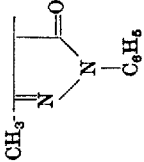
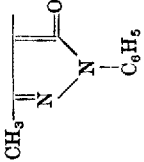
TABLE III. 4,4'-Bis(2-pyrazolin-5-ones) Linked by a Single Bond

R ¹	R ²	R ³	R ⁴	R ⁵	M.p.	Reference
H	H	H	H	H	> 360°	725
CH ₃	H	H	H	H	> 360°	725
H	CH ₃	H	H	H	—	1485
CH ₃	H	H	H	CH ₃	> 375°	72, 725
HO ₃ SCH ₂ CH ₂	CH ₃	H	H	HO ₃ SCH ₂ CH ₂	—	72
C ₆ H ₅	CH ₃	H	H	C ₆ H ₅	dec. without melting, 290°, 320°	114, 807, 809, 815, 885, 925, 1090, 1091, 1096, 1185, 1192, 1513, 1522, 1538, 1612
C ₆ H ₅	4-C ₄ H ₉	H	H	C ₆ H ₅	> 290°	1582
C ₆ H ₅	C ₁₀ H ₃₁	H	H	C ₆ H ₅	238°	636
C ₆ H ₅	C ₁₇ H ₃₅	H	H	C ₆ H ₅	—	72
C ₆ H ₅	H ₅ C ₂ OOCCH ₂	H	H	C ₆ H ₅	—	72
4-CH ₃ C ₆ H ₄	CH ₃	H	H	4-CH ₃ C ₆ H ₄	—	72
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	H	H	4-C ₂ H ₅ OC ₆ H ₄	—	72
4-ClC ₆ H ₄	CH ₃	H	H	4-ClC ₆ H ₄	—	72
4-NO ₂ C ₆ H ₄	CH ₃	H	H	4-NO ₂ C ₆ H ₄	dec.	296
3-HOOCCH ₂ H ₄	C ₁₇ H ₃₅	H	H	3-HOOCCH ₂ H ₄	255° (dec.)	690
4-HO ₃ SC ₆ H ₄	CH ₃	H	H	4-HO ₃ SC ₆ H ₄	—	72
4-HO ₃ SC ₆ H ₄	C ₁₇ H ₃₅	H	H	4-HO ₃ SC ₆ H ₄	—	72

(Table continued)

TABLE III (continued)

R ¹	R ²	R ³	R ⁴	R ⁵	M.p.	Reference
2-C ₁₀ H ₇	4-ClC ₃ H ₄ NHCOCH ₃	H	H	2-C ₁₀ H ₇	—	72
4-HO ₃ S-1-C ₁₀ H ₆	CH ₃	H	H	4-HO ₃ S-1-C ₁₀ H ₆	—	72
C ₆ H ₅ CH ₂	CH ₃	H	H	C ₆ H ₅ CH ₂	> 280°	333
C ₆ H ₅	C ₆ H ₅	H	H	C ₆ H ₅	> 330°	72, 129, 818, 1022
C ₆ H ₅	4-CH ₃ OC ₆ H ₄	H	H	C ₆ H ₅	—	129
C ₆ H ₅	CH ₃	CH ₃	CH ₃	C ₆ H ₅	166°	729, 809, 1299, 1528, 1606, 1611
C ₆ H ₅	CH ₃	C ₂ H ₅	C ₂ H ₅	C ₆ H ₅	149°, 161°	809, 1526, 1528, 1645
1-C ₁₀ H ₇	CH ₃	C ₆ H ₅ CH ₂	C ₆ H ₅ CH ₂	1-C ₁₀ H ₇	215°	849
C ₆ H ₅	CH ₃	C ₂ H ₅	H	C ₆ H ₅	161°	1522
C ₆ H ₅	CH ₃	NCHC—	H	C ₆ H ₅	116°	1613
		COOC ₂ H ₅				
C ₆ H ₅	CH ₃	NCHC—	H	C ₆ H ₅	160° (dec.)	1613
		COOH				
C ₆ H ₅	CH ₃	HOOCCH ₂	H	C ₆ H ₅	213° (dec.)	1613
C ₆ H ₅	CH ₃	NCOCH ₂	H	C ₆ H ₅	160°	1613
C ₆ H ₅	CH ₃	H ₅ C ₂ OOCCH	H	C ₆ H ₅	106°	1613
		COCH ₃				
C ₆ H ₅	CH ₃	(CN) ₂ CH	H	C ₆ H ₅	230° (dec.)	1614
C ₆ H ₅	CH ₃	NCH	H	C ₆ H ₅	—	1614
		CONH ₂				
C ₆ H ₅	CH ₃	C ₂ H ₅ O	H	C ₆ H ₅	94° (dec.)	1609
C ₆ H ₅	CH ₃	CH ₃ O	H	C ₆ H ₅	—	1609
C ₆ H ₅	CH ₃	C ₃ H ₇ O	H	C ₆ H ₅	—	1609
C ₆ H ₅	CH ₃	NC	H	C ₆ H ₅	—	1612
H ₂ NOC	CH ₃	H	H	H ₂ NOC	128°	73, 357
H ₂ NSC	CH ₃	H	H	H ₂ NSC	197°	73, 357
H ₂ NSC	C ₁₇ H ₃₅	H	H	H ₂ NSC	—	73

∞	$\text{H}_5\text{C}_6\text{HNHC}$	CH_3	H	$\text{H}_5\text{C}_6\text{HNHC}$	191°	357
$+$	$4\text{-CH}_3\text{C}_6\text{H}_4\text{NHSC}$	CH_3	H	$4\text{-CH}_3\text{C}_6\text{H}_4\text{NHSC}$	201°	357
C_2H_5	$\text{C}_2\text{H}_5\text{NHSC}$	CH_3	H	$\text{C}_2\text{H}_5\text{NHSC}$	191°	357
C_6H_5	$\text{H}_5\text{C}_2\text{OOC}$	$\text{H}_5\text{C}_2\text{OOC}$	H	C_6H_5	272°	$1082, 1229$
20	C_6H_5	CH_3	H	C_6H_5	$262^\circ, 200^\circ (\text{dec.})$	$688, 1607, 1609$
						
	C_6H_5	CH_3	H	$4\text{-BrC}_6\text{H}_4$	$200^\circ (\text{dec.})$	1607
						

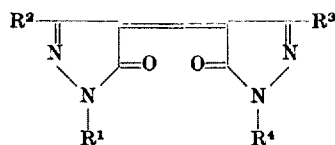


TABLE IV. 4,4'-Bis(2-pyrazolin-5-ones) Linked by a Double Bond

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	C ₆ H ₅	C ₆ H ₅	H	—	1560
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅	230°	323, 807, 809, 816, 1090, 1091
3-ClC ₆ H ₄	CH ₃	CH ₃	3-ClC ₆ H ₄	—	296
4-ClC ₆ H ₄	CH ₃	CH ₃	4-ClC ₆ H ₄	300°	296
C ₆ H ₅	CH ₃	CH ₃	4-BrC ₆ H ₄	219°	1607, 1608
C ₆ H ₅ CH ₂	CH ₃	CH ₃	C ₆ H ₅ CH ₂	142°	333

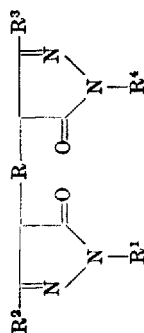


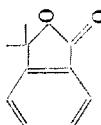
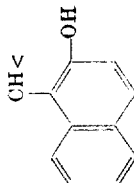
TABLE V. 4,4'-Bis(2-pyrazolin-5-ones) Linked by a Carbon Chain

Section A. 1,1'-Phenyl-3,3'-methyl Substituents

R	M.p.	Reference
—CH=	185°	93, 117, 365, 611, 675, 825, 926, 1070, 1088, 1089, 1093, 1185, 1187, 1188, 1189, 1190, 1193, 1262, 1669, 1682
—CH₂— CH₃COCH₃	220°	22, 24, 117, 300, 1262
—CH₂CH₂— —CH=CHCH=CHCH=	138°	809
—CH₂CH₂— —CH=CHCH=CHCH=	—	451
—CH₂CH₂— —CH=CHCH=CHCH=	205°	1070
CH₂C— O CH₂C=O	184°	297
C₆H₅CH< 4-CH₃C₆H₄CH<	174° 166° (0.5 C₂H₅OH)	686, 977, 1135 1094

(Table continued)

TABLE V, Section A (continued)

R	M.p.	Reference
2-HOC ₆ H ₄ CH<	228°	93, 1135
3-HOC ₆ H ₄ CH<	181°	1135
4-HOC ₆ H ₄ CH<	162°	1135
4-CH ₃ OC ₆ H ₄ CH<	175°	1094, 1255
2-ClC ₆ H ₄ CH<	231°	1135
3-ClC ₆ H ₄ CH<	149°	1135
4-ClC ₆ H ₄ CH<	208°	1135
2-NO ₂ C ₆ H ₄ CH<	146° (dec.), 203°	633, 1135
3-NO ₂ C ₆ H ₄ CH<	150° (dec.), 227°	376, 633, 1134
	(164° enol)	
4-NO ₂ C ₆ H ₄ CH<	226°	110
2-HOOC ₆ H ₄ CH<	208°	1279
2-CH ₃ OOC ₆ H ₄ CH<	178°	1279
2-C ₂ H ₅ OOCCH ₂ OC ₆ H ₄ CH<	204°	832
4-HO-3-CH ₃ OC ₆ H ₄ CH<	191°	22
3,4-(CH ₃ O) ₂ C ₆ H ₃ CH<	122°	22
2,4,6-(CH ₃ O) ₃ C ₆ H ₂ CH<	204°	1036
3-CH ₃ O-4-HO-5-HO ₃ SC ₆ H ₂ CH<	—	22
	220°	1224
	212°	297
	118-140°	93

<chem>COc1ccc2cc(C=O)ccc2c1</chem>	195°	1036
<chem>CCOC(=O)C(=O)OCC</chem>	163°	1109
<chem>COC(=O)C(=O)OC</chem>	193°	1109
<chem>O=C(O)C(=O)O</chem>	237°	1109
<chem>CCOC(=O)C(=O)O</chem>	208°	1109
<chem>CC1=CN(C(=O)O)C=C1</chem>	175°	187
<chem>CC1=CC(=C(C=C1)C(=O)O)C(=O)O</chem>	—	187

(Table continued)

TABLE V, Section A (continued)

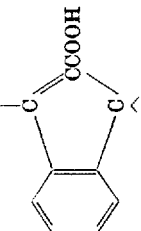
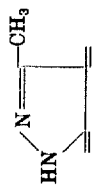
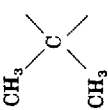
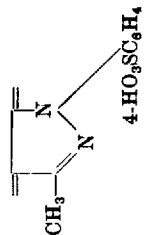
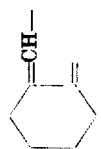
R	M.p.	Reference
	—	187

TABLE V (continued)

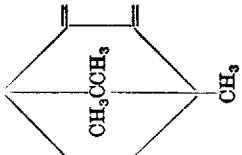
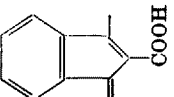
Section B. Alkyl and Aryl Substituents

R	R ¹	R ²	R ³	R ⁴	M.p.	Reference
—CH=	H	CH ₃	CH ₃	H	130–140° 315° (dec.)	93, 923, 925, 1262
—CH ₂ —	H	CH ₃	CH ₃	H	326°	1154
CH ₃ CH<	H	CH ₃	CH ₃	H	253°	514
—CH ₂ CH ₂ —	H	CH ₃	CH ₃	H	250°	1154
HOOCCH ₂ CH<	C ₆ H ₅	H	H	C ₆ H ₅	—	1351
H ₅ C ₂ OOCH ₂ CH<	C ₆ H ₅	H	H	C ₆ H ₅	173°	1351

	H	CH ₃	CH ₃	H	—	703
—CH=	H	C ₆ H ₅	C ₆ H ₅	H	> 300°	1188, 1189
C ₆ H ₅ CH<	H	C ₆ H ₅	C ₆ H ₅	H	280° (dec.)	1154, 1188
—CH=	H	C ₆ H ₅	C ₆ H ₅	H	—	1154
—CH=	2-CH ₃ C ₆ H ₄	CH ₃	CH ₃	2-CH ₃ C ₆ H ₄	190°	351
—CH=	4-CH ₃ C ₆ H ₄	CH ₃	CH ₃	4-CH ₃ C ₆ H ₄	249°	351
—CH ₂ —	4-C ₂ H ₅ OC ₆ H ₄	CH ₃	CH ₃	4-C ₂ H ₅ OC ₆ H ₄	202°	1186
CH ₃ —	4-C ₂ H ₅ OC ₆ H ₄	CH ₃	CH ₃	4-C ₂ H ₅ OC ₆ H ₄	202°	1097
	4-FC ₆ H ₄	CH ₃	CH ₃	4-FC ₆ H ₄	141°	1263
2-NO ₂ C ₆ H ₄ CH<	2-ClC ₆ H ₄	CH ₃	CH ₃	2-ClC ₆ H ₄	249°	1494
	C ₆ H ₅	CH ₃	CH ₃	4-HO ₃ SC ₆ H ₄	—	187
	C ₆ H ₅	CH ₃	CH ₃	4-HO ₃ SC ₆ H ₄	—	187
	4-HO ₃ SC ₆ H ₄	CH ₃	CH ₃	4-HO ₃ SC ₆ H ₄	—	187

(Table continued)

TABLE V, Section B (continued)

R	R ¹	R ²	R ³	R ⁴	M.p.	Reference
	4-HO ₃ SC ₆ H ₄	CH ₃	CH ₃	4-HO ₃ SC ₆ H ₄	—	187
	4-HO ₃ SC ₆ H ₄	CH ₃	CH ₃	4-HO ₃ SC ₆ H ₄	—	187, 703
—CH=	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	249°	93, 923, 925, 1185, 1188, 1189, 1262
—CH ₂ CH ₂ —	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	—	1189
	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	220°	818
—CH=	2-CH ₃ C ₆ H ₄	C ₆ H ₅	C ₆ H ₅	2-CH ₃ C ₆ H ₄	179°	351
—CH=	4-BrC ₆ H ₄	C ₆ H ₅	C ₆ H ₅	4-BrC ₆ H ₄	> 265°	351
	4-BrC ₆ H ₄	C ₆ H ₅	C ₆ H ₅	4-BrC ₆ H ₄	290° (dec.)	1154
—CH=	C ₆ H ₅	COOH	COOH	C ₆ H ₅	248° (dec.)	1262

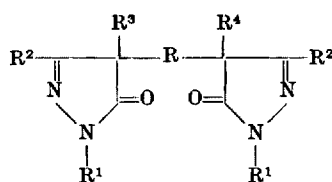


TABLE VI. Miscellaneous 4,4'-Bis(2-pyrazolin-5-ones)

R	R ¹	R ²	R ³	R ⁴	M.p.	Reference
$\begin{array}{c} \text{—CH=} \\ \text{OC}_2\text{H}_5 \quad \text{OC}_2\text{H}_5 \\ \quad \quad \\ \text{—C—} \quad \quad \text{C—} \\ \quad \quad \\ \text{Br} \quad \quad \text{Br} \end{array}$	C ₆ H ₅	CH ₃	Br		138°	1682
$\begin{array}{c} \text{—C—} \quad \quad \text{C—} \\ \quad \quad \\ \text{Br} \quad \quad \text{Br} \end{array}$	C ₆ H ₅	CH ₃	Br	Br	80°	1109
CH ₃ CH<	H	CH ₃	CH ₃ CH— OH	H	267°	513
3-NO ₂ C ₆ H ₄ CH<	C ₆ H ₅	CH ₃	CH ₃	CH ₃	178°	1134
C ₆ H ₅ CH<	H	CH ₃	CH ₃	CH ₃	129°	1560

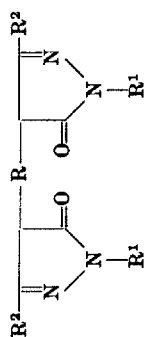
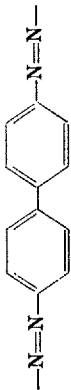
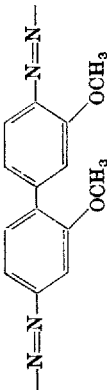
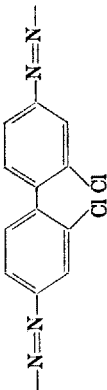
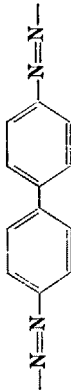


TABLE VII. 4,4'-Bis(2-pyrazolin-5-ones) Linked by Chains Containing N and S

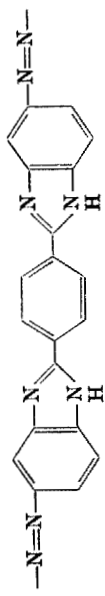
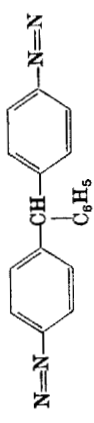
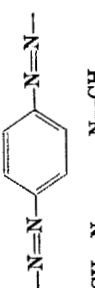
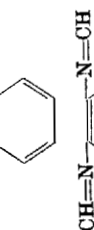
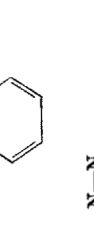
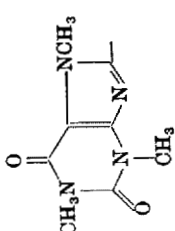
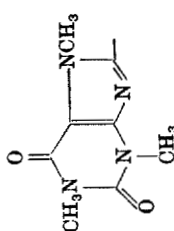
R ¹	R ²	R	M.p.	Reference
C ₆ H ₅	CH ₃	S	181°	579, 580
C ₆ H ₅	H		257°	578
C ₆ H ₅	H		270°	578
C ₆ H ₅	CH ₃		281°	578
H	CH ₃	=N—	238° (dec.)	262
H	CH ₃	—NH—	247° (dec.)	480
H	C ₂ H ₅	=N—	(HCl)	1576
H	C ₃ H ₇	=N—	235° (dec.)	1576
C ₆ H ₅ CH ₂	CH ₃	=N—	260° (dec.)	1576
C ₆ H ₅ CH ₂ CH ₂	CH ₃	=N—	160°	333
H	C ₆ H ₅	=N—	95°	1566
		=N—	124°	1552, 1576
			267° (dec.)	

C_6H_5	---N---	181°	327, 611, 809
C_6H_5	---N---	199°	397
$C_6H_5CH_2CH_2$	---N---	165°	1567
$4\text{-Br}C_6H_4$	---N---	305°	1642
C_6H_5	---N---	251°	1022, 1552
C_6H_5	---N---	222°	670
2-HOC_6H_4	---N=N---	184°, 260°	995, 1564
C_6H_5	---N=N---	> 200°	593
$3\text{-HO}_3SC_6H_4$	---N=N---	> 250°	593
$4\text{-HO}_3SC_6H_4$	---N=N---	—	1062
$4\text{-NaO}_3SC_6H_4$	---N=N---	104°	1111
C_6H_5	$CONH(CH_2CH_2)_3NHCO$	—	782
C_6H_5		—	782
C_6H_5		—	782
C_6H_5		—	782
C_6H_5		—	782
C_6H_5		98°	327

(Table continued)

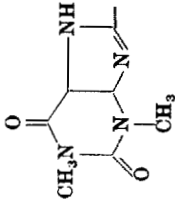
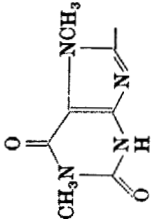
TABLE VII (continued)

R ¹	R ²	R	M.p.	Reference
C ₆ H ₅	CH ₃		—	1359
3-NO ₂ C ₆ H ₄	CH ₃		—	1359
3-H ₂ NO ₂ SC ₆ H ₄	CH ₃		—	1359
3-HOOC-4-HOC ₆ H ₃	CH ₃		—	1359
C ₆ H ₅	CH ₃		—	1245
C ₆ H ₅	C ₆ H ₅		> 270°	259
3-NH ₂ C ₆ H ₄	HOOC		—	727

2-Cl-4-HO ₃ SC ₆ H ₃	HOOC		—	727
2,5-Cl ₂ -4-HO ₃ SOCH ₂ CH ₂ O ₂ SC ₆ H ₄	CH ₃		—	651
C ₆ H ₅	H ₅ C ₂ OOC		250°	767
C ₆ H ₅	CH ₃		260°	1190
C ₆ H ₅	C ₆ H ₅		221°	1190
	CH ₃	—N=N—	298° (dec., Na salt)	1147
	CH ₃	—NHNH—	272° (dec.)	1147

(Table continued)

TABLE VII (continued)

R ¹	R ²	R	M.p.	Reference
	CH ₃	—NHNH—	224°	1147
	CH ₃	—NHNH—	330° (dec.)	1147

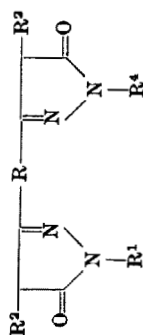


TABLE VIII. 3,3'-Bis(2-pyrazolin-5-ones)

R	R ¹	R ²	R ³	R ⁴	M.p.	Reference
	H	H	H	H	b ₇₆₀ 1549 203°	

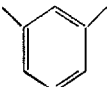
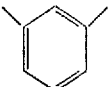
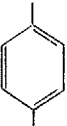
$\text{C}_6\text{H}_5\text{NHN}=\text{C} \begin{array}{l} \diagup \text{H} \\ \diagdown \end{array}$	H	H	H	113°	1549
	C_6H_5	H	H	263°	1225
	$4\text{-HO}_3\text{SC}_6\text{H}_4$	H	H	—	462
	$2\text{-HO}_3\text{S-4-NO}_2\text{C}_6\text{H}_3$	H	H	—	462
$\begin{array}{l} \text{—CH}_2\text{CH}_2\text{—} \\ \text{—CH}_2\text{CH}_2\text{—} \end{array}$	$\begin{array}{l} \text{C}_6\text{H}_5 \\ \text{H}_2\text{NOC} \end{array}$	$\begin{array}{l} \text{H}_5\text{C}_2\text{OOC} \\ \text{H}_5\text{C}_2\text{OOC} \end{array}$	$\begin{array}{l} \text{H}_5\text{C}_2\text{OOC} \\ \text{H}_5\text{C}_2\text{OOC} \end{array}$	$\begin{array}{l} 188^\circ \\ 207^\circ \end{array}$	$\begin{array}{l} 1222 \\ 1222 \end{array}$
$\begin{array}{l} \text{—CH}_2\text{CH}_2\text{—} \\ \text{—HC=CH—} \end{array}$	$\begin{array}{l} \text{H}_2\text{NOC} \\ \text{C}_6\text{H}_5 \end{array}$	$\begin{array}{l} \text{H}_2\text{NCONHNHCOCH}_2\text{CH}_2 \\ \text{C}_6\text{H}_5\text{NHNH} \end{array}$	$\begin{array}{l} \text{H}_2\text{NCONHNHCOCH}_2\text{CH}_2 \\ \text{C}_6\text{H}_5\text{NHNH} \end{array}$	$\begin{array}{l} \text{—} \\ 291^\circ \end{array}$	$\begin{array}{l} 1222 \\ 419 \end{array}$
$\begin{array}{l} \text{—NH—} \\ \text{C}_2\text{H}_5 \\ \\ \text{—N—} \end{array}$	C_6H_5	H	H	$\begin{array}{l} \text{—} \\ 290^\circ \end{array}$	$\begin{array}{l} 595, 596 \\ 595, 596 \end{array}$
$\begin{array}{l} \text{C}_4\text{H}_9 \\ \\ \text{—N—} \end{array}$	C_6H_5	H	H	265°	595, 596
$\begin{array}{l} \text{C}_4\text{H}_9 \\ \\ \text{—N—} \end{array}$	C_6H_5	H	H	223°	595, 596
$\begin{array}{l} \text{C}_6\text{H}_{11} \\ \\ \text{—N—} \end{array}$	C_6H_5	H	H	227°	595, 596

Table continued)

TABLE VIII (continued)

R	R ¹	R ²	R ³	R ⁴	M.p.	Reference
$\begin{array}{c} \text{CH}_2\text{C}_6\text{H}_5 \\ \\ -\text{N}- \end{array}$	C_6H_5	H	H	C_6H_5	245°	595, 596
$\begin{array}{c} \text{H} \\ \\ -\text{N}- \end{array}$	$4-(4\text{-C}_1\text{H}_9\text{C}_8\text{H}_4\text{O})\text{C}_6\text{H}_4$	H	H	$4-(4\text{-C}_4\text{H}_9\text{C}_8\text{H}_4\text{O})\text{C}_6\text{H}_4$	260°	595, 596
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{N}- \end{array}$	$4\text{-HO}_3\text{SC}_6\text{H}_4$	H	H	C_6H_5	—	705

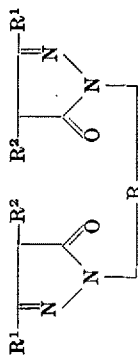
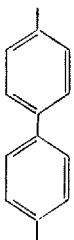
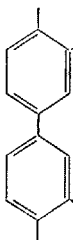
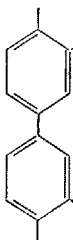
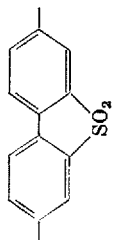
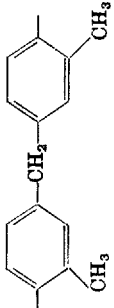
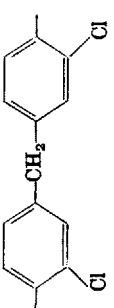
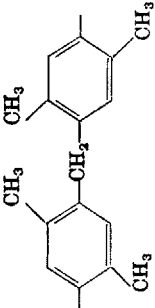


TABLE IX. 1,1'-Bis(2-pyrazolin-5-ones)

R	R ¹	R ²	M.p.	Reference
	H	H	—	656
	CH_3	H	183°	1037, 1632

1,3-C ₆ H ₄ 1,4-C ₆ H ₄		CH ₃ CH ₃	H H	185° —	116 116
		CH ₃	H	—	386, 849
		CH ₃	H	—	386
		CH ₃	H	—	711
		CH ₃	H	—	544
		CH ₃	H	—	544
		CH ₃	H	—	544

(Table continued)

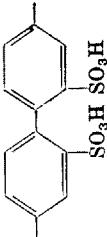
TABLE IX (continued)

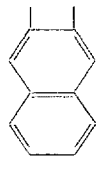
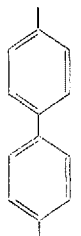
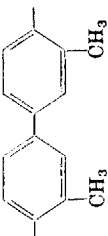
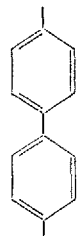
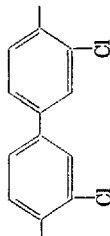
R	R ¹	R ²	M.p.	Reference
	CH ₃	H	—	544
	CH ₃	H	220	517
	CH ₃	H	—	212
	CH ₃	H	—	711
	CH ₃	H	—	711
	CH ₃	H	—	209

	CH ₃	H	—	656
	CH ₃	H	—	656
	CH ₃	H	—	656
	CH ₃	H	—	656
	CH ₃	H	—	656
	CH ₃	H	—	656
	CH ₃	H	—	656

(Table continued)

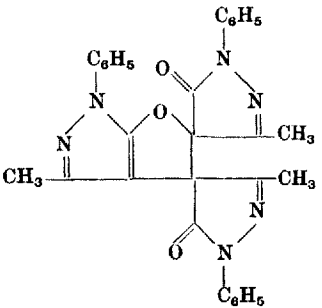
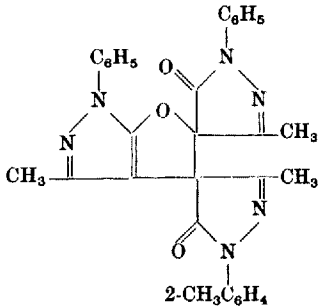
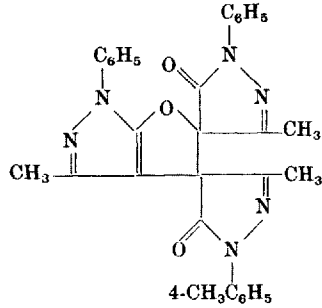
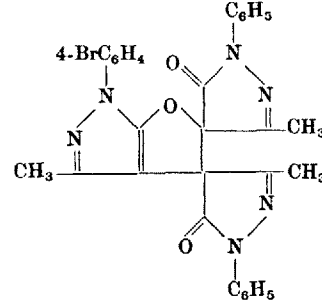
TABLE IX (continued)

R	R ¹	R ²	M.p.	Reference
	CH ₃	H	—	656
	CH ₃	H	—	656
	CH ₃	H	—	656
	CH ₃	H	—	656
	C ₂ H ₅	H	—	656
	HOOC	H	—	511
	HOOC	H	—	511
	HOOC	H	—	152

	C_6H_5	H	245°	459
	C_6H_5	H	—	656
	C_6H_5	H	—	656
	CH_3	$4-(\text{C}_2\text{H}_5)_2\text{NC}_6\text{H}_4\text{N}=\text{N}$	—	494
	CH_3	$4-(\text{C}_2\text{H}_5)_2\text{NC}_6\text{H}_4\text{N}=\text{N}$	—	494
	CH_3	$4-(\text{C}_2\text{H}_5)_2\text{NC}_6\text{H}_4\text{N}=\text{N}$	—	494
	CH_3	$2\text{-HO-4-(4-HO}_3\text{SC}_6\text{H}_4\text{NHCO)}\text{C}_6\text{H}_4$	—	209
	CH_3	$2\text{-HO-4-(4-HO}_3\text{SC}_6\text{H}_4\text{NHCO)}\text{C}_6\text{H}_4$	—	209

(Table continued)

TABLE X. Furlones

Compounds	M.p.	Reference
	158°	1608, 1611
	151°	1608
	134°	1608
	161°	1608

(Table continued)

TABLE X (continued)

Compounds	M.p.	Reference
	147°	1608
	164°	1608
	162.5° (dec.)	1610
	172° (dec.)	1610

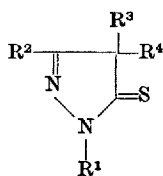


TABLE XI. 2-Pyrazolin-5-thiones

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	CH ₃	CH ₃	CH ₃	112°	759
H	CH ₃	C ₂ H ₅	C ₂ H ₅	141°	759
C ₆ H ₅	CH ₃	H	H	109°	990, 1343
4-CH ₃ C ₆ H ₄	CH ₃	H	H	212°	990
2,4-(NO ₂)C ₆ H ₃	CH ₃	H	H	179°	1207
C ₆ H ₅	CH ₃	CH ₃	CH ₃	—	785
C ₆ H ₅	CH ₃	C ₂ H ₅	C ₂ H ₅	80°	1343
C ₆ H ₅	CH ₃		(CH ₃) ₂ C=	204°	990
4-CH ₃ C ₆ H ₄	CH ₃		(CH ₃) ₂ C=	206°	990
C ₆ H ₅	C ₆ H ₅	H	H	163°	1003
C ₆ H ₅	CH ₃		C ₆ H ₅ CH=	183°	990
C ₆ H ₅	CH ₃		C ₆ H ₅ C=	185°	990
			CH ₃		
4-CH ₃ C ₆ H ₄	CH ₃		C ₆ H ₅ CH=	212°	990
4-CH ₃ C ₆ H ₄	CH ₃		C ₆ H ₅ C=	106°	990
			CH ₃		
C ₆ H ₅	CH ₃	C ₆ H ₅ CO	H	217°	977, 990
C ₆ H ₅	CH ₃	C ₆ H ₅ N=N	H	97°	990

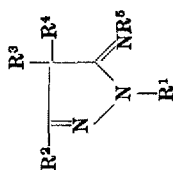
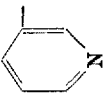
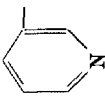


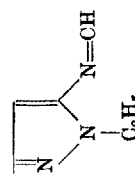
TABLE XII. 5-Imino-2-pyrazolines

R ¹	R ²	R ³	R ⁴	R ⁵	M.p.	Reference
H	H	H	H	H	b ₁₁ , 140°	819, 1266
H	H	H	H	C ₂ H ₅ OOC	153°	819
H	H	H	H	4-H ₅ NC ₆ H ₄ SO ₂	235°	714
H	CH ₃	H	H	H	94°	368, 1049
H	CH ₃	H	H	C ₂ H ₅ OOC	158°	368, 1049
H	CH ₃	H	H	4-H ₅ NC ₆ H ₄ SO ₂	253°	368
H	C ₆ H ₁₁	H	H	H	41°	1025, 1026
H	C ₆ H ₁₃	H	H	H	32°	1025, 1026
H	C ₆ H ₁₉	H	H	H	—	1065
H	H	CH ₃	C ₄ H ₉	H	172°	391
H	H	C ₂ H ₅	C ₂ H ₅	H	232°	391
CH ₃ C(=O)CHCN	CH ₃	H	H	H	—	1543
CH ₃	H	C ₂ H ₅	C ₂ H ₅	H	b ₁₀ , 91°	391
H	H	C ₆ H ₅	H	H	172°	1086
H	C ₆ H ₅	H	H	H	125°	342, 344, 1025
H	C ₆ H ₅	H	H	CH ₃ C(=O)CHCN	115°	299
H	C ₆ H ₅	H	H	C ₆ H ₅	166°	1652, 1656
H	C ₆ H ₅	H	H	4-CH ₃ C ₆ H ₄	157°	1656
H	C ₆ H ₅	H	H	4-ClC ₆ H ₄	174°	1655, 1656

H	C ₆ H ₅	H	H	3-BrC ₆ H ₄	205°	1656
H	C ₆ H ₅	H	H	4-BrC ₆ H ₄	176°	1654
H	C ₆ H ₅	H	H	4-IC ₆ H ₄	175°	1656
H	C ₆ H ₅	H	H	4-C ₆ H ₅ -C ₆ H ₅	219°	1656
H	C ₆ H ₅	H	H	HCO	214°	301
H	C ₆ H ₅	H	H	CH ₃ CO	—	301
H	C ₆ H ₅	H	H	C ₆ H ₅ CO	190°	301
H	C ₆ H ₅	H	H	C ₂ H ₅ OCO	160°	301
H	C ₆ H ₅	H	H	C ₂ H ₅ OCOCO	164°	301
C ₆ H ₅	H	H	H	C ₆ H ₅	138°	1002
H	4-CH ₃ C ₆ H ₄	H	H	H	143°	1542
H	4-NO ₂ C ₆ H ₄	H	H	H	255°	342, 344
H		H	H	H	—	931
H	C ₆ H ₅	CH ₃	H	H	58°	299, 301
H		H	H	CH ₃ CO	308°	931
C ₆ H ₅	CH ₃	H	H	H	110°	322, 341, 838, 1010, 1043
C ₆ H ₅	CH ₃	H	H	C ₂ H ₅	b315°	975
C ₆ H ₅	CH ₃	H	H	C ₆ H ₅ CH ₂	b13228°	975
C ₆ H ₅	CH ₃	H	H	C ₆ H ₅	120°, 146°	826, 827, 1002

(Table continued)

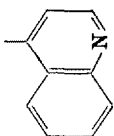
TABLE XII (continued)

R ¹	R ²	R ³	R ⁴	R ⁵	M.P.	Reference
C ₆ H ₅	CH ₃	H	H	2-CH ₃ C ₆ H ₄	72°	1002
C ₆ H ₅	CH ₃	H	H	4-CH ₃ C ₆ H ₄	109°	827, 1002
C ₆ H ₅	CH ₃	H	H	4-ClC ₆ H ₄	139°	1002
C ₆ H ₅	CH ₃	H	H	4-BrC ₆ H ₄	136°	1002
C ₆ H ₅	CH ₃	H	H	4-HOOCCH ₃	140°	996
C ₆ H ₅	CH ₃	H	H	4-C ₂ H ₅ OOCCH ₃	76°	996
C ₆ H ₅	CH ₃	H	H	3-NO ₂ C ₆ H ₄	138°	1002
C ₆ H ₅	CH ₃	H	H	4-NO ₂ C ₆ H ₄	153°	1002
C ₆ H ₅	CH ₃	H	H	1-C ₁₀ H ₇	137°	828
C ₆ H ₅	CH ₃	H	H	HCO	135°	322, 996
C ₆ H ₅	CH ₃	H	H	CH ₃ CO	110°	996
C ₆ H ₅	CH ₃	H	H	C ₆ H ₅ CO	113°	996
C ₆ H ₅	CH ₃	H	H	C ₆ H ₅ SO ₂	170°	996
C ₆ H ₅	CH ₃	H	H	4-H ₂ NC ₆ H ₄ SO ₂	180°	325
C ₆ H ₅	CH ₃	H	H	4-NO ₂ C ₆ H ₄ SO ₂	220°	325
C ₆ H ₅	CH ₃	H	H	H ₂ NOC	215°	996
C ₆ H ₅	CH ₃	H	H	C ₆ H ₅ HNOC	205°	996
C ₆ H ₅	CH ₃	H	H	C ₆ H ₅ HNOC	150°	996
C ₆ H ₅	CH ₃	H	H	CH ₃	—	322
						
C ₆ H ₅	C ₆ H ₁₁	H	H	H	b ₁₈ 231°	1025, 1026
2-CH ₃ C ₆ H ₄	CH ₃	H	H	H	93°	996
2-CH ₃ C ₆ H ₄	CH ₃	H	H	C ₆ H ₅	131°	1002
4-CH ₃ C ₆ H ₄	CH ₃	H	H	CH ₃ CO	157°	996
4-CH ₃ C ₆ H ₄	CH ₃	H	H	H	120°	996
4-CH ₃ C ₆ H ₄	CH ₃	H	H	C ₆ H ₅	106°	1002
2-ClC ₆ H ₄	CH ₃	H	H	H	—	86

4-BrC ₆ H ₄	CH ₃	H	H	C ₆ H ₅	106°	1002
4-H ₂ N ₂ O ₂ SC ₆ H ₄	CH ₃	H	H	H	98°	975
4-H ₂ N ₂ O ₂ SC ₆ H ₄	CH ₃	H	H	H	245°	324
2,5-Cl ₂ C ₆ H ₃	CH ₃	H	H	H	—	86
2,4-(NH ₂) ₂ C ₆ H ₃	CH ₃	H	H	C ₆ H ₅	184°	1207
2,4-(NO ₂) ₂ C ₆ H ₃	CH ₃	H	H	H	204°	1207
2,4-(NO ₂) ₂ C ₆ H ₃	CH ₃	H	H	C ₆ H ₅ CH ₂	286°	1207
2,4-(NO ₂) ₂ C ₆ H ₃	CH ₃	H	H	C ₆ H ₅	190°	1207
2,4-(NO ₂) ₂ C ₆ H ₃	CH ₃	H	H	4-CH ₃ C ₆ H ₄	166°	1207
2,4-(NO ₂) ₂ C ₆ H ₃	CH ₃	H	H	C ₆ H ₅ NH	216° (dec.)	1207
2-C ₁₀ H ₇	CH ₃	H	H	C ₆ H ₅	122°	975
2-C ₁₀ H ₇	CH ₃	H	H	1-C ₁₀ H ₇	145°	975
C ₆ H ₅	CH ₃	H	H	H	128°	129, 340, 342, 345
C ₆ H ₅	H	C ₆ H ₅	H	H	—	506
C ₆ H ₅	C ₆ H ₅	H	H	CH ₃ C— CHCOOC ₂ H ₅	125°	299
C ₆ H ₅	C ₆ H ₅	H	H	C ₆ H ₅	153°	1652
C ₆ H ₅	C ₆ H ₅	H	H	CH ₃ CO	149°	1287
C ₆ H ₅	C ₆ H ₅	H	H	C ₆ H ₅ — N—N=N C ₆ H ₅	217°	340
C ₆ H ₅	4-CH ₃ C ₆ H ₄	H	H	H	169°	1287
C ₆ H ₅	4-CH ₃ C ₆ H ₄	H	H	CH ₃ CO	—	1287
C ₆ H ₅	4-CH ₃ OC ₆ H ₄	H	H	H	188°	90, 129
C ₆ H ₅	4-C ₂ H ₅ OC ₆ H ₄	H	H	H	127°	1543
C ₆ H ₅	4-H ₂ NC ₆ H ₄	H	H	H	110°	340
C ₆ H ₅	4-CH ₃ COHNC ₆ H ₄	H	H	CH ₃ CO	235°	340
C ₆ H ₅	2-ClC ₆ H ₄	H	H	H	137°	1543

(Table continued)

TABLE XII (continued)

R ¹	R ²	R ³	R ⁴	R ⁵	M.P.	Reference
C ₆ H ₅	3-ClC ₆ H ₄	H	H	H	108°	1543
C ₆ H ₅	4-ClC ₆ H ₄	H	H	H	185°	1543
C ₆ H ₅	H	4-ClC ₆ H ₄	H	CH ₃ CO	219°	1562
C ₆ H ₅	H	4-ClC ₆ H ₄	H	C ₆ H ₅ CO	219°	1562
C ₆ H ₅	4-NO ₂ C ₆ H ₄	H	H	H	185°	340, 342
C ₆ H ₅	4-NO ₂ C ₆ H ₄	H	H	CH ₃ CO	218°	340
C ₆ H ₅		H	H	H	—	127
C ₆ H ₅	CH ₃	CH ₃	H	H	102°	975, 1011
C ₆ H ₅	CH ₃	CH ₃	H	C ₆ H ₅ CO	196°	1011
C ₆ H ₅	C ₂ H ₅	CH ₃	H	H	81°	132
C ₆ H ₅	CH ₃	C ₂ H ₅	H	H	53°	1011
C ₆ H ₅	CH ₃	C ₂ H ₅	H	C ₆ H ₅ CO	233°	1011
C ₆ H ₅	CH ₃	C ₃ H ₇	H	H	55°	1011
C ₆ H ₅	CH ₃	C ₃ H ₇	H	C ₆ H ₅ CO	150°	1011
C ₆ H ₅	CH ₃	C ₆ H ₅ CH ₂	H	H	77°	975, 1011
C ₆ H ₅	CH ₃	C ₆ H ₅ CH ₂	H	CH ₃	120°	975
C ₆ H ₅	CH ₃	C ₆ H ₅ CH ₂	H	C ₆ H ₅ CO	184°	975, 1011
C ₆ H ₅	CH ₃	C ₆ H ₅ CH=	H	C ₆ H ₅	164°	1002
C ₆ H ₅	CH ₃	C ₆ H ₅ CH=		4-CH ₃ C ₆ H ₄	163°	1002
C ₆ H ₅	CH ₃	4-CH ₃ OC ₆ H ₄ CH=		C ₆ H ₅	295°	1002
C ₆ H ₅	CH ₃	4-CH ₃ OC ₆ H ₄ CH=		4-CH ₃ C ₆ H ₄	184°	1002
C ₆ H ₅	CH ₃	4-ClC ₆ H ₄	H	H	100°	918
C ₆ H ₅	C ₂ H ₅	C ₆ H ₅	H	H	120°	1562
C ₆ H ₅	C ₆ H ₅ OCH ₂	C ₆ H ₅	H	CH ₃ CO	174°	1562

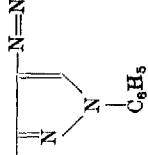
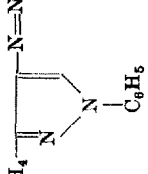
(Table continued)

TABLE XII (continued)

R ¹	R ²	R ³	R ⁴	R ⁵	M.p.	Reference
C ₆ H ₅	C ₆ H ₅ OCH ₂	C ₆ H ₅	H	C ₆ H ₅ CO	163°	1562
C ₆ H ₅	C ₆ H ₅	4-ClC ₆ H ₄	H	H	149°	1563
2,4-(NO ₂) ₂ C ₆ H ₃	C ₆ H ₅ CH ₂	C ₆ H ₅	H	H	127°	310
2,4-(NO ₂) ₂ C ₆ H ₃	4-CH ₃ C ₆ H ₄ CH ₂	C ₆ H ₅	H	H	140°	310
2,4-(NO ₂) ₂ C ₆ H ₃	4-CH ₃ OC ₆ H ₄ CH ₂	C ₆ H ₅	H	H	114°	310
2,4-(NO ₂) ₂ C ₆ H ₃	4-BrC ₆ H ₄ CH ₂	C ₆ H ₅	H	H	155°	310
2,4-(NO ₂) ₂ C ₆ H ₃	C ₆ H ₅	4-FC ₆ H ₅	H	H	175°	310
2,4-(NO ₂) ₂ C ₆ H ₃	C ₆ H ₅	4-ClC ₆ H ₅	H	H	155°	310
CH ₃	C ₆ H ₅ COO	H	H	C ₆ H ₅ CO	150°	594
H	CH ₃ COO	C ₆ H ₅	C ₂ H ₅	H	183°	391
H	CH ₃ COO	C ₂ H ₅	C ₂ H ₅	CH ₃ CO	202°	391
C ₆ H ₅	C ₆ H ₅ COO	H	H	H	105°	1599
C ₆ H ₅	C ₆ H ₅ COO	H	H	C ₆ H ₅ CO	193°	1599
C ₆ H ₅	CH ₃	4-NO ₂ C ₆ H ₄ S	H	H	170°	325
C ₆ H ₅	CH ₃	4-NO ₂ C ₆ H ₄ S	H	CH ₃ CO	201°	325
H	CH ₃	H ₂ N	H	H	—	1044
C ₆ H ₅	CH ₃	H ₂ N	H	H	—	1043, 1044
C ₆ H ₅	CH ₃	H ₂ N	H	C ₆ H ₅	140°	995, 1002
C ₆ H ₅	CH ₃	H ₂ N	H	4-CH ₃ C ₆ H ₄	131°	1002
C ₆ H ₅	CH ₃	H ₂ N	H	3-NO ₂ -4-CH ₃ C ₆ H ₃	97°	1002
C ₆ H ₅	CH ₃	CH ₃ C≡N	H	C ₆ H ₅	127°	995
C ₆ H ₅	CH ₃	CH ₂ COOC ₂ H ₅				
C ₆ H ₅	CH ₃	C ₆ H ₅ CH=N	H	C ₆ H ₅	147°	995
C ₆ H ₅	CH ₃	4-CH ₃ OC ₆ H ₄ CH=N	H	C ₆ H ₅	191°	995
C ₆ H ₅	CH ₃	C ₆ H ₅ CONH	H	C ₆ H ₅	187°	995
C ₆ H ₅	CH ₃	H ₂ NOCHN	H	C ₆ H ₅	201°	995
C ₆ H ₅	CH ₃	C ₆ H ₅ NHOCHN	H	H	220°	1002
C ₆ H ₅	CH ₃	C ₆ H ₅ NHSCHN	H	H	160°	1002

(Table continued)

TABLE XII (continued)

R ¹	R ²	R ³	R ⁴	R ⁵	M.P.	Reference
H	4-CH ₃ C ₆ H ₄	C ₆ H ₅ N=N	H	H	233°	1542
C ₆ H ₅	CH ₃	C ₆ H ₅ N=N	H	H	140°	975, 996
C ₆ H ₅	CH ₃	2-CH ₃ OC ₆ H ₄ N=N	H	H	93°	1039
C ₆ H ₅	CH ₃	2-C ₂ H ₅ OC ₆ H ₄ N=N	H	H	89°	1040
C ₆ H ₅	CH ₃	1-C ₁₀ H ₇ N=N	H	H	117°	996
2-CH ₃ C ₆ H ₄	CH ₃	C ₆ H ₅ N=N	H	H	118°	996
4-HO ₃ SCH ₂ CH ₂ O ₃ SC ₆ H ₄	CH ₃	2-HOOC ₆ H ₄ N=N	H	H	—	651
C ₆ H ₅	C ₆ H ₅		H	H	217°	1287
C ₆ H ₅	4-CH ₃ C ₆ H ₄	4-CH ₃ C ₆ H ₄ - 	H	H	212°	1287
H	CH ₃	Br	H	H	258°	1046
H	Cl	CH ₃	C ₄ H ₉	H	150°	391
H	Cl	C ₂ H ₅	C ₂ H ₅	H	161°	391
H	Cl	C ₂ H ₅	C ₂ H ₅	CH ₃ CO	182°	391
H	Br	CH ₃	C ₄ H ₉	H	144°	391
H	Br	C ₂ H ₅	C ₂ H ₅	H	165°	391
C ₂ H ₅	Br	C ₂ H ₅	C ₂ H ₅	H	b ₁₁ , 102°	391
H	C ₆ H ₅	Cl	H	2-Cl-4-BrC ₆ H ₃	197°	1654
H	C ₆ H ₅	Br	H	3-BrC ₆ H ₄	178°	1656
H	C ₆ H ₅	Br	H	2-Br-4-CH ₃ C ₆ H ₃	181°	1656

H	C ₆ H ₅	Br	H	2-Br-4-ClC ₆ H ₃	198°	1655, 1656
H	C ₆ H ₅	Br	H	2,4-Br ₂ C ₆ H ₃	206° (dec.)	1652, 1654
H	C ₆ H ₅	Br	H	2-Br-4-IC ₆ H ₃	201°	1656
C ₆ H ₅	CH ₃	Cl	H	H	118°	975
C ₆ H ₅	CH ₃	Cl	H	CH ₃ CO	132°	975
C ₆ H ₅	Cl ₂ CH	Cl	H	C ₆ H ₅	138°	1201
C ₆ H ₅	CH ₃	Br	H	H	106°	975
C ₆ H ₅	CH ₃	Br	H	C ₆ H ₅ CO	172°	996
C ₆ H ₅	CH ₃	I	H	H	75°	975
2-CH ₃ C ₆ H ₄	CH ₃	Cl	H	H	114°	996
2-CH ₃ C ₆ H ₄	CH ₃	Br	H	H	134°	996
2-CH ₃ C ₆ H ₄	CH ₃	I	H	H	141°	996
4-CH ₃ C ₆ H ₄	CH ₃	Br	H	H	128°	996
4-BrC ₆ H ₄	CH ₃	Br	H	4-BrC ₆ H ₄	131°	1002
X.Y-Cl ₂ C ₆ H ₃	CH ₃	Cl	H	H	—	975
CH ₃ C— CHCN	CH ₃	NO	H	H	167°	1643
H	C ₆ H ₅	NO	H	H	270° (dec.)	301
H	C ₆ H ₅	NO	H	CH ₃ CO	237°	301
H	C ₆ H ₅	NO	H	C ₆ H ₅ CO	271°	301
H	C ₆ H ₅	NO	H	C ₆ H ₅ OCOCO	240° (dec.)	301
C ₆ H ₅	H	NO	H	C ₆ H ₅	113°	1002
C ₆ H ₅	CH ₃	NO	H	H	168°, 199°	1002, 1010
C ₆ H ₅	CH ₃	NO	H	4-CH ₃ C ₆ H ₄	117°	1002
2-CH ₃ C ₆ H ₄	CH ₃	NO	H	H	195°	996
4-CH ₃ C ₆ H ₄	CH ₃	NO	H	H	198°	996
C ₆ H ₅	C ₆ H ₅	NO	H	H	207°	340, 1153
4-CH ₃ C ₆ H ₄	NO	NO	H	H	230°	1152, 1153
4-CH ₃ OC ₆ H ₄	NO	NO	H	H	208°	1153
4-NO ₂ C ₆ H ₄	NO	NO	H	H	—	340
H	H	NO ₂	H	H	228°	1043
H	H	NO ₂	H	CH ₃ CO	180°	1043
H	CH ₃	NO ₂	H	H	225°	1044, 1045

(Table continued)

TABLE XII (continued)

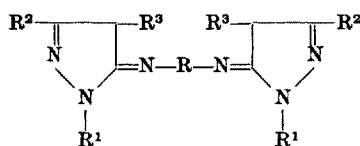
R ¹	R ²	R ³	R ⁴	R ⁵	M.p.	Reference
H	CH ₃	NO ₂	H	C ₂ H ₅ OOC	200°	1049
H	C ₆ H ₅	NO ₂	H	2,4-(NO ₂) ₂ C ₆ H ₃	286° (dec.)	1652, 1654
H	C ₆ H ₅	NO ₂	H	2,4-(NO ₂) ₂ -6-CH ₃ C ₆ H ₂	245°	1656
H		NO ₂	H	H	—	932
H		NO ₂	H	CH ₃ CO	175°	932
C ₆ H ₅	CH ₃	NO ₂	H	H	167°	1010, 1043, 1044
C ₆ H ₅	CH ₃	C ₆ H ₅ CO	H	H	153°	973, 977
C ₆ H ₅	CH ₃	C ₆ H ₅ CO	H	C ₆ H ₅	171°	973
H	H	HOOC	H	H	—	1266
H	H	C ₂ H ₅ OOC	H	H	102°	1266
C ₆ H ₅	HOOC	C ₆ H ₅	H	H	—	506
C ₆ H ₅	C ₆ H ₅ OOC	C ₆ H ₅	H	H	—	506
H	HOOCCH ₂	H ₂ NCO	H	H	—	1478
CH ₃	HOOCCH ₂	H ₂ NCO	H	H	—	1478
C ₆ H ₅	HOOCCH ₂	H ₂ NCO	H	H	—	1478
C ₆ H ₅	CH ₃	C ₆ H ₅ NHCO	H	C ₆ H ₅	171°	826
C ₆ H ₅	CH ₃	C ₆ H ₅ NHCO	H	1-C ₁₀ H ₇	168°	828
C ₆ H ₅	CH ₃	1-C ₁₀ H ₇ NHCO	H	1-C ₁₀ H ₇	224°	828
C ₆ H ₅	CH ₃	C ₆ H ₅ NHCS	H	C ₆ H ₅	224°	827
C ₆ H ₅	CH ₃	C ₆ H ₅ NHCS	H	1-C ₁₀ H ₇	259°	828
H	H	NC	H	H	174°	1196
H	NCCH ₂	NC	H	H	198°	1478
CH ₃	NCCH ₂	NC	H	H	—	1478

C_6H_5	H_2NCO	H	H	186°	726
C_6H_5	CH_3HNCO	H	H	153°	726
C_6H_5	NC	H	H	168°	726
C_6H_5	$NCCH_2$	H	H	—	1478
CH_3CO	H	H	CH_3C	162°	1542
CH_3CO		H	CH_3CO	148°	299
			$\parallel$ $CHCOOC_2H_5$		
CH_3CO	H	H	CH_3CO	159°	301, 342, 344
CH_3CO	H	H	C_2H_5OOC	144°	301
CH_3CO	H	H	CH_3CO	221°	1542
CH_3CO	H	H	CH_3CO	163°	1542
CH_3CO	H	H	CH_3CO	203°	344
C_6H_5CO	H	H	CH_3CO	159°	301
C_6H_5CO	H	H	C_6H_5CO	—	301
H_2NCO	H	H	H	170°	343, 344
H_2NCO	H	H	H	180°	1542
H_2NCO	H	H	H	338°	343
H_2NCO	$4-ClC_6H_4$	H	H	168°	918
C_6H_5NHCO	H	H	H	173°	1542
C_6H_5NHCO	H	H	CH_3CO	161°	1542
$C_6H_5N=C$	H	H	H	206°	1542
$C_6H_5N=C$	H	H	CH_3CO	184°	1542
C_6H_5NHCS	H	H	H	187°	1542
C_6H_5NHCS	H	H	H	196°	1542
C_6H_5	Cl	Br	H	124°	996
C_6H_5	Br	H	H	125°	996
C_6H_5	$4-NO_2C_6H_4SO_2$	H	H	174°	325
C_6H_5	$4-NO_2C_6H_4SO_2$	H	CH_3CO	210°	325

(Table continued)

TABLE XII (continued)

R ¹	R ²	R ³	R ⁴	R ⁵	M.p.	Reference
C ₆ H ₅	H ₃ C ₂ OOC	C ₆ H ₅ N=N	H	H	105°	126
CH ₃ CO	CH ₃ COO	H	H	C ₆ H ₅	—	1598
CH ₃ CO	CH ₃ COO	H	H	CH ₃ CO	131°	594
CH ₃ CO	Cl	C ₂ H ₅	C ₂ H ₅	CH ₃ CO	50°	391

TABLE XIII. *N,N'*-Bis(5-imino-2-pyrazolines)

R ¹	R ²	R ³	R	M.p.	Reference
H	C ₆ H ₅	H		310° (dec.)	301
H	C ₆ H ₅	H		> 310°	301
C ₆ H ₅	CH ₃	H		184°	996
C ₆ H ₅	CH ₃	H		—	322
CH ₃ CO	C ₆ H ₅	H		243°	301
C ₆ H ₅	CH ₃	C ₆ H ₅ CO	none	—	973

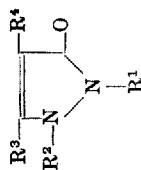


TABLE XIV. 3-Pyrazolin-5-ones

Section A. Alkyl and Alicyclic Substituents

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	CH ₃	CH ₃	H	174°	54, 788, 860, 1205
H	C ₃ H ₇	CH ₃	H	135°	1205
CH ₃	CH ₃	CH ₃	H	40°	54, 788, 789, 985
	CH ₃	CH ₃	H	b ₃ 161°	101
	CH ₃	CH ₃	H	66°	101, 103, 859
	CH ₃	CH ₃	H	85°	101
C ₂ H ₅	CH ₃	CH ₃	iso-C ₃ H ₇	b ₀ .06, 97°	250
C ₃ H ₇	CH ₃	CH ₃	iso-C ₃ H ₇	b ₀ .12, 107°	250
iso-C ₃ H ₇	CH ₃	CH ₃	iso-C ₃ H ₇	b ₀ .07, 81°	250
C ₄ H ₉	CH ₃	CH ₃	iso-C ₃ H ₇	b ₀ .07, 98°	250
iso-C ₄ H ₉	CH ₃	CH ₃	iso-C ₃ H ₇	b ₀ .06, 90°	250

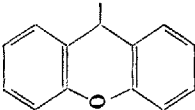
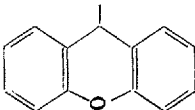
TABLE XIV (continued)

Section B. Alkyl and Aryl Substituents

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	C ₆ H ₅	H	H	155°	450, 858, 993, 1122, 1254, 1559
H	4-IC ₆ H ₄	H	H	126°	446
C ₆ H ₅	CH ₃	H	H	117°	108
H	CH ₃	C ₆ H ₅	H	165°	54, 1205
H	C ₆ H ₅	CH ₃	H	166°	95, 247, 788, 826, 885, 888, 988, 1522, 1524, 1559, 1569
H	C ₆ H ₅	H	CH ₃	—	972, 1569
H	C ₆ H ₅	C ₅ H ₁₁	H	280°	1023, 1024
H	C ₆ H ₅	C ₆ H ₁₃	H	270°	1023, 1024
H	2-CH ₃ C ₆ H ₄	CH ₃	H	169°	988, 1524
H	4-CH ₃ C ₆ H ₄	CH ₃	H	196°	988
H	4-CH ₃ C ₆ H ₄	H	CH ₃	217°	446
H	4-BrC ₆ H ₄	CH ₃	H	227°	1001
H	4-BrC ₆ H ₄	H	CH ₃	245°	446
H	3-NO ₂ C ₆ H ₄	CH ₃	H	239°	1001
H	4-NO ₂ C ₆ H ₄	CH ₃	H	233°	885
H	4-NO ₂ C ₆ H ₄	H	CH ₃	266°	446
H	2,5-(CH ₃) ₂ C ₆ H ₃	CH ₃	H	180°	679
H	2,5-Cl ₂ C ₆ H ₃	CH ₃	H	231°	885
H	1-C ₁₀ H ₇	CH ₃	H	240°	885
C ₆ H ₅	C ₆ H ₅	H	H	130°	370

(Table continued)

TABLE XIV, Section B (continued)

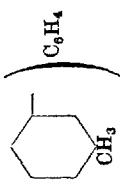
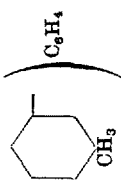
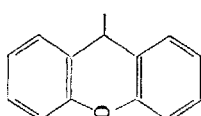
R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	C ₆ H ₅	C ₆ H ₅	H	256°	95, 808, 1023, 1024, 1042, 1071, 1333, 1522, 1524
H	2-CH ₃ C ₆ H ₄	C ₆ H ₅	H	207°	1524
H	C ₆ H ₅	2-CH ₃ OC ₆ H ₄	H	222°	670
		H	H	—	457
C ₆ H ₅	CH ₃	CH ₃	H	113°	781, 785, 801, 806, 807, 1173, 1174, 1198, 1508
CH ₃	C ₆ H ₅	CH ₃	H	113°	95, 888, 1522
CH ₃	CH ₃	C ₆ H ₅	H	108°	992
H	C ₆ H ₅	CH ₃	CH ₃	256°	95, 984
C ₆ H ₅	CH ₃	C ₆ H ₅	H	65°	1252
C ₆ H ₅	CH ₃	H	C ₂ H ₅	121°	303
H	C ₆ H ₅	CH ₃	C ₂ H ₅	172°	95, 984, 1522, 1524
C ₆ H ₅	C ₃ H ₇	CH ₃	H	90°	1321
H	iso-C ₃ H ₇	CH ₃	C ₆ H ₅	219°	250
C ₆ H ₅	CH ₃		H	115°	1477

Φ^*	C_6H_5	CH_3	$C_{15}H_{31}$	H	66°	636
	C_6H_5	C_2H_6	C_2H_6	H	$b_{2.5}178^\circ$	1252
	C_6H_5	CH_3	CH_3	$HOCH_2CH_2$	115°	1171
	C_6H_5	CH_3	CH_3	$HOOCCH_2$	186°	638
	C_6H_5	CH_3	CH_3	$H_5C_2OOCCH_2$	—	638
	C_6H_5	CH_3	CH_3	H_2NOCCH_2	147°	638
	C_6H_5	CH_3	CH_3	$HOOCCHCH_2$ NH_2	—	638
	C_6H_5	CH_3	CH_3	$HOOCCHCH_2$ $NHCOC_6H_5$	228°	638
	C_6H_5	CH_3	CH_3	$H_5C_2OOCCHCH_2$ NO_2	—	638
	C_6H_5	CH_3	CH_3	$(H_3COOC)_2CCH_2$ $NHCHO$	161°	638
	C_6H_5	CH_3	CH_3	$(H_5C_2OOC)_2CCH_2$ $NHCHO$	143°	638
	C_6H_5	CH_3	CH_3	$(H_5C_2OOC)_2CCH_2$ $NHCHO$	—	638
	C_6H_5	CH_3	CH_3	$(H_5C_2OOC)_2CCH_2$ NO_2	96°	806
	$2-CH_3C_6H_4$	CH_3	CH_3	H	169°	988
	CH_3	$2-CH_3C_6H_4$	CH_3	H	161.5°	1524
	H	$2-CH_3C_6H_4$	CH_3	C_2H_5	$b_{0.01}201^\circ$	1477
	$3-CH_3C_6H_4$	CH_3		H	137°	806
	$4-CH_3C_6H_4$	CH_3	CH_3	H	98°	988
	CH_3	$4-CH_3C_6H_4$	CH_3	H	—	145
	$4-CH_3C_6H_4$	C_2H_5	CH_3	H	$b_{0.06}185^\circ$	1477
	$4-CH_3C_6H_4$	CH_3		H		

(Table continued)

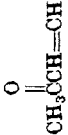
TABLE XIV, Section B (continued)

R ¹	R ²	R ³	R ⁴	M.P.	Reference
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	CH ₃	H	81°	902
4-C ₂ H ₅ OC ₆ H ₄	C ₂ H ₅	CH ₃	H	—	145
4-C ₃ H ₇ OC ₆ H ₄	CH ₃	CH ₃	H	55°	1149
2-H ₂ NC ₆ H ₄	CH ₃	CH ₃	H	165°	978
3-H ₂ NC ₆ H ₄	CH ₃	CH ₃	H	148°	978
4-H ₂ NC ₆ H ₄	CH ₃	CH ₃	H	210°	978
3-(CH ₃) ₂ NC ₆ H ₄	CH ₃	CH ₃	H	270° (dec., chloroplatinate)	978
4-HO.SCH ₂ NHC ₆ H ₄	CH ₃	CH ₃	H	—	541
3-CH ₃ CONHC ₆ H ₄	CH ₃	CH ₃	H	167°	978
3-C ₂ H ₅ CONHC ₆ H ₄	CH ₃	CH ₃	H	119°	978
3-C ₆ H ₅ SO ₂ NHC ₆ H ₄	CH ₃	CH ₃	H	199°	978
4-CH ₃ CONHC ₆ H ₄	CH ₃	CH ₃	H	221°	978
4-C ₂ H ₅ CONHC ₆ H ₄	CH ₃	CH ₃	H	261°	978
4-C ₆ H ₅ SO ₂ NHC ₆ H ₄	CH ₃	CH ₃	H	251°	978
4-(4-H ₂ NC ₆ H ₄ SO ₂ NH)C ₆ H ₄	CH ₃	CH ₃	H	256°	674, 1290
4-(4-CH ₃ CONHC ₆ H ₄ SO ₂ NH)C ₆ H ₄	CH ₃	CH ₃	H	—	674
4-H ₂ NHNC ₆ H ₄	CH ₃	CH ₃	H	—	645
4-H ₂ NCNHNHC ₆ H ₄	CH ₃	CH ₃	H	—	645
2-ClC ₆ H ₄	CH ₃	CH ₃	H	113°	296
3-ClC ₆ H ₄	CH ₃	CH ₃	H	89°	296
4-ClC ₆ H ₄	CH ₃	CH ₃	H	126°	296
4-BrC ₆ H ₄	CH ₃	CH ₃	H	—	540
CH ₃	4-BrC ₆ H ₄	CH ₃	H	150°	1001
4-IC ₆ H ₄	CH ₃	CH ₃	H	126°	446
2-NO ₂ C ₆ H ₄	CH ₃	CH ₃	H	188°	978
3-NO ₂ C ₆ H ₄	CH ₃	CH ₃	H	98°	978
4-NO ₂ C ₆ H ₄	CH ₃	CH ₃	H	132°	978
4-H ₂ NO ₂ SC ₆ H ₄	CH ₃	CH ₃	H	248°	1475, 1476
X-H ₂ NO ₂ SC ₆ H ₄	CH ₃	CH ₃	H	239°	361

$4\text{-H}_2\text{O}_2\text{AsC}_6\text{H}_4$ $2,5\text{-(CH}_3)_2\text{C}_6\text{H}_3$ $2,4\text{Cl}_2\text{C}_6\text{H}_3$	CH_3 CH_3 CH_3	CH_3 CH_3 CH_3	H H H	— 97.5° 143°	546 679 296
$4\text{-}\left(\text{C}_6\text{H}_4\right)$ 	CH_3	CH_3	H	87° (opt. act.)	141
$4\text{-}\left(\text{C}_6\text{H}_4\right)$ 	CH_3	CH_3	H	147° (racemic)	141
$2\text{-C}_{10}\text{H}_7$ C_6H_5 C_6H_5 C_6H_5	CH_3 BrCH_2 C_6H_5 CH_3	CH_3 BrCH_2 CH_3 C_6H_5	H H H H	129° 175° 130° 150°	806 899 647, 789 818
	CH_3	H	CH_3	202°	457
H C_6H_5	C_6H_5 CH_3	C_6H_5 CH_3	CH_3 CH_3	274° 82°	1333 95, 362, 809, 814, 1056, 1252

(Table continued)

TABLE XIV, Section B (continued)

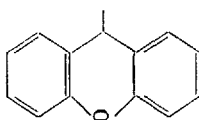
R ¹	R ²	R ³	R ⁴	M.p.	Reference
CH ₃	C ₆ H ₅	CH ₃	CH ₃	97°	95, 984
CH ₃	CH ₃	CH ₃	C ₆ H ₅	215°	250
C ₆ H ₅	C ₂ H ₅	CH ₃	CH ₃	b ₃ 183°	1252
CH ₃	C ₆ H ₅	CH ₃	C ₂ H ₅	65°	95, 984
C ₆ H ₅	CH ₃	CH ₃	C ₃ H ₇	57°	1252, 1337
C ₆ H ₅	CH ₃	CH ₃	iso-C ₃ H ₇	101°	1252, 1337, 1522
C ₆ H ₅	CH ₃	CH ₃	C ₃ H ₅	52°	1252, 1337
C ₆ H ₅	CH ₃	CH ₃	C ₄ H ₉	44°	560, 1252
C ₆ H ₅	CH ₃	CH ₃	sec.-C ₄ H ₉	91°	1252
C ₆ H ₅	CH ₃	CH ₃	iso-C ₄ H ₉	56°	560, 1074, 1252
C ₆ H ₅	CH ₃	CH ₃	iso-C ₃ H ₁₁	61°	1252
C ₆ H ₅	C ₂ H ₅	CH ₃	C ₃ H ₇	b _{1,s} 175°	1252
C ₆ H ₅	C ₂ H ₅	CH ₃	iso-C ₃ H ₇	88°	1252
C ₆ H ₅	C ₂ H ₅	CH ₃	C ₃ H ₅	b _{1,s} 181°	1252
C ₆ H ₅	C ₂ H ₅	CH ₃	C ₄ H ₉	b ₃ 194°	1252
C ₆ H ₅	C ₂ H ₅	CH ₃	iso-C ₄ H ₉	b ₃ 187°	1252
C ₆ H ₅	C ₂ H ₅	CH ₃	sec.-C ₄ H ₉	91°	1252
C ₆ H ₅	C ₂ H ₅	CH ₃	iso-C ₃ H ₁₁	b ₃ 193°	1252
C ₆ H ₅	C ₃ H ₆	CH ₃	iso-C ₃ H ₇	84°	1447
C ₆ H ₅	CH ₃		iso-C ₃ H ₇	108°	1477
C ₆ H ₅	CH ₃	BrCH ₂	CH ₃	—	1320
C ₆ H ₅	CH ₃	CH ₃		87°	113
C ₆ H ₅	CH ₃	CH ₃		161°	316

C_6H_5	CH_3	CH_3	$C_2H_5C(=O)CH=CH$	128°	316
C_6H_5	CH_3	CH_3	$O_2NCH=CH$	160°	696
C_6H_5	CH_3	CH_3	$HOOCCH=CH$	208° (dec.)	898
C_6H_5	CH_3	CH_3	$(H_5C_2OOC)_2C=CH$	135°	898
C_6H_5	CH_3	CH_3	H_5C_2OOC		
C_6H_5	CH_3	CH_3	$CH_3CH_2C(=O)CH_2$	115°	1320
C_6H_5	CH_3	CH_3	H_5C_2OOC		
C_6H_5	CH_3	CH_3	O_2N		
C_6H_5	CH_3	CH_3	$CHCH_2$	84° ($(C_2H_5)_2NH$ salt)	384
C_6H_5	CH_3	CH_3	H_5C_2OOC		
C_6H_5	CH_3	CH_3	$HON=CCH_2$	—	113
C_6H_5	CH_3	CH_3	CH_3		
C_6H_5	CH_3	CH_3	O		
C_6H_5	CH_3	CH_3	$H_2NC(=O)NHN=C(=O)CH_2$	255° (dec.)	113
C_6H_5	CH_3	CH_3	CH_3		
C_6H_5	CH_3	CH_3	$H_2NC(=O)NHN=C(=O)CH$	228°	316
C_6H_5	CH_3	CH_3	CH_3		
C_6H_5	CH_3	CH_3	$H_2NC(=O)NHN=C(=O)CH$	254°	799
C_6H_5	CH_3	CH_3	CH_3		
C_6H_5	$(CH_3)_2NCH_2CH_2$	CH_3	CH_3	$b_{0.9} 149^\circ$	249

(Table continued)

TABLE XIV, Section B (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	(CH ₃) ₂ NCH ₂ CH CH ₃	CH ₃	CH ₃	b _{1,s} 170°	249
C ₆ H ₅		CH ₃	CH ₃	b _{0,s} 158°	249
C ₆ H ₅		CH ₃	C ₂ H ₅	b _{0,s} 174°	249
C ₆ H ₅ C ₆ H ₅	(CH ₃) ₂ NCH ₂ CH ₂ (CH ₃) ₂ NCH ₂ CH CH ₃	CH ₃ CH ₃	iso-C ₃ H ₇ iso-C ₃ H ₇	b _{0,s} 143° b _{0,s} 141°	249 249
C ₆ H ₅		CH ₃	iso-C ₃ H ₇	b _{0,s} 141°	249
C ₆ H ₅ 4-H ₂ NC ₆ H ₄ 4-(CH ₃) ₂ NC ₆ H ₄	CH ₃ CH ₃ CH ₃	BrCH ₂ CH ₃ CH ₃	iso-C ₃ H ₇ CH ₃ CH ₃	— — 140°, 212°	1318 535 535, 1355, 1506
4-HO ₂ SCH ₂ NEC ₆ H ₄ 4-NO ₂ C ₆ H ₄ 4-NO ₂ C ₆ H ₄ C ₆ H ₅	CH ₃ CH ₃ CH ₃ CH ₃	CH ₃ CH ₃ BrCH ₂ BrCH ₂	CH ₃ C ₂ H ₅ C ₂ H ₅ BrCH ₂	— 129° 163° 175°	541 532 532 362



434

CH₃CH₃C₆H₅

TABLE XIV (continued)

Section C. Alkyl, Aryl, Heterocyclicalkyl and Aryl Substituents

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	C ₆ H ₅ CH ₂	CH ₃	H	224°	54
C ₆ H ₅	C ₆ H ₅ CH ₂	H	H	125°	1321
C ₆ H ₅ CH ₂	CH ₃	CH ₃	H	84°	333
4-CH ₃ C ₆ H ₄ CH ₂	CH ₃	CH ₃	H	78°	333
C ₆ H ₅ CH ₂ CH ₂	CH ₃	CH ₃	H	102°	1566
C ₆ H ₅	C ₆ H ₅ CH ₂	CH ₃	H	103°	1321
C ₆ H ₅	CH ₃	C ₆ H ₅ CH ₂	H	105°	1320
C ₆ H ₆	CH ₃	H	C ₆ H ₅ CH ₂	77.5°	1320
H	2-C ₁₀ H ₇	CH ₃	C ₆ H ₅ CH ₂	202°	849
C ₆ H ₅ CH ₂ CH ₂	CH ₃	C ₆ H ₅	H	—	1567

(Table continued)

TABLE XIV, Section C (continued)

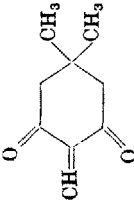
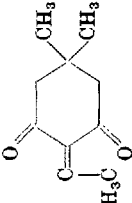
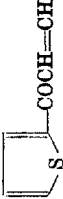
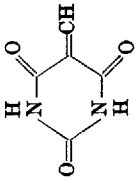
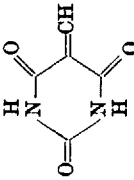
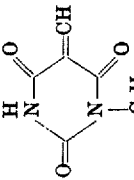
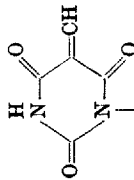
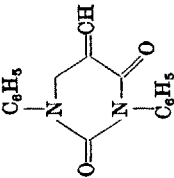
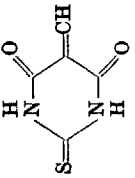
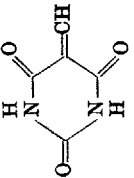
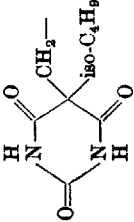
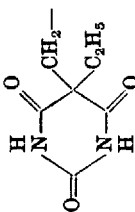
R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	H		196°	897
C ₆ H ₅	CH ₃	H		258°	897
C ₆ H ₅	CH ₃	H		118°	378
C ₆ H ₅ CH ₂	CH ₃	CH ₃	iso-C ₃ H ₇	87°	250
C ₆ H ₅	C ₆ H ₅ CH ₂	CH ₃	CH ₃	128.5°	1321
C ₆ H ₅	CH ₃	CH ₃	4-HOC ₆ H ₄ CH ₂	204°	21, 553
C ₆ H ₅	CH ₃	CH ₃	4-H ₂ NC ₆ H ₄ CH ₂	140°	110, 1483
C ₆ H ₅	CH ₃	CH ₃	4-CH ₃ NHC ₆ H ₄ CH ₂	99°	110
C ₆ H ₅	CH ₃	CH ₃	4-(CH ₃) ₂ NC ₆ H ₄ CH ₂	152°	110, 1483
C ₆ H ₅	CH ₃	CH ₃	4-CH ₃ CONHC ₆ H ₄ CH ₂	220°	110
C ₆ H ₅	CH ₃	CH ₃	4-CH ₃ CONC ₆ H ₄ CH ₂	114°	110
C ₆ H ₅	CH ₃	CH ₃		149°	110
C ₆ H ₅	CH ₃	CH ₃	NO		

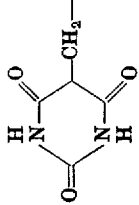
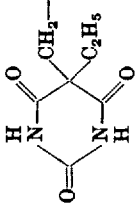
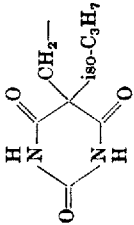
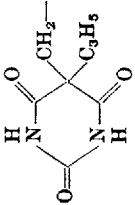
TABLE XIV, Section C (*continued*)

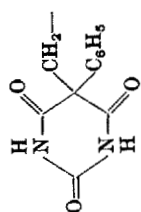
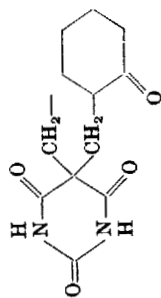
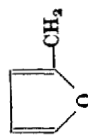
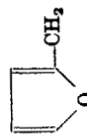
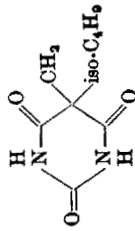
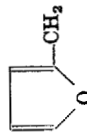
R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃		202°	316
C ₆ H ₅	CH ₃	CH ₃		254°	890, 898
CH ₃	C ₆ H ₅	CH ₃		268°	1190
C ₆ H ₅	CH ₃	CH ₃		190°	890, 898
CH ₃	C ₆ H ₅	CH ₃		276°	1190

C_6H_5	CH_3	CH_3		280° (dec.)	890, 898
C_6H_5	CH_3	CH_3		238° (dec.)	890, 898
C_6H_5	CH_3	CH_3		274°	890, 898
C_6H_5	CH_3	CH_3		251°	728
C_6H_5	CH_3		CH_3	$> 250^\circ$	1320

(Table continued)

TABLE XIV, Section C (*continued*)

R ¹	R ²	R ³	R [•]	M. p.	Reference
C ₆ H ₅	CH ₃	CH ₃		247° (dec.)	481
C ₆ H ₅	CH ₃	CH ₃		270° (dec.)	481
C ₆ H ₅	CH ₃	CH ₃		274° (dec.)	481
C ₆ H ₅	CH ₃	CH ₃		272° (dec.)	481

C_6H_5	CH_3	CH_3		250° (dec.)	481
C_6H_5	CH_3	CH_3		220° (dec.)	481
$4\cdot CH_3C_6H_4$	CH_3	CH_3		90°	378
$4\cdot C_2H_5OC_6H_4$	CH_3	CH_3		—	378
C_6H_5	CH_3	CH_3		251°	728
$4\cdot H_2NC_6H_4$	CH_3	CH_3		—	378

(Table continued)

TABLE XIV, Section C (continued)

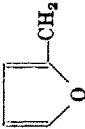
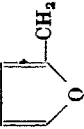
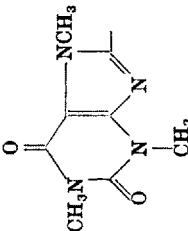
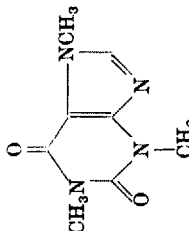
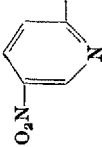
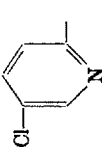
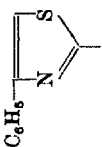
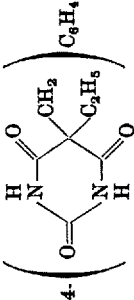
R ¹	R ²	R ³	R ⁴	M.p.	Reference
4-BrC ₆ H ₄	CH ₃	CH ₃		—	378
4-NO ₂ C ₆ H ₄	CH ₃	CH ₃		—	378
	CH ₃	CH ₃	H	251° (dec.)	1147
	CH ₃	CH ₃	CH ₃	335° (dec.)	1147

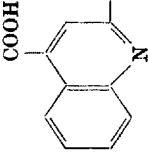
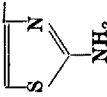
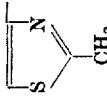
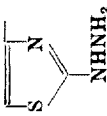
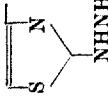
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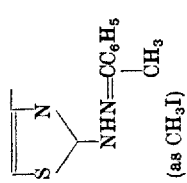
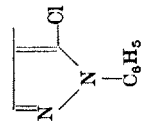
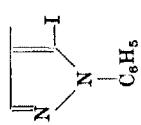
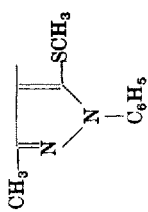
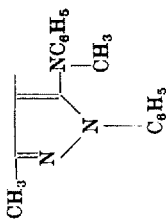
Section D. Alkyl, Aryl and Heterocyclic Substituents

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃		H	—	1499
	CH ₃	CH ₃	H	172°	1159
	CH ₃	CH ₃	H	135°	1159
	CH ₃	CH ₃	H	110°	94
	CH ₃	CH ₃	H	300°	1160

(Table continued)

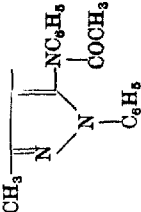
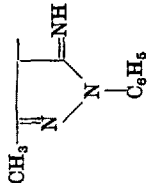
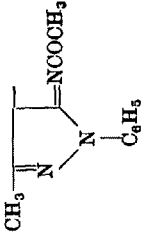
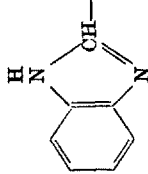
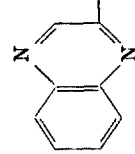
TABLE XIV, Section D (continued)

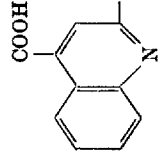
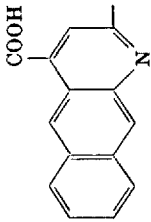
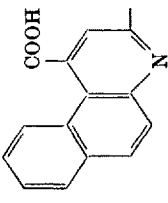
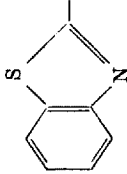
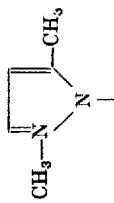
R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	H		284°	903
C ₆ H ₅	CH ₃	CH ₃		235°	94
C ₆ H ₅	CH ₃	CH ₃		130°	94
C ₆ H ₅	CH ₃	CH ₃		152°	94
C ₆ H ₅	CH ₃	CH ₃		231°	94

C_6H_5	CH_3	CH_3		216°	94
C_6H_5	CH_3	CH_3		203°	991
C_6H_5	CH_3	CH_3		—	991
C_6H_5	CH_3	CH_3		168°	991
C_6H_5	CH_3	CH_3		101°	991

(Table continued)

TABLE XIV, Section D (continued)

R ¹	R ²	R ³	R ⁴	M.P.	Reference
C ₆ H ₅	CH ₃	CH ₃		238°	991
C ₆ H ₅	CH ₃	CH ₃		220°	991
C ₆ H ₅	CH ₃	CH ₃		237°	991
C ₆ H ₅	CH ₃	CH ₃		202°, 280°	799, 1190
C ₆ H ₅	CH ₃	CH ₃		194°	799

C_6H_5	CH_3	CH_3		266°	903
C_6H_6	CH_3	CH_3		278° (dec.)	1190
C_6H_5	CH_3	CH_3		278°	903
CH_3	C_6H_6	CH_3		208°	829
C_6H_5	CH_3	CH_3		178°	452

(Table continued)

TABLE XIV, Section D (continued)

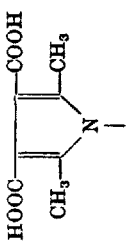
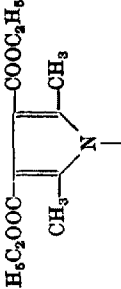
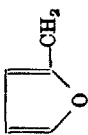
R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃		256°	452
C ₆ H ₅	CH ₃	CH ₃		145°	452
C ₆ H ₅	CH ₃			144°	378

TABLE XIV (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	HOCH ₂	H	145	698
4-H ₂ NC ₆ H ₄	CH ₃	HOCH ₂	H	223	532
4-NO ₂ C ₆ H ₄	CH ₃	HOCH ₂	H	—	532
C ₆ H ₅	CH ₃	CH ₃	HOCH ₂	158	17
C ₆ H ₅	CH ₃	HOCH ₂	CH ₃	170	528
4-H ₂ NC ₆ H ₄	CH ₃	HOCH ₂	CH ₃	—	532

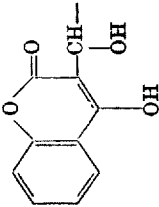
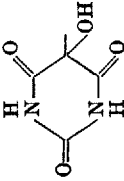
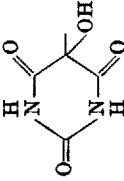
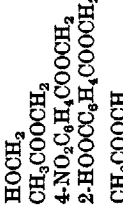
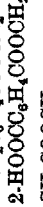
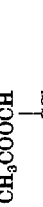
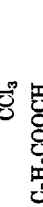
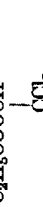
Section E. α -Hydroxy-, α -Acyloxy-, and α -Alkylthioalkyl, Alkyl and Aryl Substituents

4-(CH ₃) ₂ NC ₆ H ₄	CH ₃	HOCH ₂	CH ₃	186	532
4-NCCH ₂ NHC ₆ H ₄	CH ₃	HOCH ₂	CH ₃	—	532
4-NCCH ₂ NC ₆ H ₄	CH ₃	HOCH ₂	CH ₃	—	532
4-(HOOCCH ₂) ₂ NC ₆ H ₄	CH ₃	HOCH ₂	CH ₃	—	532
4-H ₂ NC ₆ H ₄	CH ₃	HOCH ₂	C ₂ H ₅	244	532
4-(CH ₃) ₂ NC ₆ H ₄	CH ₃	HOCH ₂	C ₂ H ₅	183	532
4-NO ₂ C ₆ H ₄	CH ₃	HOCH ₂	C ₂ H ₅	169	532
C ₆ H ₅	CH ₃	CH ₃	Cl ₃ CCH	197	107, 196, 889, 895
CH ₃	C ₆ H ₅	CH ₃	OH	190	1190
CH ₃	CH ₃	C ₆ H ₅	Cl ₃ CCH	173	1190
C ₆ H ₅	CH ₃	C ₆ H ₅	OH	156°	901
4-CH ₃ C ₆ H ₄	CH ₃	CH ₃	Cl ₃ CCH	191°	889
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	CH ₃	OH	146°	902
C ₆ H ₅	CH ₃	C ₆ H ₅	Cl ₃ CCH	188°	889, 902
C ₆ H ₅	CH ₃	CH ₃	OH	188°	895
C ₆ H ₅	CH ₃	CH ₃	Br ₃ CCH	—	107
			NCCH		
			OH		

(Table continued)

TABLE XIV, Section E (*continued*)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃	CH ₃ CHCH(HCl) OH NH ₂	—	113
C ₆ H ₅	CH ₃	CH ₃	CH ₃ CHCH(HCl) OH NHCH ₃	163° (threo) 220° (erythro)	112, 113
C ₆ H ₅	CH ₃	CH ₃	CH ₃ CHCH OH C ₂ H ₅ NH	123°	112
C ₆ H ₅	CH ₃	CH ₃	CH ₃ CHCH OH iso-C ₃ H ₇ NH	162°	112
C ₆ H ₅	CH ₃	CH ₃	CH ₃ CHCH OH (CH ₃) ₂ N	165°	112
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ CH OH	173°	977

C_6H_6	CH_3	CH_3		152°	800
C_9H_5	CH_3	CH_3		240°	1194
CH_3	CH_3	CH_3		227°	1194
C_6H_6	CH_3	CH_3		164°	698
C_6H_5	CH_3	CH_3		—	970
C_6H_5	CH_3	CH_3		—	970
C_6H_5	CH_3	CH_3		—	970
C_6H_5	CH_3	CH_3		154°	895
C_6H_5	CH_3	CH_3		141°	895

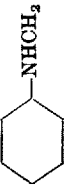
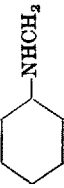
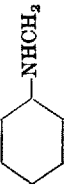
(Table continued)

TABLE XIV, Section E (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃	C ₄ H ₉ COOCH CCl ₃	136°	895
C ₆ H ₅	CH ₃	CH ₃	iso-C ₄ H ₉ COOCH CCl ₃	135°	895
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ COOCH CCl ₃	214°	895
C ₆ H ₅	CH ₃	CH ₃	4-NO ₂ C ₆ H ₄ COOCH CCl ₃	160°	895
C ₆ H ₅	CH ₃	CH ₃	3 HO ₃ SC ₆ H ₄ COOCH CCl ₃	230°	895
C ₆ H ₅	CH ₃	CH ₃	CH ₃ COOCH CBr ₃	138°	895
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ COOCH CBr ₃	170°	895
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ NHCOOCH ₂	271.5°	402
C ₆ H ₅	CH ₃	CH ₃	C ₂ H ₅ SCH ₂	97°	1127
C ₆ H ₅	CH ₃	CH ₃	C ₃ H ₇ SCH ₂	64°	1127
C ₆ H ₅	CH ₃	CH ₃	C ₄ H ₉ SCH ₂	53°	1127
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ CH ₂ SCH ₂	100°	1127
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ SCH ₂	102°	1127

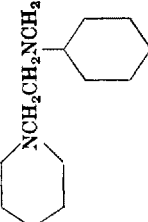
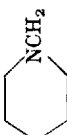
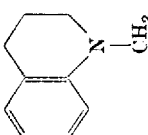
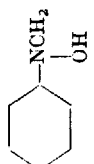
TABLE XIV (continued)

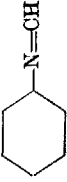
Section F. α -Amino-, α -Imino-, α -Oximino-, α -Amido- and α -Hydrazinoalkyl, Alkyl and Aryl Substituents

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃ NHCH ₂	H	70°	697
C ₆ H ₅	CH ₃	(CH ₃) ₂ NCH ₂	H	83°	697
C ₆ H ₅	CH ₃	CH ₃	H ₂ NCH ₂	—	901
C ₆ H ₅	CH ₃	CH ₃	CH ₃ NHCH ₂ (HNO ₃)	168°	107
C ₆ H ₅	CH ₃	CH ₃	C ₂ H ₅ NHCH ₂	—	107
C ₆ H ₅	CH ₃	CH ₃		88°	107
C ₆ H ₅	CH ₃	CH ₃ CHNHCH ₂	iso-C ₃ H ₇	65°	1319
C ₆ H ₅	CH ₃	CH ₃ CH ₂ CH ₂ CH ₂	C ₆ H ₅ NHCH ₂	171°, 143°	110, 111, 1483
C ₆ H ₅	CH ₃	CH ₃ CH ₂ CH ₂ CH ₂	4-CH ₃ C ₆ H ₄ NHCH ₂	140°	110
C ₆ H ₅	CH ₃	CH ₃	CH ₃ NHCH	105°	112
C ₆ H ₅	CH ₃	CH ₃		185°	1094
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ NHCH	—	—
C ₆ H ₅	CH ₃	CH ₃		93°	945
C ₆ H ₅	CH ₃	CH ₃	(CH ₃) ₂ NCH ₂	66°	945
C ₆ H ₅	CH ₃	CH ₃	(CH ₃) ₂ NCH ₂	68°	945
C ₆ H ₅	CH ₃	CH ₃	(C ₂ H ₅) ₂ NCH ₂	132°	1318
C ₆ H ₅	CH ₃	CH ₃	iso-C ₃ H ₇	—	—

(Table continued)

TABLE XIV, Section F (continued)

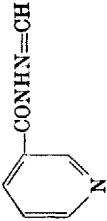
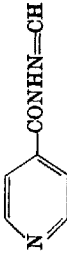
R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃		oil	111
C ₆ H ₅	CH ₃	CH ₃	(C ₆ H ₅ CH ₂) ₂ NCH ₃	131°	910
C ₆ H ₅	CH ₃	CH ₃		100°	637
C ₆ H ₅	CH ₃	CH ₃		153°	945
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ COCH ₂ CH ₂ NCH ₂ - CH ₃	86°	944
C ₆ H ₅	CH ₃	CH ₃		132°	1482
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ CONHCH ₂	140°	1014

C_6H_5	CH_3	CH_3	$H_2NCONCH_2$ CH_3	167°	107
C_6H_5	CH_3	CH_3	$H_2NCONCH_2$ C_2H_5	165°	107
C_6H_5	CH_3	CH_3	CH_3CONCH_2 C_6H_5	128°	110, 1483
C_6H_5	CH_3	CH_3	C_6H_5NHCH SO_3Na	170°	202, 891
C_6H_5	CH_3	CH_3	$4-H_2NO_2SC_6H_4NHCH$ SO_3Na	—	202, 891, 894
$4-C_2H_5OC_6H_4$	CH_3	CH_3	$4-C_2H_5OC_6H_4NHCH$ SO_3Na	150° (dec.)	202, 891
C_6H_5	CH_3	CH_3	C_6H_5NHCH SO_3Na	120° (dec.)	202, 891
C_6H_5 C_6H_5	CH_3 CH_3	CH_3 CH_3	$C_2H_5N=CH$ $CH_3N=CH$ SO_3Na	— —	107 107
C_6H_5	CH_3	CH_3		148°	107, 891
C_6H_5	CH_3	CH_3	$C_6H_5N=CH$	162°	107, 202, 891, 897
C_6H_5	CH_3	CH_3	$2-CH_3C_6H_4N=CH$	192°	891
C_6H_5	CH_3	CH_3	$4-C_2H_5OC_6H_4N=CH$	163°	891
C_6H_5	CH_3	CH_3	$2-H_2NC_6H_4N=CH$	215°	1190
C_6H_5	CH_3	CH_3	$4-OHCC_6H_4N=CH$	232°	891

(Table continued)

TABLE XIV, Section F (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃	4-H ₃ NO ₂ SC ₆ H ₄ N=CH	—	202
C ₆ H ₅	CH ₃	CH ₃	3-HO-4-HOOC ₆ H ₄ N=CH	190°	891
C ₆ H ₅	CH ₃	CH ₃	1-C ₁₀ H ₇ N=CH	97°	891
CH ₃	C ₆ H ₅	CH ₃	4-C ₂ H ₅ OC ₆ H ₄ NH=CH	135°	1190
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	CH ₃	4-C ₂ H ₅ OC ₆ H ₄ N=CH	161°	1186
C ₆ H ₅	CH ₃	C ₆ H ₅	C ₆ H ₅ N=CH	140°	202, 891, 902
C ₆ H ₅	CH ₃	C ₆ H ₅	C ₆ H ₅ N=CH	—	1183
C ₆ H ₅	CH ₃	CH ₃	HON=CH	220°	196, 201, 889, 1092, 1181
CH ₃	C ₆ H ₅	CH ₃	HON=CH	221°	1190
C ₆ H ₅	CH ₃	CH ₃	HON=C C ₆ H ₅	197°	977
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	CH ₃	HON=CH	210°	902, 1186
C ₆ H ₅	CH ₃	C ₆ H ₅	HON=CH	239°	201, 1183
C ₆ H ₅	CH ₃	C ₆ H ₅ NHN=CH	H	227°	698
C ₆ H ₅	CH ₃	CH ₃	H ₂ NN=C CH ₂ Cl	211°	799
C ₆ H ₅	CH ₃	CH ₃	H ₂ NN=C C ₆ H ₅	215°	977
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ NHN=CH	225°, 236°, 255°	196, 201, 889, 1181, 1182
CH ₃	C ₆ H ₅	CH ₃	C ₆ H ₅ NHN=CH	230°	1190
C ₆ H ₅	CH ₃	CH ₃	4-N ₂ O ₂ C ₆ H ₄ NHN=CH	272°	201, 1181
C ₆ H ₅	CH ₃	CH ₃	2,4-(NO ₂) ₂ C ₆ H ₃ NHN=CH	260°	201
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ NHN=C C ₆ H ₅	160°	977

C_6H_5	CH_3	CH_3		263°	696
C_6H_5	CH_3	CH_3		270°	412
$4-C_2H_5OC_6H_4$ $4-C_2H_5OC_6H_4$ C_6H_5	CH_3 CH_3 CH_3	CH_3 CH_3 CH_3	$C_6H_5NHN=CH$ $4-C_2H_5OC_6H_4NHN=CH$ $C_6H_5CH=CHCHN=C$	260° — 160°	1186 1186 799
C_6H_5	CH_3	CH_3	$3-CH_3O-4-HOC_6H_3CH=NN=C$ CH_2Cl	235°	799
C_6H_5	CH_3	CH_3	$2-HOC_6H_4CH=NN=C$ CH_2Cl	164°	799
C_6H_5	CH_3	CH_3	$C_6H_5C=NN=C$ CH_3 CH_2Cl	104°	799
C_6H_5 C_6H_5	CH_3 CH_3	CH_3 CH_3	$C_6H_5NHN=CH$ $H_2NCONHN=CH$	216° (dec.) 204°, 223°, 245°	698 201, 204, 892, 1181
$4-C_2H_5OC_6H_4$ C_6H_5 C_6H_5	CH_3 CH_3 CH_3	CH_3 C_6H_5 CH_3	$H_2NCONHN=CH$ $H_2NCONHN=CH$ $H_2NCONHN=CH$	256° 210°, 256° 226°, 246°	1186 201, 1180 510, 616, 799, 900
CH_3 C_6H_5 C_6H_5 $4-C_2H_5OC_6H_4$ C_6H_5	C_6H_5 CH_3 CH_3 CH_3 CH_3	CH_3 CH_3 CH_3 CH_3 C_6H_5	$H_2NCONHN=CH$ $C_2H_5NHCSNHN=CH$ $C_6H_5NHCSNHN=CH$ $H_2NCONHN=CH$ $H_2NCONHN=CH$	238° (dec.) 246° 215° 233° 233°	1190 900 900 900 900

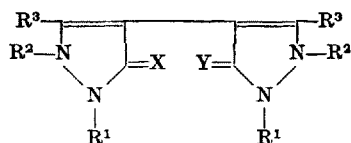


TABLE XV. 4,4'-Bis(3-pyrazolin-5-ones) Linked by a Single Bond

R ¹	R ²	R ³	X	Y	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃	O	O	254°	785, 807, 809, 991
C ₆ H ₅	CH ₃	CH ₃	S	S	237°	785, 991
C ₆ H ₅	CH ₃	CH ₃	Se	Se	270°	986
C ₆ H ₅	CH ₃	CH ₃	NH	HN	250°	991
C ₆ H ₅	CH ₃	CH ₃	O	S	225°	991
C ₆ H ₅	CH ₃	CH ₃	O	HN	259°	991
C ₆ H ₅	CH ₃	CH ₃	O	C ₆ H ₅ N	215°	991
C ₆ H ₅	C ₂ H ₅	CH ₃	O	O	240°	807
C ₆ H ₅	C ₆ H ₅ CO	CH ₃	O	O	203°	1056

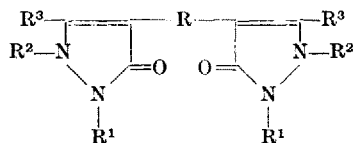
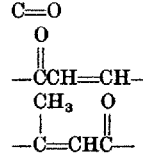
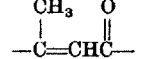
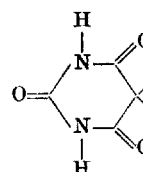


TABLE XVI. 4,4'-Bis(3-pyrazolin-5-ones) Linked by Carbon or Heteroatoms

R	R ¹	R ²	R ³	M.p.	Reference
CH ₂	C ₆ H ₅	CH ₃	H	180°	902
CH ₃ CH ₂ CH<	C ₆ H ₅	C ₆ H ₅	H	192°	1042
CH ₂	C ₆ H ₅	CH ₃	CH ₃	155°, 178°	19, 740, 910, 1192, 1483
HOOCCH<	C ₆ H ₅	CH ₃	CH ₃	239°	107, 896
H ₃ COOCH<	C ₆ H ₅	CH ₃	CH ₃	204°	107
C ₂ H ₅ OOCH<	C ₆ H ₅	CH ₃	CH ₃	92°	107
CH=CHC(=O)CH=CH	C ₆ H ₅	CH ₃	CH ₃	270°	316
(CH ₃) ₂ CHCH ₂ CH<	C ₆ H ₅	CH ₃	CH ₃	160°	409
C ₆ H ₅ CH<	H	C ₆ H ₅	CH ₃	270°	988
4-CH ₃ OC ₆ H ₄ CH<	H	C ₆ H ₅	CH ₃	287°	988
C ₆ H ₅ CH<	H	4-CH ₃ C ₆ H ₄	CH ₃	278°	988
4-CH ₃ OC ₆ H ₄ CH<	H	4-CH ₃ C ₆ H ₄	CH ₃	270°	988

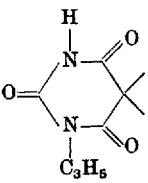
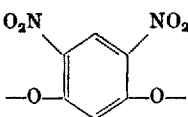
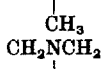
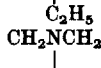
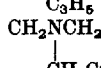
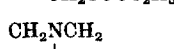
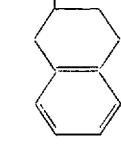
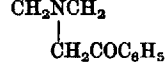
(Table continued)

TABLE XVI (continued)

R	R ¹	R ²	R ³	M. p.	Reference
C ₆ H ₅ CH<	C ₆ H ₅	CH ₃	CH ₃	201°	807, 809, 1133
C ₆ H ₅ CH<	CH ₃	CH ₃	C ₆ H ₅	213°	992
2-HOC ₆ H ₄ CH<	C ₆ H ₅	CH ₃	CH ₃	193°	21
2-CH ₃ OC ₆ H ₄ CH<	C ₆ H ₅	CH ₃	CH ₃	216°	568
3-CH ₃ OC ₆ H ₄ CH<	C ₆ H ₅	CH ₃	CH ₃	186°	569
4-(CH ₃) ₂ NC ₆ H ₄ CH<	C ₆ H ₅	CH ₃	CH ₃	—	1133
2-ClC ₆ H ₄ CH<	C ₆ H ₅	CH ₃	CH ₃	260°	568
4-ClC ₆ H ₄ CH<	C ₆ H ₅	CH ₃	CH ₃	169°	566
2-NO ₂ C ₆ H ₄ CH<	C ₆ H ₅	CH ₃	CH ₃	214°	566, 568
3-NO ₂ C ₆ H ₄ CH<	C ₆ H ₅	CH ₃	CH ₃	214°	566
4-NO ₂ C ₆ H ₄ CH<	C ₆ H ₅	CH ₃	CH ₃	232°	566
2-HO ₃ SC ₆ H ₄ CH<	C ₆ H ₅	CH ₃	CH ₃	288° (dec.)	568
4-HO ₃ SC ₆ H ₄ CH<	C ₆ H ₅	CH ₃	CH ₃	300° (dec.)	568
3-CH ₃ -4-HOC ₆ H ₃ CH<	C ₆ H ₅	CH ₃	CH ₃	119°	21
3-CH ₃ O-4-HOC ₆ H ₃ CH<	C ₆ H ₅	CH ₃	CH ₃	146°	566
3,4-(CH ₃ O) ₂ C ₆ H ₃ CH<	C ₆ H ₅	CH ₃	CH ₃	200°	569
1-C ₁₀ H ₇ CH<	C ₆ H ₅	CH ₃	CH ₃	254°	566
C ₆ H ₅ COH	C ₆ H ₅	CH ₃	CH ₃	172°	569
3-CH ₃ OC ₆ H ₄ COH	C ₆ H ₅	CH ₃	CH ₃	111°	569
				(picrate)	
4-(CH ₃) ₂ NC ₆ H ₄ COH	C ₆ H ₅	CH ₃	CH ₃	135°	569
2-ClC ₆ H ₄ COH	C ₆ H ₅	CH ₃	CH ₃	109°	568
				(picrate)	
4-ClC ₆ H ₄ COH	C ₆ H ₅	CH ₃	CH ₃	137°	566
2-NO ₂ C ₆ H ₄ COH	C ₆ H ₅	CH ₃	CH ₃	130°	568
				(picrate)	
3-NO ₂ C ₆ H ₄ COH	C ₆ H ₅	CH ₃	CH ₃	148°	569
				(picrate)	
4-NO ₂ C ₆ H ₄ COH	C ₆ H ₅	CH ₃	CH ₃	180°	566, 569
2-HO ₃ SC ₆ H ₄ COH	C ₆ H ₅	CH ₃	CH ₃	—	568
4-HO ₃ SC ₆ H ₄ COH	C ₆ H ₅	CH ₃	CH ₃	—	568
3,4-(CH ₃ O) ₂ C ₆ H ₃ COH	C ₆ H ₅	CH ₃	CH ₃	118°	569
				(picrate)	
1-C ₁₀ H ₇ COH	C ₆ H ₅	CH ₃	CH ₃	235°	566, 569
				(picrate)	
C=O	C ₆ H ₅	CH ₃	CH ₃	246°	740
	C ₆ H ₅	CH ₃	H	256°	902
	C ₆ H ₅	CH ₃	H	256°	901
	C ₆ H ₅	CH ₃	CH ₃	269° (dec.)	481

(Table continued)

TABLE XVI (continued)

R	R ¹	R ²	R ³	M.p.	Reference
	C ₆ H ₅	CH ₃	CH ₃	221°	481
—COOCH ₂ CO—	C ₆ H ₅	CH ₃	CH ₃	256°	740, 741
	C ₆ H ₅	CH ₃	CH ₃	243°	744
—S—S—	C ₆ H ₅	CH ₃	CH ₃	256°	8, 742, 848
—S—S—	C ₆ H ₅	C ₂ H ₅	CH ₃	199°	848
—S—Hg—S—	C ₆ H ₅	CH ₃	CH ₃	—	848
—S—Hg—S—	C ₆ H ₅	C ₂ H ₅	CH ₃	230°	848
—Se—	C ₆ H ₅	CH ₃	CH ₃	240°	545, 850
Se ← Se <	C ₆ H ₅	CH ₃	CH ₃	215°	850
Cl ₂ Se <	C ₆ H ₅	CH ₃	CH ₃	225°	850
CONHN=CH	C ₆ H ₅	CH ₃	CH ₃	232°	696
CH ₂ NCH ₂	C ₆ H ₅	CH ₃	CH ₃	111°	945
	C ₆ H ₅	CH ₃	CH ₃	143°	945
	C ₆ H ₅	CH ₃	CH ₃	163°	945
	C ₆ H ₅	CH ₃	CH ₃	174°	945
	C ₆ H ₅	CH ₃	CH ₃	217°	945
	C ₆ H ₅	CH ₃	CH ₃	93°	945
	C ₆ H ₅	CH ₃	CH ₃	163°	1483

(Table continued)

TABLE XVI (continued)

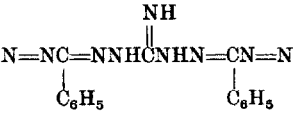
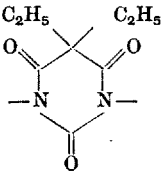
R	R ¹	R ²	R ³	M.p.	Reference
	C ₆ H ₅	CH ₃	CH ₃	262°	927
	C ₆ H ₅	CH ₃	CH ₃	248°	945
SO ₂ NHCH ₂ CH ₂ NHSO ₂	C ₆ H ₅	CH ₃	CH ₃	275°	745
N=N	H	4-BrC ₆ H ₄	CH ₃	175°	1001
N=N	H	C ₆ H ₅	CH ₃	160°	984
N=N	C ₆ H ₅	CH ₃	CH ₃	165°	456
	C ₆ H ₅	CH ₃	CH ₃	154°	1284
CH=N	C ₆ H ₅	CH ₃	CH ₃	224°	891
	C ₆ H ₅	CH ₃	CH ₃	312°	589

TABLE XVII. Miscellaneous Bis(3-pyrazolin-5-ones) and Bis(5-imino-3-pyrazolines)

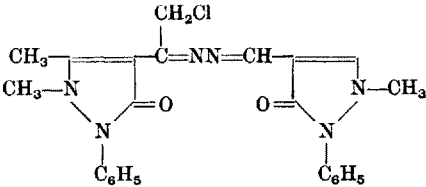
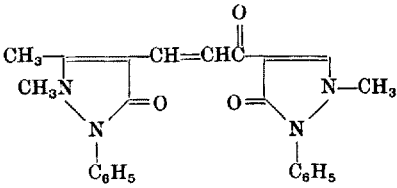
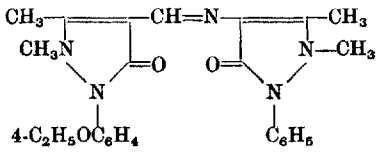
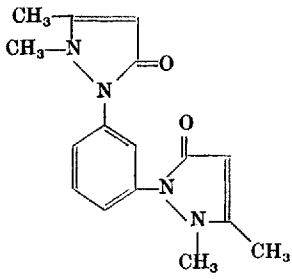
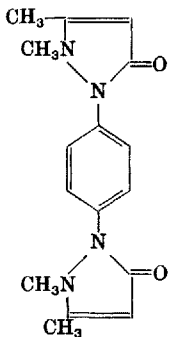
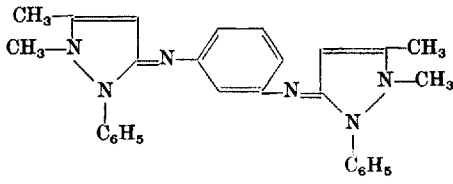
Structure	M.p.	Reference
	226°	799
	258° (hydrate)	108, 696

TABLE XVII (continued)

Structure	M.p.	Reference
	220°	891, 1186
	177°	116
	300°	116
	204°	1002

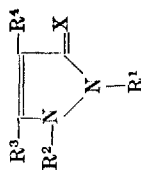


TABLE XVIII. 3-Pyrazolin-5-thiones and -5-selenones

R ¹	R ²	R ³	R ⁴	M.p.	Reference
X = S					
H		C ₆ H ₅	H	169°	1653
CH ₃	CH ₃	CH ₃	H	147°	789, 985
C ₆ H ₅	CH ₃	CH ₃	H	182°	785, 844, 845
CH ₃	C ₆ H ₅	CH ₃	H	136°	988
CH ₃	CH ₃	C ₆ H ₅	H	178°	992
CH ₃	2-CH ₃ C ₆ H ₄	CH ₃	H	133°	988
CH ₃	4-CH ₃ C ₆ H ₄	CH ₃	H	223°	988
2-H ₂ NC ₆ H ₄	CH ₃	CH ₃	H	172°	978
3-H ₂ NC ₆ H ₄	CH ₃	CH ₃	H	199°	978
4-H ₂ NC ₆ H ₄	CH ₃	CH ₃	H	255°	978
4-CH ₃ CONHC ₆ H ₄	CH ₃	CH ₃	H	271°	978
4-C ₆ H ₅ CONHC ₆ H ₄	CH ₃	CH ₃	H	265°	978
CH ₃	3-H ₂ NC ₆ H ₄	CH ₃	H	97°	1001
CH ₃	4-BrC ₆ H ₄	CH ₃	H	236°	1001
2-NO ₂ C ₆ H ₄	CH ₃	CH ₃	H	190°	978
3-NO ₂ C ₆ H ₄	CH ₃	CH ₃	H	204°	978
CH ₃	3-NO ₂ C ₆ H ₄	CH ₃	H	242°	1001

(Table continued)

TABLE XVIII (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
4-NO ₂ C ₆ H ₄	CH ₃	CH ₃	H	240°	978
C ₆ H ₅	C ₆ H ₅	CH ₃	H	185°	789
CH ₃	C ₆ H ₅	C ₆ H ₅	H	185°	1001
3-NO ₂ C ₆ H ₄	CH ₃	C ₆ H ₅	H	106°	1003
CH ₃	3-NO ₂ C ₆ H ₄	C ₆ H ₅	H	112°	1001
CH ₃	C ₆ H ₅	CH ₃	CH ₃	103°	984
CH ₃	C ₆ H ₅	CH ₃	C ₂ H ₅	126	984
C ₆ H ₅	CH ₃	CH ₃	(CH ₃) ₂ N	—	986, 1000
CH ₃	C ₆ H ₅	Cl	H	123°	981
C ₆ H ₅	CH ₃	CH ₃	Cl	188.5°	795
CH ₃	C ₆ H ₅	Cl	Br	173°	981
4-NO ₂ C ₆ H ₄	CH ₃	CH ₃	NO ₂	240°	978

X = Se

CH ₃	C ₆ H ₅	CH ₃	H	168°	988
CH ₃	CH ₃	C ₆ H ₅	H	198°	992

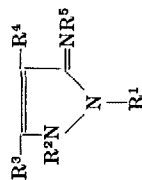
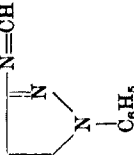


TABLE XIX. 5-Imino-3-pyrazolines

R ¹	R ²	R ³	R ⁴	R ⁵	M.p.	Reference
H	C ₆ H ₅	H	H	H	93°	398

H	C ₆ H ₅	H	H		—	398
H	3-CH ₃ C ₆ H ₄	H	H	H	100°	398
H	4-CH ₃ OC ₆ H ₄	H	H	H	124°	398
H	4-ClC ₆ H ₄	H	H	H	108°	398
H	4-BrC ₆ H ₄	H	H	H	176°	398
H	C ₃ H ₅	CH ₃	H	H	112°	398
H	C ₃ H ₅	CH ₃	H	H	146°	826
H	C ₃ H ₅	CH ₃	H	H	116°	826
H	C ₃ H ₅	CH ₃	H	H	128°	1002
C ₆ H ₅	CH ₃	H	H	4-CH ₃ C ₆ H ₄	155°	1002
C ₆ H ₅	C ₂ H ₅	H	H	C ₆ H ₅	124°	1002
C ₆ H ₅	C ₃ H ₇	H	H	C ₆ H ₅	b ₁₈ 231°	1025
H	C ₃ H ₅	C ₆ H ₁₁	H	H	135°	398, 1025
H	C ₆ H ₅	C ₆ H ₅	H	H	234°	1653
H	C ₆ H ₅	C ₆ H ₅	H	C ₆ H ₅ NH		
CH ₃	CH ₃	CH ₃	H	H	—	985
C ₆ H ₅	CH ₃	CH ₃	H	H	63°, 211°	975, 1352
C ₆ H ₅	CH ₃	CH ₃	H	CH ₃	131°	1352
C ₆ H ₅	CH ₃	CH ₃	H	C ₂ H ₅	—	1352
C ₆ H ₅	CH ₃	CH ₃	H	C ₆ H ₅ CH ₂	oil	975
C ₆ H ₅	CH ₃	CH ₃	H	C ₆ H ₅	79°	827, 975
C ₆ H ₅	CH ₃	CH ₃	H	2-CH ₃ C ₆ H ₄	69°	1002
C ₆ H ₅	CH ₃	CH ₃	H	4-CH ₃ C ₆ H ₄	106°	1002
C ₆ H ₅	CH ₃	CH ₃	H	3-H ₂ NC ₆ H ₄	45°	1002
C ₆ H ₅	CH ₃	CH ₃	H	3-CH ₃ COHNC ₆ H ₄	212°	1002

(Table continued)

TABLE XIX (continued)

R ¹	R ²	R ³	R ⁴	R ⁵	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃	H	3-C ₆ H ₅ COHNC ₆ H ₄	172°	1002
C ₆ H ₅	CH ₃	CH ₃	H	4-H ₃ NC ₆ H ₄	112°	1002
C ₆ H ₅	CH ₃	CH ₃	H	4-CH ₃ HNC ₆ H ₄	143°	1002
C ₆ H ₅	CH ₃	CH ₃	H	4-(CH ₃) ₂ NC ₆ H ₄	120°	1002
C ₆ H ₅	CH ₃	CH ₃	H	4-CH ₃ COHNC ₆ H ₄	196°	1002
C ₆ H ₅	CH ₃	CH ₃	H	4-CH ₃ NC ₆ H ₄	142°	1002
				COCH ₃		
C ₆ H ₅	CH ₃	CH ₃	H	4-CH ₃ NC ₆ H ₄	169°	1002
				NO		
C ₆ H ₅	CH ₃	CH ₃	H	4-C ₂ H ₅ NC ₆ H ₄	—	1002
				NO		
C ₆ H ₅	CH ₃	CH ₃	H	4-ClC ₆ H ₄	78°	1002
C ₆ H ₅	CH ₃	CH ₃	H	3-BrC ₆ H ₄	205°	1002
C ₆ H ₅	CH ₃	CH ₃	H	4-BrC ₆ H ₄	81°	1002
C ₆ H ₅	CH ₃	CH ₃	H	3-NO ₂ C ₆ H ₄	114°	1002
C ₆ H ₅	CH ₃	CH ₃	H	4-NO ₂ C ₆ H ₄	129°	1002
C ₆ H ₅	CH ₃	CH ₃	H	4-HOOC ₆ H ₄	150°	996
C ₆ H ₅	CH ₃	CH ₃	H	4-CH ₃ OOC ₆ H ₄	155°	996
C ₆ H ₅	CH ₃	CH ₃	H	3-NO ₂ -4-CH ₃ C ₆ H ₄	100°	1002
C ₆ H ₅	CH ₃	CH ₃	H	3,4-Cl ₂ C ₆ H ₄	—	1002
C ₆ H ₅	CH ₃	CH ₃	H	1-C ₁₀ H ₇	161°	975
C ₆ H ₅	CH ₃	CH ₃	H	2-C ₁₀ H ₇	70°	975
C ₆ H ₅	CH ₃	CH ₃	H	C ₆ H ₅ CO	176°	1352
C ₆ H ₅	CH ₃	CH ₃	H	C ₆ H ₅ SO ₂	211°	1352
C ₆ H ₅	CH ₃	CH ₃	H	C ₆ H ₅ NH	oil	983
C ₆ H ₅	CH ₃	CH ₃	H	⁶ H ₅ N	128°	983
				CH ₃		

C_6H_5	CH_3	CH_3	H	C_6H_5N $\begin{array}{c} \\ C_2H_5 \end{array}$	78°	983
CH_3	CH_3	CH_3	H	H	—	1352
C_6H_5	C_6H_5	C_6H_5	H	H	170°	975
C_6H_5	C_2H_5	C_2H_5	H	$C_6H_5SO_2$	173°	975
$2-CH_3C_6H_4$	CH_3	CH_3	H	H	35°	996
$2-CH_3C_6H_4$	CH_3	CH_3	H	C_6H_5	129°	1002
$2-CH_3C_6H_4$	CH_3	CH_3	H	C_6H_5CO	186°	996
$2-CH_3C_6H_4$	CH_3	CH_3	H	$C_6H_5SO_2$	179°	996
$4-CH_3C_6H_4$	CH_3	CH_3	H	H	177°	996
$4-CH_3C_6H_4$	CH_3	CH_3	H	C_6H_5	106°	1002
$4-CH_3C_6H_4$	CH_3	CH_3	H	$C_6H_5SO_2$	203°	996
$4-CH_3C_6H_4$	CH_3	CH_3	H	C_6H_5	96°	1002
$4-CH_3C_6H_4$	CH_3	CH_3	H	C_6H_5	119°	1002
$4-BrC_6H_4$	CH_3	CH_3	H	C_6H_5	182°	975
$2-C_{10}H_7$	CH_3	CH_3	H	$2-C_{10}H_7$	122°	975
$2-C_{10}H_7$	CH_3	CH_3	CH_3	H	—	1352
C_6H_5	CH_3	CH_3	CH_3	CH_3	—	1352
C_6H_5	CH_3	CH_3	$C_6H_5CH_2$	H	148°	975
C_6H_5	CH_3	CH_3	$C_6H_5CH_2$	CH_3	—	975
C_6H_5	CH_3	CH_3	$C_6H_5CH_2$	C_6H_5CO	124°	975
C_6H_5	CH_3	CH_3	$C_6H_5CH_2$	$C_6H_5SO_2$	141°	975
C_6H_5	CH_3	CH_3	$C_6H_5N=N$	H	188°	996
$2-CH_3C_6H_4$	CH_3	CH_3	$C_6H_5N=N$	H	191°	996
$4-CH_3C_6H_4$	CH_3	CH_3	Br	$4-CH_3OCCC_6H_4$	170°	996
C_6H_5	CH_3	CH_3	C_6H_5CO	H	155°	977
C_6H_5	CH_3	CH_3	C_6H_5CO	C_6H_5	159°	977
C_6H_5	CH_3	CH_3	$C_6H_5C=$ $\begin{array}{c} \\ NNHC_6H_5 \end{array}$	C_6H_5	178°	977
C_6H_5	CH_3	CH_3	C_6H_5HNCS	C_6H_5	224°	826
H	CH_3	CH_3	C_6H_5HNCO	C_6H_5	215°	826
C_6H_5	CH_3COO	CH_3COO	H	CH_3CO	202°	594
C_6H_5	CH_3COO	CH_3COO	H	CH_3CO	83°	1599

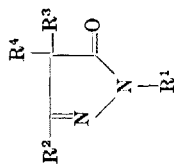
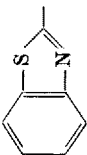
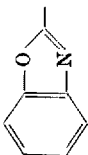
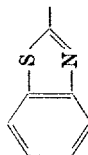
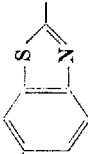


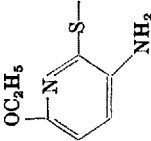
TABLE XX. 2-Pyrazolin-5-ones. Hydroxy and Mercapto Derivatives

R¹	R²	R³	R⁴	M. P.	Reference
H	CH₃	H	OH	205°	262
H	CH₃	CH₃	OH	96°	1526
H	CH₃	C₂H₅	OH	128°	1526
H	CH₃	C₃H₇	OH	117°	1526
H	CH₃	C₃H₅ (allyl)	OH	103°	1526
H	CH₃	C₄H₉	OH	101°	1526
H	CH₃	C₆H₁₁	OH	140°	1526
C₆H₅	CH₃	H	OH	190°, 225°	99, 372, 1491
H	CH₃	C₃H₅CH₂	OH	143°	1526
H	C₆H₅	C₆H₅CH₂	OH	185°	1526
CH₃	CH₃	C₂H₅	OH	39°	1525, 1526
CH₃	CH₃	C₆H₅	OH	126°	1527
CH₃	CH₃	C₃H₅CH₂	OH	143°, 155°	1525, 1526
C₆H₅	CH₃	CH₃	OH	105°, 113°	1525, 1526, 1528
C₆H₅	CH₃	C₂H₅	OH	117°, 130°	1525, 1526, 1528
C₆H₅	CH₃	C₃H₇	OH	116°	1525, 1526
C₆H₅	CH₃	iso-C₃H₇	OH	115°	1525
C₆H₅	CH₃	C₄H₉	OH	95°	1525, 1526
C₆H₅	CH₃	C₃H₅CH₂	OH	145°	1525, 1526
C₆H₅	CH₃	C₆H₁₁	OH	110°	1525

C_6H_5 C_6H_5 H C_6H_5 $4-NO_2C_6H_4$ $4-H_2NO_2SC_6H_4$	  C_6H_5 	$4-(t-C_4H_9)C_6H_4O$ 	CH_3O CH_3O C_2H_5O C_2H_5O C_2H_5O C_2H_5O C_2H_5O C_2H_5O C_2H_5O C_2H_5O C_4H_9O C_4H_9O C_4H_9O C_4H_9O C_4H_9O CH_3COO CH_3COO CH_3 C_6H_5COO CH_3COO C_6H_5COO $(CH_3)_2NCOO$	CH_3 C_2H_5 H H H H H H H H H H H H H 4- $NO_2C_6H_4COO$ C_6H_5 $C_6H_5CH_2COO$ CH_3 C_2H_5 C_2H_5 H	C_2H_5 C_2H_5 H H H H H H H H H H H H H H C_2H_5 C_2H_5 H CH_3 H CH_3 C_2H_5 C_2H_5 C_2H_5 H	70° 94° 177° 116.5° 151° 197° 200° 152° 59° 59° 185° 162° 159.5° — 80° 97° 110° 115°	994 41, 317 1143 598 1143 598, 1143 1143 1143 1143 1143 1143 783 1234 320 998 317 317 200

(Table continued)

TABLE XX (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	C ₆ H ₅	OH	H	200°	1243
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ COO	H		1243
C ₆ H ₅	C ₆ H ₅	OH	OH	82°	1243
C ₆ H ₅	C ₆ H ₅	OH	C ₂ H ₅ O	165°	1243
C ₆ H ₅	C ₆ H ₅	OH	NaO ₃ S	—	1243
H	CH ₃		H	226° (dec.)	1474
C ₆ H ₅	CH ₃	4-CH ₃ C ₆ H ₄ S	H	212°	28
C ₆ H ₅	CH ₃	2-NH ₂ C ₆ H ₄ S	H	181°	28
C ₆ H ₅	CH ₃	4-NH ₂ C ₆ H ₄ S	H	217°	28
C ₆ H ₅	CH ₃	4-ClC ₆ H ₄ S	H	205°	28
C ₆ H ₅	CH ₃	4-BrC ₆ H ₄ S	H	221°	28
C ₆ H ₅	CH ₃	2,4-Cl ₂ C ₆ H ₃ S	H	225°	28
C ₆ H ₅	CH ₃	2-NO ₂ C ₆ H ₄ S	H	207°	28
C ₆ H ₅	CH ₃	4-NO ₂ C ₆ H ₄ S	H	236°	27
4-NO ₂ C ₆ H ₄	CH ₃	OH	OH	185°	690
4-NO ₂ C ₆ H ₄	CH ₃	OH	CH ₃ O	192°	690

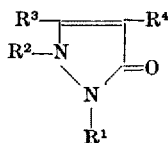
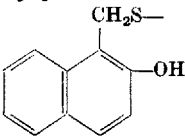
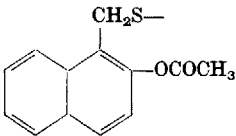


TABLE XXI. 3-Pyrazolin-5-ones. Alkoxy, Aryloxy, Acyloxy, and Alkylthio Substituents

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	C ₆ H ₅	CH ₃ O	H	92°	41
C ₆ H ₅	C ₆ H ₅		H	188°	200
C ₆ H ₅	C ₆ H ₅		H	314°	1048
C ₆ H ₅	C ₆ H ₅		H	337°	1048
C ₆ H ₅	CH ₃	CH ₃	CH ₃ O	75°	820
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ O	60°	820
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ COO	139°	820
C ₆ H ₅	CH ₃	CH ₃	2-NO ₂ -5-ClC ₆ H ₃ O	176°	744
C ₆ H ₅	CH ₃	CH ₃	2,4-(NO ₂) ₂ C ₆ H ₃ O	174°	744
C ₆ H ₅	CH ₃	CH ₃	2-CH ₃ OOC-4-NO ₂ C ₆ H ₃ O	191°	744
C ₆ H ₅	CH ₃	CH ₃	2-HOOC-4-NO ₂ C ₆ H ₃ O	250°	744
C ₆ H ₅	CH ₃	CH ₃	2-C ₂ H ₅ OOC-4-NO ₂ C ₆ H ₃ O	171°	744
C ₆ H ₅	CH ₃	CH ₃	2,4-(NO ₂) ₂ -5-ClC ₆ H ₃ O	205°	744
C ₆ H ₅	CH ₃	CH ₃	2,4-(NO ₂) ₂ -5-CH ₃ OC ₆ H ₂ O	195	744
C ₆ H ₅	CH ₃	CH ₃	2,4-(NO ₂) ₂ -5-H ₂ NC ₆ H ₂ O	267°	744
C ₆ H ₅	CH ₃	CH ₃	2,4-(NO ₂) ₂ -5-C ₆ H ₅ NHC ₆ H ₂ O	(dec.) 240°	744
C ₆ H ₅	CH ₃	CH ₃	2,4-(NO ₂) ₂ -5-(2-C ₂ H ₅ OC ₆ H ₂ NH) C ₆ H ₂ O	246°	744
C ₆ H ₅	CH ₃	CH ₃	2,4,6-(NO ₂) ₃ C ₆ H ₂ O	150°	744
C ₆ H ₅	CH ₃	CH ₃		142°	744
C ₆ H ₅	CH ₃	CH ₃		126°	744

(Table continued)

TABLE XXI (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃	4-H ₂ NC ₆ H ₄ COO	194°	783
C ₆ H ₅	CH ₃	CH ₃	4-O ₂ NC ₆ H ₄ COO	143°	783
C ₆ H ₅	C ₆ H ₅	CH ₃	CH ₃ O	—	887
C ₆ H ₅	C ₆ H ₅	(CH ₃) ₂ NCOO	C ₄ H ₉	135°	200
C ₆ H ₅	CH ₃	CH ₃		201°	1127
C ₆ H ₅	CH ₃	CH ₃		133°	1127
C ₆ H ₅	CH ₃	C ₆ H ₅	CH ₃ O	155°	1243
C ₆ H ₅	CH ₃	C ₆ H ₅	C ₆ H ₅ COO	—	1243

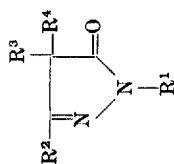


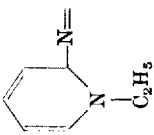
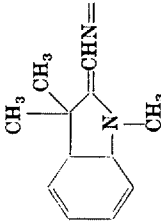
TABLE XXII. 2-Pyrazolin-5-ones. Amino, Imino, Hydrazino, Azo, and Related Derivatives

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	CH ₃	H	NH ₂	247° (dec., HCl salt)	480
CH ₃	CH ₃	CH ₃	NH ₂	225° (HCl salt)	478
H	CH ₃		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	202°	519
H	CH ₃		2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=	195°	244
CH ₃	CH ₃	CH ₃	4-CH ₃ OC ₆ H ₄ CH=N	202°	478
CH ₃	CH ₃	CH ₃	3,4-(OCH ₂ O)C ₆ H ₃ CH=N	245°	478
CH ₃	CH ₃	CH ₃	4-NO ₂ C ₆ H ₄ CH=N	257°	478
H	H	H	C ₆ H ₅ CONH CH ₃	200°	59, 319
H	H	H	C ₆ H ₅ CON—	237°	318
H	H	H	C ₆ H ₅ CH ₂ CONH	215°, 222°	243, 1027
H		H	H	165°	705
H	C ₂ H ₅ OOCCCH ₃		C ₂ H ₅ ON=	116°	866
C ₆ H ₅ CH ₂	CH ₃		AgO ₂ N=	—	333

(Table continued)

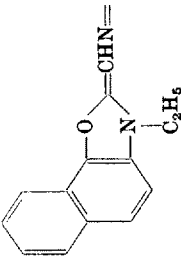
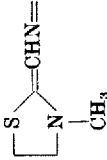
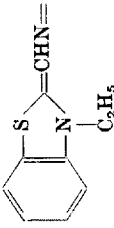
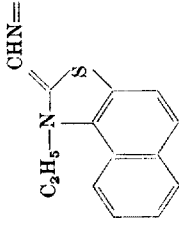
TABLE XXII (continued)

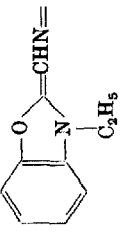
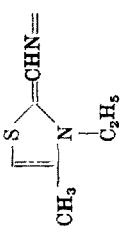
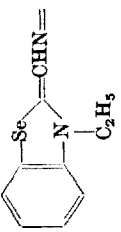
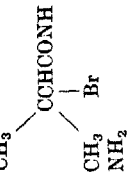
R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅ CH ₂	CH ₃		(C ₆ H ₅ NH) ₂ N= OAg 2-HOC ₆ H ₄ CH=	—	333
H	2-HOC ₆ H ₄ CH=N			> 245°	1083
H	C ₆ H ₅	H		—	1560
H	C ₆ H ₅	H	NH ₂ C ₆ H ₅ CH=N	152°	1560
C ₆ H ₅	H		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	165°	519
C ₆ H ₅	H		2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=	134°	244
C ₆ H ₅	H	H	C ₆ H ₃ NHN=CHCHN— CH ₃ COOC ₂ H ₅	224°	1537
H	C ₆ H ₅			153°	1560
H	C ₆ H ₅		C ₂ H ₅ ON= CH ₃ COON= C ₆ H ₅ COON=	82°	1560
H	C ₆ H ₅			142°	1560
C ₆ H ₅	H	H	C ₆ H ₅ CONH C ₆ H ₅ CH ₂ CONH H	198°	319
C ₆ H ₅	H	H		173°	1102
C ₆ H ₅	C ₆ H ₅ CON— C ₂ H ₅	H		111°	595
H	C ₆ H ₅			192°	519
H	C ₆ H ₅		4-(C ₂ H ₅) ₂ NC ₆ H ₅ N=	209°	244
C ₆ H ₅	CH ₃	H	2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N= NH ₂	—	809, 996
C ₆ H ₅	CH ₃	H	HOOCCH ₂ NH— C ₂ H ₅ OOCNH	—	525
C ₆ H ₅	CH ₃	H	C ₆ H ₅ CONH	—	525
C ₆ H ₅	CH ₃	H	C ₆ H ₅ CONH	183°	52
C ₆ H ₅	CH ₃	H	N ₂ C ₆ H ₅ NH	—	1144
C ₆ H ₅	CH ₃	H		198°	1107
C ₆ H ₅	CH ₃		4-(CH ₃) ₂ NC ₆ H ₄ N=	158°, 187°	519, 1242
C ₆ H ₅	CH ₃		4-(C ₂ H ₅ N)C ₆ H ₄ N= CH ₃	102°	519

C_6H_5 C_6H_5 C_6H_5	CH_3 CH_3 CH_3	$4-(C_2H_5)_2NC_6H_4N=$ $4-(C_4H_9)_2NC_6H_4N=$ $4-(HOCH_2CH_2N)C_6H_4N=$ C_2H_5	117° 90° 45°	$494, 519$ 519 519
C_6H_5	CH_3	CH_3 CH_3 $4-(NOCHN)C_6H_4N=$ CH_3 CH_3	190°	1244
C_6H_5 C_6H_5 C_6H_5	CH_3 CH_3 CH_3	$4-(H_2NOCCHN)C_6H_4N=$ $4-CH_3-2-(C_2H_5)_2NC_6H_3N=$ $2-CH_3-4-(C_2H_5)_2NC_6H_3N=$ CH_3	159° 124° 129°	1244 1638 $244, 519,$ 1255
C_6H_5 C_6H_5 C_6H_5	CH_3 CH_3 CH_3	$C_6H_5CH=N$ $2-NO_2C_6H_5CH=N$ $C_6H_5CH=CHCH=N$	186° 198° 192°	809 633 633
C_6H_5	CH_3		185°	1072
C_6H_5	CH_3		185° (dec.)	240

(Table continued)

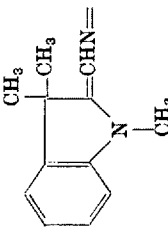
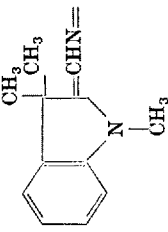
TABLE XXII (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃			214° (dec.)	240
C ₆ H ₅	CH ₃			237° (dec.)	240
C ₆ H ₅	CH ₃			256° (dec.)	240
C ₆ H ₅	CH ₃			279° (dec.)	240

C_6H_5	CH_3		220° (dec.)	240
C_6H_5	CH_3		186° (dec.)	240
C_6H_5	CH_3		225° (dec.)	240
C_6H_5	CH_3	$C_6H_5N=N-CH_3$	—	52
C_6H_5 C_6H_5	CH_3 CH_3	C_6H_5CONH $iso-C_4H_9CONH$ CH_3	183° —	52 536
C_6H_5	CH_3		—	536
CH_3	C_6H_5	H	> 175° (HCl salt)	992
CH_3	C_6H_5	$4-(C_2H_5)_2NC_6H_4N=$	96°	519
CH_3	C_6H_5	$2-HOC_6H_4CH=N$	230° (dec.)	992
CH_3	C_6H_5	$4-CH_3OC_6H_4CH=N$	220° (dec.)	992
CH_3	C_6H_5	$4-NO_2C_6H_4CH=N$	250° (dec.)	992

(Table continued)

TABLE XXII (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
CH ₃	C ₆ H ₅	H		180°	992
C ₆ H ₅	<i>i</i> -C ₄ H ₉		2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₅ N=	131°	244
C ₆ H ₅	C ₁₀ H ₃₁		2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₅ N=	44°	244
C ₆ H ₅	HOCH ₂	H	NH ₂	201° (HCl)	397
C ₆ H ₅	H ₅ C ₇ OOCH ₂		2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₅ N=	96°	244
3-CH ₃ C ₆ H ₄	CH ₃			203° (dec.)	240
4-CH ₃ C ₆ H ₄	CH ₃			246° (dec.)	240
3-NH ₂ C ₆ H ₄	CH ₃		(C ₂ H ₅) ₂ N-C ₆ H ₄ N=	—	494
4-NH ₂ C ₆ H ₄	CH ₃		(C ₂ H ₅) ₂ N-C ₆ H ₄ N=	144°	494, 519
4-NH ₂ C ₆ H ₄	CH ₃		2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₅ N=	189°	244
2-ClC ₆ H ₄	CH ₃		2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₅ N=	148°	244
4-ClC ₆ H ₄	CH ₃		2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₅ N=	169°	244
3-BrC ₆ H ₄	CH ₃		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	118°	519

4-BrC ₆ H ₄	CH ₃	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	139°	519
4-NO ₂ C ₆ H ₄	CH ₃	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	163°	519
4-NO ₂ C ₆ H ₄	CH ₃	2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=	189°	244
4-HOCC ₆ H ₄	CH ₃	2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=	243°	244
3-HOCC ₆ H ₄	C ₁₇ H ₃₅	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	73°	519
4-HOCC ₆ H ₄	C ₁₇ H ₃₅	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	135°	519
4-NCC ₆ H ₄	CH ₃	2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=	201°	244
3-HO ₃ SC ₆ H ₄	CH ₃	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	280°	519
4-KO ₃ SC ₆ H ₄	CH ₃	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	—	494
3-HO ₃ SC ₆ H ₄	C ₁₇ H ₃₅	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	180°	519
4-HO ₃ SC ₆ H ₄	C ₁₇ H ₃₅	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	150°	519
4-NH ₂ O ₂ SC ₆ H ₄	CH ₃	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	213°	519
4-NH ₂ O ₂ SC ₆ H ₄	CH ₃	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	215°	695
2,4-Cl ₂ C ₆ H ₃	CH ₃	2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=	229° (dec.)	244
2,4-(NO ₂) ₂ C ₆ H ₃	CH ₃	2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=	141°	244
3-HO ₃ S-4-(C ₂ H ₅ O)C ₆ H ₃	C ₁₇ H ₃₅	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	201°	11
2,4,6-Cl ₃ C ₆ H ₂	CH ₃	2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=	100°	519
1-C ₁₀ H ₇	CH ₃	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	176°	244
			—	494
		H		
		4-(C ₂ H ₅)NC ₆ H ₄ NH		
		2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=	215°	695
		2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=	229° (dec.)	244
		CH ₃ CONH	141°	244
		H		
		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	201°	11
		2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=	100°	519
		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	176°	244
			—	494
		2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=	200°	244
		2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=	153°	244
		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	218°	519

(Table continued)

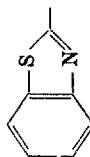
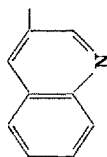
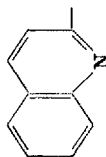
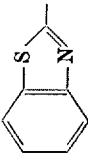
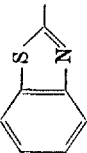
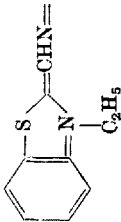
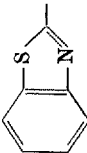
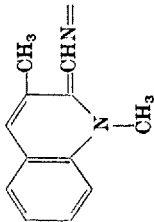
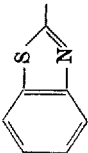
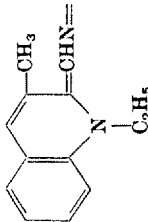
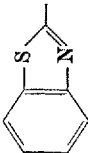
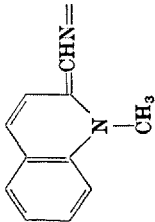
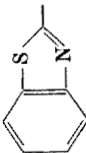
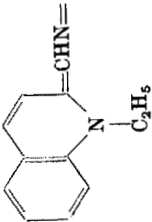
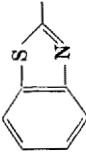
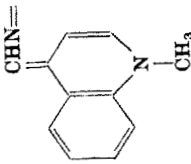
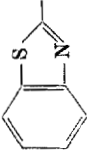
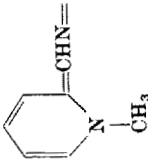
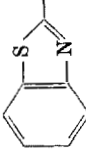
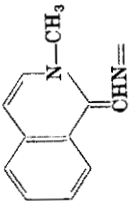
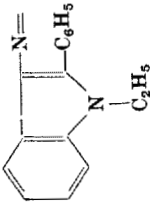


TABLE XXII (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
	CH ₃		2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	204°	244
	CH ₃			> 300°	240
	CH ₃			278° (dec.)	240
	CH ₃			270° (dec.)	240
	CH ₃			> 300°	240

	CH ₃		> 300°	240
	CH ₃		303° (dec.)	240
	CH ₃		303° (dec.)	240
	CH ₃		261° (dec.)	240
C ₆ H ₅	CH ₃		207°	943

(Table continued)

TABLE XXII (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅			2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=	191°	244
4-HO ₃ SC ₆ H ₄	4-NO ₂ C ₆ H ₄ CH ₂		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	> 350°	519
C ₆ H ₅	C ₆ H ₅		2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=	166°	244
C ₆ H ₅	C ₆ H ₅		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	136°	519
C ₆ H ₅	2-CH ₃ C ₆ H ₄		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	129°	519
C ₆ H ₅	2-HOC ₆ H ₄		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	172°	670
C ₆ H ₅	3-NH ₂ C ₆ H ₄		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	169°	519
C ₆ H ₅	4-NH ₂ C ₆ H ₄		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	163°	519
C ₆ H ₅	3-NO ₂ C ₆ H ₄		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	170°	519
C ₆ H ₅	4-NO ₂ C ₆ H ₄		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	168°	519
C ₆ H ₅	C ₆ H ₅	H	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	—	494
4-NH ₂ C ₆ H ₄	4-NO ₂ C ₆ H ₄		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	—	494
3-NO ₂ C ₆ H ₄	C ₆ H ₅		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	—	494
4-NO ₂ C ₆ H ₄	C ₆ H ₅		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	—	494
3-HOCC ₆ H ₄	3-C ₁₇ H ₃₅ CONHC ₆ H ₄		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	145°	519
3-HOCC ₆ H ₄	4-C ₁₇ H ₃₅ CONHC ₆ H ₄		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	213°	519
3-HOCC ₆ H ₄	3-NO ₂ C ₆ H ₄		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	254°	519
3-HOCC ₆ H ₄	4-NO ₂ C ₆ H ₄		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	> 350°	519
3-KOCC ₆ H ₄	4-NO ₂ C ₆ H ₄		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	—	494
4-KOCC ₆ H ₄	C ₆ H ₅		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	—	494
4-KOCC ₆ H ₄	4-NO ₂ C ₆ H ₄		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	—	494
3-HO ₃ SC ₆ H ₄	3-C ₁₇ H ₃₅ CONHC ₆ H ₄		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	193°	519
3-HO ₃ SC ₆ H ₄	4-C ₁₇ H ₃₅ CONHC ₆ H ₄		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	> 350°	519
3-HO ₃ SC ₆ H ₄	3-NO ₂ C ₆ H ₄		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	245°	519
4-HO ₃ SC ₆ H ₄	C ₆ H ₅		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	219°	519
4-HO ₃ SC ₆ H ₄	3-NH ₂ C ₆ H ₄		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	> 350°	519
4-HO ₃ SC ₆ H ₄	4-NH ₂ C ₆ H ₄		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	> 300°	519
4-HO ₃ SC ₆ H ₄	3-C ₁₇ H ₃₅ CONHC ₆ H ₄		4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	224°	519

4-HO ₃ SC ₆ H ₄	4-C ₁₇ H ₃₃ CONHC ₆ H ₄	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	> 350°	519
4-HO ₃ SC ₆ H ₄	3-NO ₂ C ₆ H ₄	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	275°	519
4-HO ₃ SC ₆ H ₄	4-NO ₂ C ₆ H ₄	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	> 250°	519
4-NH ₂ O ₂ SC ₆ H ₄	C ₆ H ₅	4-(C ₂ H ₅) ₂ NC ₆ H ₄ NH	225°	695
2-C ₁₀ H ₇	C ₆ H ₅	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	—	494
2-C ₁₀ H ₇	4-NO ₂ C ₆ H ₄	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	—	494
C ₆ H ₅	CH ₃	(CH ₃) ₂ N	96°	938
C ₆ H ₅	C ₆ H ₅ CH=N	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	152°	519
C ₆ H ₅	CH ₃	CH ₃ OOCCH ₂ NH	—	525
CH ₃ CO	CH ₃	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	119°	519
CH ₃ CO	C ₆ H ₅	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=	113°	519

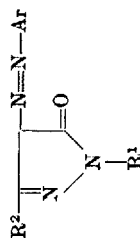


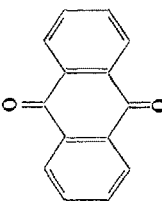
TABLE XXIII. 4-Arylazo-2-pyrazolin-5-ones

Section A. Alkyl and Aryl Substituents

R ¹	R ²	Ar	M.p.	Reference
H	H	C ₆ H ₅	196°	813
H	H	4-CH ₃ C ₆ H ₄	223° (dec.)	813, 1548, 1553
H	H	2-Cl-4-H ₃ C ₂ NHHSO ₂ -6-NO ₂ C ₆ H ₂	—	963
H	CH ₃	C ₆ H ₅	197°	255, 257, 262, 263, 264, 1553

(Table continued)

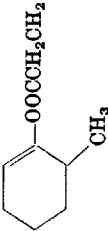
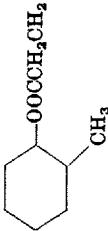
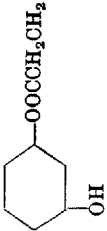
TABLE XXIII, Section A (continued)

R ¹	R ²	Ar	M.p.	Reference
H	CH ₃	2-CH ₃ C ₆ H ₅	223°	263, 264
H	CH ₃	3-CH ₃ C ₆ H ₄	190°	262, 263, 264
H	CH ₃	4-CH ₃ C ₆ H ₄	234°	263, 264
H	CH ₃	4-NO ₂ C ₆ H ₄	267° (dec.)	262, 263
H	CH ₃	2-HOOC ₆ H ₄	> 280°	263, 264
H	CH ₃	2-H ₂ O ₃ AsC ₆ H ₄	268°	314
H	CH ₃	3-H ₂ O ₃ AsC ₆ H ₄	> 250°	314
H	CH ₃	4-H ₂ O ₃ AsC ₆ H ₄	> 250°	314
H	CH ₃	2-CH ₃ -X-NO ₂ C ₆ H ₃	223° (dec.)	260
H	CH ₃	3-CH ₃ -4-NO ₂ C ₆ H ₃	—	262
H	CH ₃	4-CH ₃ -X-NO ₂ C ₆ H ₃	235°	260
H	CH ₃	2-HO-5-C ₆ H ₄ NHSO ₂ C ₆ H ₃	—	1457
H	CH ₃	2,4-(NO ₂) ₂ C ₆ H ₃	277°	263
H	CH ₃	2-(2-HO ₃ S-4-ClC ₆ H ₃ O)-5-ClC ₆ H ₃	—	582
H	CH ₃	4-C ₆ H ₁₁ -2-HO ₃ SC ₆ H ₃	—	582
H	CH ₃	4-C ₆ H ₅ -2-HO ₃ SC ₆ H ₃	—	582
H	CH ₃	2-NO ₂ -4-C ₆ H ₄ NHSO ₂ C ₆ H ₃	—	963
H	CH ₃	2-NO ₂ -4-H ₂ O ₃ AsC ₆ H ₃	> 250°	314
H	CH ₃	2-HO-3-Cl-5-NO ₂ C ₆ H ₂	—	865
H	CH ₃	2-HO-4-NO ₂ -5-ClC ₆ H ₂	—	865
H	CH ₃	1-C ₁₀ H ₇	247°	263, 264
H	CH ₃	2-C ₁₀ H ₇	238°	263, 264
				
H	CH ₃		—	1251
H	H ₅ C ₂ OOCCH ₂	4-CH ₃ C ₆ H ₄	172°	866

H	CH ₃	C ₆ H ₅	188°	1560
—	CH ₃	2-NO ₂ -4-CH ₃ C ₆ H ₃	—	206
—	CH ₃	2-HO-4-NH ₂ O ₂ SC ₆ H ₃	—	206
—	CH ₃	2-HO-4-CH ₃ NHO ₂ SC ₆ H ₃	—	228, 1681
—	CH ₃	2-HO-3-HO ₂ S-5-NO ₂ C ₆ H ₂	—	206
—	CH ₃	2-HO-4-NO ₂ C ₆ H ₃	—	253
—	CH ₃	2-HO-5-CH ₃ O ₂ SC ₆ H ₃	—	253
—	CH ₃	2-HO-4-H ₂ NO ₂ SC ₆ H ₃	—	253
—	CH ₃	2-HO-5-H ₂ NO ₂ SC ₆ H ₃	—	253
—	CH ₃	2-HO-4-H ₂ NO ₂ SC ₆ H ₃	—	253
—	CH ₃	2-HO-5-H ₂ NO ₂ SC ₆ H ₃	—	253
—	CH ₃	2-HO-5-H ₂ NO ₂ SC ₆ H ₃	—	253
—	CH ₃	2-HO-4-H ₂ NO ₂ S-6-NO ₂ C ₆ H ₂	—	253, 1463
—	CH ₃	2-HO-3-NO ₂ -5-H ₂ NO ₂ SC ₆ H ₂	—	253
—	CH ₃	4-HO ₂ SC ₆ H ₄	—	206
—	CH ₃	2,5-(HO ₂ S) ₂ C ₆ H ₃	—	206
—	CH ₃	4,8-(HO ₂ S) ₂ -2-C ₁₀ H ₅	—	206
—	CH ₃	2-CH ₃ C ₆ H ₄	83°	1118
—	CH ₃	2-CH ₃ C ₆ H ₄	—	1118
—	CH ₃	2-NO ₂ C ₆ H ₄	—	1118
—	CH ₃	2-NO ₂ C ₆ H ₄	112°	1118
—	CH ₃	2-NO ₂ C ₆ H ₄	101°	1118
—	CH ₃	2-CH ₃ C ₆ H ₄	59°	1118
—	CH ₃	2-NO ₂ C ₆ H ₄	96°	1118
—	CH ₃	2-NO ₂ C ₆ H ₄	85°	1118
—	CH ₃	2-NO ₂ C ₆ H ₄	70°	1118
—	CH ₃	2-NO ₂ C ₆ H ₄	112°	1118
—	CH ₃	2-NO ₂ C ₆ H ₄	54°	1118
—	CH ₃	2-NO ₂ C ₆ H ₄	92°	1118
—	CH ₃	2-NO ₂ C ₆ H ₄	120°	1118

(Table continued)

TABLE XXIII, Section A (continued)

R ¹	R ²	Ar	M.p.	Reference
C ₄ H ₉ OCH ₂ CH ₂ OOCCH ₂ CH ₂ HOCH ₂ CH ₂ OCH ₂ CH ₂ OOCCH ₂ CH ₂ CH ₃ CHCH ₂ OOCCH ₂ CH ₂ OH	CH ₃ CH ₃ CH ₃	2-NO ₂ C ₆ H ₄ 2-NO ₂ C ₆ H ₄ 2-NO ₂ C ₆ H ₄	60° 107° 115°	1118 1118 1118
HOCH ₂ CHCH ₂ OOCCH ₂ CH ₂ Cl	CH ₃	2-NO ₂ C ₆ H ₄	135°	1118
	CH ₃	2-NO ₂ C ₆ H ₄	97°	1118
	CH ₃	2-NO ₂ C ₆ H ₄	122°	1118
4-C ₄ H ₉ - 	CH ₃	2-NO ₂ C ₆ H ₄	150°	1118
	CH ₃	2-NO ₂ C ₆ H ₄	125°	1118
	CH ₃	2-NO ₂ C ₆ H ₄	110°	1118

CNCH ₂ CH ₂ HOOCCH	CH ₃ CH ₃	2-NO ₂ C ₆ H ₄ 2-NO ₂ C ₆ H ₄	— —	1118 1118
— CH ₃ C ₄ H ₉ OOCCH	CH ₃	2-NO ₂ C ₆ H ₄	80°	1118
— CH ₃ C ₄ H ₉ OOCCH ₂ CH ₂ C ₄ H ₉ OOCCH ₂ CH ₂ C ₆ H ₅ CH ₂	CH ₃ CH ₃ CH ₃	2-CH ₃ -3-ClC ₆ H ₃ 2-NO ₂ -4-Cl-C ₆ H ₃ 4-CH ₃ C ₆ H ₄	59° 132° 123°	1118 1118 333

TABLE XXIII (continued)

Section B. Alkyl, Aryl, and Heterocyclic Substituents

R ¹	R ²	Ar	M. p.	Reference
C ₆ H ₅	H	C ₆ H ₅	150°	283, 352
H	C ₆ H ₅	C ₆ H ₅	208°	992, 1552, 1553
C ₆ H ₅	H	4-CH ₃ C ₆ H ₄	149°	1550
H	C ₆ H ₅	2-CH ₃ C ₆ H ₄	179°	1552
H	C ₆ H ₅	4-CH ₃ C ₆ H ₄	185°	1552
H	C ₆ H ₅	1-C ₁₀ H ₇	216°	1552
H	C ₆ H ₅	2-C ₁₀ H ₇	250°	1552
H	H	4-ClC ₆ H ₄	—	782
C ₆ H ₅	H	3-NO ₂ C ₆ H ₄	—	782
C ₆ H ₅	H	4-NO ₂ C ₆ H ₄	—	782

(Table continued)

TABLE XXIII, Section B (continued)

R ¹	R ²	Ar	M.p.	Reference
C ₆ H ₅	H	4-HO ₃ SC ₆ H ₄	—	782
C ₆ H ₅	H	2-NO ₂ -4-CH ₃ C ₆ H ₃	—	782
C ₆ H ₅	H	2-NO ₂ -4-(t-C ₄ H ₉)C ₆ H ₃	—	782
C ₆ H ₅	H	2-HO-5-HO ₃ SC ₆ H ₃	—	782
C ₆ H ₅	H	2-HOOC-4-HO ₃ SC ₆ H ₃	—	782
C ₆ H ₅	H	2-HOOC-5-HO ₃ SC ₆ H ₃	—	782
C ₆ H ₅	H	2-HO-3-HO ₃ S-5-ClC ₆ H ₂	—	782
C ₆ H ₅	H	2-HO-3-NO ₂ -5-HO ₃ SC ₆ H ₂	—	782
C ₆ H ₅	H	2-HO-3-HO ₃ S-5-NO ₂ C ₆ H ₂	—	782
C ₆ H ₅	H	1-C ₁₀ H ₇	—	782
C ₆ H ₅	H	2-C ₁₀ H ₇	—	782
C ₆ H ₅	H	6-HO ₃ S-2-C ₁₀ H ₆	—	782
C ₆ H ₅	H	2-HO-6-HO ₃ S-1-C ₁₀ H ₅	—	782
C ₆ H ₅	H	5,7-(HO ₃ S) ₂ -2-C ₁₀ H ₅	—	782
C ₆ H ₅	H	3,6-(NaO ₃ S) ₂ -2-C ₁₀ H ₅	—	782
C ₆ H ₅	H	2-HO-4-HO ₃ S-6-NO ₂ -1-C ₁₀ H ₄	—	782
C ₆ H ₅	H	2-HO-3-HO ₃ S-5-ClC ₆ H ₂	—	782
4-NO ₂ C ₆ H ₄	H	2-HO ₃ C ₆ H ₄	—	782
4-HO ₃ SC ₆ H ₄	H	4-NO ₂ C ₆ H ₄	—	782
4-HO ₃ SC ₆ H ₄	H	2-HOOC ₆ H ₄	—	782
4-HO ₃ SC ₆ H ₄	H	4-HO ₃ SC ₆ H ₄	—	782
4-HO ₃ SC ₆ H ₄	H	2-HO-5-ClC ₆ H ₃	—	782
4-HO ₃ SC ₆ H ₄	H	2-HO-5-NO ₂ C ₆ H ₃	—	782
4-HO ₃ SC ₆ H ₄	H	2-HO-5-HO ₃ SC ₆ H ₃	—	782
4-HO ₃ SC ₆ H ₄	H	2-HOOC-4-HO ₃ SC ₆ H ₃	—	782
4-HO ₃ SC ₆ H ₄	H	2-HO-3-HO ₃ S-5-ClC ₆ H ₂	—	782
4-HO ₃ SC ₆ H ₄	H	2-HO-3-HO ₃ S-5-NO ₂ C ₆ H ₂	—	782
4-HO ₃ SC ₆ H ₄	H	2-HO-4-HO ₃ S-1-C ₁₀ H ₅	—	782
4-HO ₃ SC ₆ H ₄	H	1-HO-4-HO ₃ S-2-C ₁₀ H ₅	—	782
4-HO ₃ SC ₆ H ₄	H	2-HO-4-HO ₃ S-6-NO ₂ -1-C ₁₀ H ₄	—	782
2,4,5-Cl ₃ C ₆ H ₂	H	2,4,5-Cl ₃ C ₆ H ₂	308° (dec.)	285

TABLE XXIII, Section B (continued)

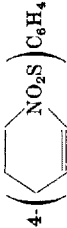
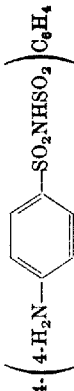
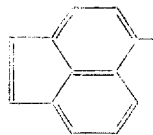
R ¹	R ²	Ar	M.p.	Reference
C ₆ H ₅	CH ₃	4-ClC ₆ H ₄	140°	278, 327
C ₆ H ₅	CH ₃	4-BrC ₆ H ₄	151°	278, 327
C ₆ H ₅	CH ₃	2-NO ₂ C ₆ H ₄	209°	278, 327
C ₆ H ₅	CH ₃	3-NO ₂ C ₆ H ₄	183°	278, 327
C ₆ H ₅	CH ₃	4-NO ₂ C ₆ H ₄	198°	263, 278, 732
C ₆ H ₅	CH ₃	4-CH ₃ COC ₆ H ₄	136°	327
C ₆ H ₅	CH ₃	4-CH ₃ CC ₆ H ₄ = NOH NNHC ₆ H ₅ =	187°	327
C ₆ H ₅	CH ₃	4-CH ₃ CC ₆ H ₄ = NNHCONH ₂ =	148°	327
C ₆ H ₅	CH ₃	4-CH ₃ CC ₆ H ₄ =	260°	327
C ₆ H ₅	CH ₃	2-(C ₆ H ₅ SO ₂ NHOC)C ₆ H ₄	—	864
C ₆ H ₅	CH ₃	4-(4-NO ₂ C ₆ H ₄ SO ₂)C ₆ H ₄	240°	1677
C ₆ H ₅	CH ₃	3-NaO ₃ SC ₆ H ₄	—	280
C ₆ H ₅	CH ₃	4-NaO ₃ SC ₆ H ₄	—	280
C ₆ H ₅	CH ₃	4-ClO ₂ SC ₆ H ₄	150°	1591
C ₆ H ₅	CH ₃	4-H ₂ NO ₂ SC ₆ H ₄	247°	1591
C ₆ H ₅	CH ₃	4-CH ₃ NHO ₂ SC ₆ H ₄	192°	1591
C ₆ H ₅	CH ₃	4-(C ₂ H ₅) ₂ NO ₂ SC ₆ H ₄	154°	1591
C ₆ H ₅	CH ₃	4-C ₆ H ₅ NHO ₂ SC ₆ H ₄	243°	1591
C ₆ H ₅	CH ₃	4-( C ₆ H ₄	—	1591
C ₆ H ₅	CH ₃	4-( C ₆ H ₄	255°	1591

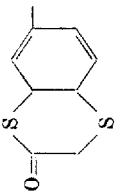
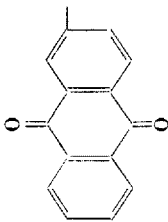
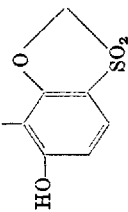
TABLE XXIII, Section B (continued)

R ¹	R ²	Ar	M.p.	Reference
C ₆ H ₅	CH ₃	3,4-(CH ₃) ₂ -2-HO ₃ SC ₆ H ₂	—	523
C ₆ H ₅	CH ₃	3-NO ₂ -4-CH ₃ -5-HO ₃ SC ₆ H ₂	—	123
C ₆ H ₅	CH ₃	2-HO-4-HS-5-ClC ₆ H ₂	—	879
C ₆ H ₅	CH ₃	2-HO-4-NO ₂ -5-CH ₃ O ₂ SC ₆ H ₂	—	1445
C ₆ H ₅	CH ₃	2-HO-3-HO ₃ S-5-ClC ₆ H ₂	—	1444
C ₆ H ₅	CH ₃	2-HO-3-H ₂ NO ₂ S-5-NO ₂ C ₆ H ₂	—	214
C ₆ H ₅	CH ₃	2,5-(C ₂ H ₅ O) ₂ -4-C ₆ H ₅ CONHC ₆ H ₂	254°	885
C ₆ H ₅	CH ₃	2-C ₆ H ₅ COO-3-HO ₃ S-5-NO ₂ C ₆ H ₂	—	442
C ₆ H ₅	CH ₃	2-C ₆ H ₅ COO-3-HO ₃ S-5-ClC ₆ H ₂	—	442
C ₆ H ₅	CH ₃	2-C ₆ H ₅ COO-3-HOOC-4-HO ₃ SC ₆ H ₂	—	442
C ₆ H ₅	CH ₃	2-(4-NO ₂ C ₆ H ₅ COO)-3-HO ₃ S-5-NO ₂ C ₆ H ₂	—	442
C ₆ H ₅	CH ₃	2-HO-3-HO ₃ S-5-[2,2,4-(CH ₃) ₃ C ₆ H ₈]C ₆ H ₂	—	1386
C ₆ H ₅	CH ₃	2-HO-3,6-Cl ₂ -5-HO ₃ SC ₆ H	—	276
C ₆ H ₅	CH ₃	2-HO-3,5-Cl ₂ -4-HSC ₆ H	—	879
C ₆ H ₅	CH ₃	1-C ₁₀ H ₇	—	263, 278, 327
C ₆ H ₅	CH ₃	2-C ₁₀ H ₇	—	263, 278, 327
C ₆ H ₅	CH ₃	2-NO ₂ -1-C ₁₀ H ₆	202°	327
C ₆ H ₅	CH ₃	4-NO ₂ -1-C ₁₀ H ₆	186°	327
C ₆ H ₅	CH ₃	1-NaO ₃ S-2-C ₁₀ H ₆	138°	327
C ₆ H ₅	CH ₃	2-C ₆ H ₇ COO-4-HO ₃ S-1-C ₁₀ H ₅	125°	280
C ₆ H ₅	CH ₃	2-C ₆ H ₅ COO-4-HO ₃ SC ₁₀ H ₅	—	442
C ₆ H ₅	CH ₃	2-HO-4-HO ₃ S-6-CH ₃ O-1-C ₁₀ H ₅	—	442
C ₆ H ₅	CH ₃	2-HO-4-HO ₃ S-1-C ₁₀ H ₅	—	189, 1616
C ₆ H ₅	CH ₃	2-C ₆ H ₅ COO-4-HO ₃ S-6-NO ₂ -1-C ₁₀ H ₄	—	441, 1618
C ₆ H ₅	CH ₃		—	442

CH₃C₆H₅

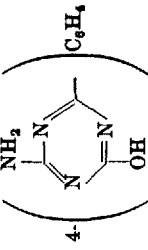
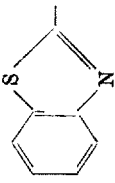
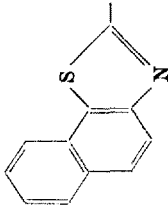
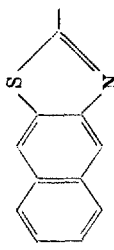
146°

327

$\equiv$ * C_6H_5	CH_3		272°	936
C_6H_5	CH_3		247°	1009
C_6H_5 C_6H_5 C_6H_5 C_6H_5	CH_3 CH_3 CH_3 CH_3	1- C_6H_5 -3- CH_3 -4-pyrazolyl 1- C_6H_5 -5-Cl-4-pyrazolyl 4-[2,5-(CH_3) ₂ -3,4-(H_5C_2OOC) ₂ -1-pyrrolyl] C_6H_4 5-Tetrazolyl	220° (dec.) 143° 154° 201°	995 974 261 256
C_6H_5	CH_3		228° (dec.)	1629
C_6H_5	CH_3		—	375
C_6H_5	CH_3	4-(HN—N—) C_6H_4	—	834, 1146

(Table continued)

TABLE XXIII, Section B (*continued*)

R ¹	R ²	Ar	M.p.	Reference
C ₆ H ₅	CH ₃		—	1493
C ₆ H ₅	CH ₃		160°	281
C ₆ H ₅	CH ₃		205°	281
C ₆ H ₅	CH ₃		215°	281
C ₆ H ₅	CH ₃		248°	281

C_6H_5	C_6H_7	C_6H_5	C_6H_5	133°	1535
C_6H_5	C_6H_6	C_6H_5	C_6H_5	119°	1576
C_6H_5	$C_{12}H_{21}$	$4-CH_3CONHC_6H_4$	$4-CH_3CONHC_6H_4$	—	403
C_6H_5	$3-HOCH_2$	C_6H_5	C_6H_5	155°	397
C_6H_5	$3-CH_3COOCH_2$	C_6H_5	C_6H_5	131°	397
C_6H_5	$3-HOCH_2$	$4-ClC_6H_4$	$4-ClC_6H_4$	186°	397
C_6H_5	$3-HOCH_2CH(OH)CH(OH)-$	C_6H_5	C_6H_5	210°	627
$HOOCCH_2CH_2$	C_6H_5	$2-CH_3-3-ClC_6H_5$	$2-CH_3-3-ClC_6H_5$	—	1118
$H_9C_4OOCCH_2CH_2$	C_6H_5	$2-CH_3-3-ClC_6H_5$	$2-CH_3-3-ClC_6H_5$	73°	1118
$2-CH_3C_6H_4$	CH_3	$2-NaOOCCH_2CH_2COOCH_2CH_2SO_2C_6H_4$	$2-NaOOCCH_2CH_2COOCH_2CH_2SO_2C_6H_4$	—	1398
$2-CH_3C_6H_4$	CH_3	$2-NaOOCCH=CHCOOCH_2CH_2SO_2C_6H_4$	$2-NaOOCCH=CHCOOCH_2CH_2SO_2C_6H_4$	—	1398
$2-CH_3C_6H_4$	CH_3	$HO_2SOCH_2CH_2SO_2C_6H_4$	$HO_2SOCH_2CH_2SO_2C_6H_4$	—	1398
$2-CH_3C_6H_4$	$HOCH_2$	$2-CH_3C_6H_4$	$2-CH_3C_6H_4$	149°	397
$2-CH_3C_6H_4$	CH_3	$2-HOOC-4-(CH_3)_2CHNHSO_2C_6H_3$	$2-HOOC-4-(CH_3)_2CHNHSO_2C_6H_3$	—	1462
$2-CH_3C_6H_4$	CH_3	$2-HOOC-4-C_6H_4NHSO_2C_6H_3$	$2-HOOC-4-C_6H_4NHSO_2C_6H_3$	—	1462
$2-CH_3C_6H_4$	CH_3	$2-HOOC-4-C_6H_4NHSO_2C_6H_3$	$2-HOOC-4-C_6H_4NHSO_2C_6H_3$	—	1462
$4-CH_3C_6H_4$	CH_3	$4-CH_3C_6H_4$	$4-CH_3C_6H_4$	216°	987
$4-CH_3C_6H_4$	CH_3	$2-NaOOC-5-ClC_6H_3$	$2-NaOOC-5-ClC_6H_3$	—	625
$4-CH_3C_6H_4$	CH_3	$2-Ca_{1/2}OOC-5-ClC_6H_3$	$2-Ca_{1/2}OOC-5-ClC_6H_3$	—	625
$4-CH_3C_6H_4$	CH_3	$2-Sr_{1/2}OOC-5-ClC_6H_3$	$2-Sr_{1/2}OOC-5-ClC_6H_3$	—	625
$4-CH_3C_6H_4$	CH_3	$3-(4-ClC_6H_4SO_2NHSO_2C_6H_4$	$3-(4-ClC_6H_4SO_2NHSO_2C_6H_4$	—	180
$4-CH_3C_6H_4$	CH_3	$2-HOOC-4-CH_3NHSO_2C_6H_3$	$2-HOOC-4-CH_3NHSO_2C_6H_3$	—	1458, 1462
$4-t-C_4H_9C_6H_4$	CH_3	$2-HO-5-NO_2C_6H_3$	$2-HO-5-NO_2C_6H_3$	—	1383
$4-CH_3OC_6H_4$	$H_8C_3OOCCH=CHCH=CH$	$2,4-(NO_2)_2C_6H_3$	$2,4-(NO_2)_2C_6H_3$	258°	125
$4-(t-C_4H_9C_6H_4O)C_6H_4$	CH_3	$4-HOC_6H_4$	$4-HOC_6H_4$	185°	403, 575
$4-(4-ClC_6H_4O)C_6H_4$	CH_3	$2-HO-3-NO_2-5-HO_3SC_6H_2$	$2-HO-3-NO_2-5-HO_3SC_6H_2$	—	79
$3-NH_2C_6H_4$	CH_3	$3-ClC_6H_4$	$3-ClC_6H_4$	—	878
$3-NH_2C_6H_4$	CH_3	$2-CH_3-4-ClC_6H_3$	$2-CH_3-4-ClC_6H_3$	—	878
$3-NH_2C_6H_4$	CH_3	$2-CH_3O-5-ClC_6H_3$	$2-CH_3O-5-ClC_6H_3$	—	877, 878
$3-NH_2C_6H_4$	CH_3	$2-F_3C-4-ClC_6H_3$	$2-F_3C-4-ClC_6H_3$	—	878
$4-NH_2C_6H_4$	CH_3	$1-C_6H_7$	$1-C_6H_7$	—	878
$4-NH_2C_6H_4$	CH_3	$2-HO-5-(4-HO_3SC_6H_4NHCO)C_6H_3$	$2-HO-5-(4-HO_3SC_6H_4NHCO)C_6H_3$	—	209
$4-NH_2C_6H_4$	CH_3	$3-ClC_6H_4$	$3-ClC_6H_4$	—	878

(Table continued)

TABLE XXIII, Section B (continued)

R ¹	R ²	Ar	M.P.	Reference
4-NH ₂ C ₆ H ₄	CH ₃	2-HOOC-4-HO ₃ SC ₆ H ₃	—	226
3-C ₆ H ₅ SO ₂ NHC ₆ H ₅	CH ₃	4-HO ₃ S-2-C ₁₀ H ₆	—	467
4-(4-HOOCCH ₂ SO ₂ NH)C ₆ H ₄	CH ₃	2,3,5-Cl ₃ -6-HOOCCH ₂ H	—	160
3-(2-HO-1-C ₁₀ H ₆ CONH)C ₆ H ₄	CH ₃	2-CH ₃ O-5-ClC ₆ H ₃	262°	877
3-(2-HO-1-C ₁₀ H ₆ CONH)C ₆ H ₄	CH ₃	2-CH ₃ O-4-ClC ₆ H ₃	277°	877
3-(2-HO-1-C ₁₀ H ₆ CONH)C ₆ H ₄	CH ₃	2-CH ₃ -4-ClC ₆ H ₃	260°	877
4-(2-HO-1-C ₁₀ H ₆ CONH)C ₆ H ₄	CH ₃	2-CH ₃ -4-ClC ₆ H ₃	283°	877
3-(2-HO-1-C ₁₀ H ₆ CONH)C ₆ H ₄	CH ₃	2-CF ₃ -4-ClC ₆ H ₃	262°	877
4-(2-HO-1-C ₁₀ H ₆ CONH)C ₆ H ₄	CH ₃	3-ClC ₆ H ₄	260°	877
3-(2-HO-1-C ₁₀ H ₆ CONH)C ₆ H ₄	CH ₃	1-C ₁₀ H ₇	226°	877
4-CH ₃ OC ₆ H ₄	CH ₃	2-HO-5-ClC ₆ H ₃	—	1456
4-CH ₃ OC ₆ H ₄	CH ₃	2-HO-4-H ₂ NO ₂ SC ₆ H ₃	—	1456
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	2-HO-4-H ₂ NO ₂ SC ₆ H ₃	—	1456
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	2-HO-5-H ₂ NO ₂ SC ₆ H ₃	—	1456
2-ClC ₆ H ₄	CH ₃	2-ClC ₆ H ₄	212°	286
2-ClC ₆ H ₄	CH ₃	4-HOOCCH ₂ CH ₂ COOCH ₂ CH ₂ SO ₂ C ₆ H ₄	—	1034
2-ClC ₆ H ₄	CH ₃	4-NaOOCCH ₂ CH ₂ COOCH ₂ CH ₂ SO ₂ C ₆ H ₄	—	1398
2-ClC ₆ H ₄	CH ₃	4-NaOOCCH=CHCOOCH ₂ CH ₂ SO ₂ C ₆ H ₄	—	1398
2-ClC ₆ H ₄	CH ₃	4-HO ₃ SOCH ₂ CH ₂ SO ₂ C ₆ H ₄	—	1398
2-ClC ₆ H ₄	CH ₃	2-HO-5-H ₃ C ₃ SO ₂ C ₆ H ₃	—	1455
2-ClC ₆ H ₄	CH ₃	2-C ₆ H ₅ COO-4-HO ₃ S-1-C ₁₀ C ₅	—	442
HOCH ₂	HOCH ₂	2-ClC ₆ H ₄	203° (dec.)	397
3-ClC ₆ H ₄	CH ₃	2-H ₂₁ C ₁₀ OOCCH ₂ H ₄	—	217
3-ClC ₆ H ₄	CH ₃	2-(3,4-Cl ₂ C ₆ H ₃ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3-ClC ₆ H ₄	CH ₃	2-(2,4,5-Cl ₃ C ₆ H ₂ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3-ClC ₆ H ₄	CH ₃	2-(4-ClC ₆ H ₄ SO ₂ NHSO ₂)-5-ClC ₆ H ₃	—	180
3-ClC ₆ H ₄	CH ₃	2-(1-C ₁₀ H ₇ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3-ClC ₆ H ₄	CH ₃	2-(2-C ₁₀ H ₇ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3-ClC ₆ H ₄	CH ₃	2-(2-CH ₃ -5-iso-C ₃ H ₇ C ₆ H ₃ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3-ClC ₆ H ₄	CH ₃	2-(5-CH ₃ -2-iso-C ₃ H ₇ C ₆ H ₃ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3-ClC ₆ H ₄	CH ₃	2-(5,6,7,8-H ₄ -1-C ₁₀ H ₇ SO ₂ NHSO ₂)C ₆ H ₄	—	180

3-ClC ₆ H ₄	CH ₃	2-(5,6,7,8-H ₄ -2-C ₁₀ H ₇ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3-ClC ₆ H ₄	CH ₃	3-(1-C ₁₀ H ₇ SO ₂ NHSO ₂)-4-CH ₃ C ₆ H ₃	—	180
3-ClC ₆ H ₄	CH ₃	3-(2,4-Cl ₂ C ₆ H ₃ SO ₂ NHSO ₂)-4-CH ₃ C ₆ H ₃	—	180
3-ClC ₆ H ₄	CH ₃	3-(2,5-Cl ₂ C ₆ H ₃ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3-ClC ₆ H ₄	CH ₃	2-(C ₆ H ₅ SO ₂ NHSO ₂)-5-ClC ₆ H ₃	—	180
3-ClC ₆ H ₄	CH ₃	2-(2,5-Cl ₂ C ₆ H ₃ SO ₂ NHSO ₂)-5-ClC ₆ H ₃	—	180
3-ClC ₆ H ₄	CH ₃	3-(2,4,5-Cl ₃ C ₆ H ₃ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3-ClC ₆ H ₄	CH ₃	3-(4,5-Cl ₂ C ₆ H ₃ SO ₂ NHSO ₂)-4-ClC ₆ H ₃	—	180
3-ClC ₆ H ₄	CH ₃	2-(2,4-Cl ₂ C ₆ H ₃ SO ₂ NHSO ₂)-5-ClC ₆ H ₃	—	180
3-ClC ₆ H ₄	CH ₃	3-(5,6,7,8-H ₄ -1-C ₁₀ H ₇ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3-ClC ₆ H ₄	CH ₃	3-(5,6,7,8-H ₄ -2-C ₁₀ H ₇ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3-ClC ₆ H ₄	CH ₃	2-(5,6,7,8-H ₄ -1-C ₁₀ H ₇ SO ₂ NHSO ₂)-5-ClC ₆ H ₃	—	180
3-ClC ₆ H ₄	CH ₃	2-(5,6,7,8-H ₄ -2-C ₁₀ H ₇ SO ₂ NHSO ₂)-5-ClC ₆ H ₃	—	180
3-ClC ₆ H ₄	CH ₃	2-(3,4-Cl ₂ C ₆ H ₃ SO ₂ NHSO ₂)-5-ClC ₆ H ₃	—	180
3-ClC ₆ H ₄	CH ₃	2-(1-C ₁₀ H ₇ SO ₂ NHSO ₂)-5-ClC ₆ H ₃	—	180
3-ClC ₆ H ₄	CH ₃	2-(4-ClC ₆ H ₄ SO ₂ NHSO ₂)-5-ClC ₆ H ₃	—	180
3-ClC ₆ H ₄	CH ₃	2-(4-BrC ₆ H ₄ SO ₂ NHSO ₂)-5-ClC ₆ H ₃	—	180
3-ClC ₆ H ₄	CH ₃	2-(4-CH ₃ OC ₆ H ₄ SO ₂ NHSO ₂)-5-ClC ₆ H ₃	—	180
3-ClC ₆ H ₄	CH ₃	2-(4-CH ₃ CONHC ₆ H ₄ SO ₂ NHSO ₂)-5-ClC ₆ H ₃	—	180
3-ClC ₆ H ₄	CH ₃	3-(C ₆ H ₅ CH ₂ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3-ClC ₆ H ₄	CH ₃	3-(4-ClC ₆ H ₄ CH ₂ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3-ClC ₆ H ₄	CH ₃	3-(4-BrC ₆ H ₄ CH ₂ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3-ClC ₆ H ₄	CH ₃	2-(3,4-Cl ₂ C ₆ H ₃ SO ₂ NHSO ₂)-5-(4-ClC ₆ H ₅ O)C ₆ H ₃	—	180
3-ClC ₆ H ₄	CH ₃	2-(3,4-Cl ₂ C ₆ H ₃ SO ₂ NHSO ₂)-5-(4-C ₆ H ₅ O)C ₆ H ₃	—	180
3-ClC ₆ H ₄	CH ₃	2-(4-ClC ₆ H ₄ SO ₂ NHSO ₂)-5-(2-CH ₃ OC ₆ H ₄ O)C ₆ H ₃	—	180
3-ClC ₆ H ₄	CH ₃	4-(4-ClC ₆ H ₄ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3-ClC ₆ H ₄	CH ₃	4-(C ₆ H ₅ CH ₂ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3-ClC ₆ H ₄	CH ₃	2,4-Cl ₂ C ₆ H ₃	190°	296
3-ClC ₆ H ₄	CH ₃	2-HOOC-4-H ₄ NO ₂ SC ₆ H ₃	—	208
3-ClC ₆ H ₄	CH ₃	2-HO-5-CH ₃ SO ₂ C ₆ H ₃	—	211, 1446
3-ClC ₆ H ₄	CH ₃	2-HO-4-CH ₂ =CHO ₂ SC ₆ H ₃	—	650
3-ClC ₆ H ₄	CH ₃	2-HO-5-NO ₂ C ₆ H ₃	—	211
3-ClC ₆ H ₄	CH ₃	2-HO-4-HOCH ₂ CH ₂ NHO ₂ SC ₆ H ₃	—	211
3-ClC ₆ H ₄	CH ₃	2-HO-5-CH ₃ NHO ₂ SC ₆ H ₃	—	1460, 1461

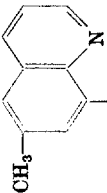
(Table continued)

TABLE XXIII, Section B (continued)

R ¹	R ²	Ar	M.p.	Reference
3-ClC ₆ H ₄	CH ₃	2-HO-4-(C ₂ H ₅) ₂ NO ₂ SC ₆ H ₃	—	211
3-ClC ₆ H ₄	CH ₃	2-HO-3-CH ₃ CONH-5-CH ₃ O ₂ SC ₆ H ₂	—	211
3-ClC ₆ H ₄	CH ₃	2-HO-5-C ₂ H ₅ O ₂ SC ₆ H ₃	—	219
3-ClC ₆ H ₄	CH ₃	2-HO-5-ClCH ₂ O ₂ SC ₆ H ₃	—	223
3-ClC ₆ H ₄	CH ₃	2-HOOC-5-ClCH ₂ O ₂ SC ₆ H ₃	—	223
3-ClC ₆ H ₄	CH ₃	2-HO-4-NO ₂ -5-CH ₃ SO ₂ C ₆ H ₂	—	1445
3-ClC ₆ H ₄	CH ₃	2-HO-3-NO ₂ -5-ClCH ₂ O ₂ SC ₆ H ₃	—	223
4-ClC ₆ H ₄	CH ₃	4-ClC ₆ H ₄	232°	296
4-ClC ₆ H ₄	CH ₃	2-HO-5-CH ₃ HNO ₂ SC ₆ H ₃	—	225, 1460, 1681
4-ClC ₆ H ₄	CH ₃	2-HO-4-CH ₃ HNO ₂ SC ₆ H ₃	—	228
4-ClC ₆ H ₄	CH ₃	2-HO-5-CH ₃ O ₂ SC ₆ H ₃	—	254
4-BrC ₆ H ₄	CH ₃	4-BrC ₆ H ₄	229°	446
4-BrC ₆ H ₄	CH ₃	2-(2-CH ₃ -5-iso-C ₂ H ₅ -C ₂ H ₅ SO ₂ NHSO ₂)C ₆ H ₄	—	180
4-BrC ₆ H ₄	CH ₃	2-(5-CH ₃ -2-iso-C ₂ H ₅ -C ₂ H ₅ SO ₂ NHSO ₂)C ₆ H ₄	—	180
4-BrC ₆ H ₄	CH ₃	2-(1-C ₁₀ H ₇ SO ₂ NHSO ₂)C ₆ H ₄	—	180
4-BrC ₆ H ₄	CH ₃	2-(2-C ₁₀ H ₇ SO ₂ NHSO ₂)C ₆ H ₄	—	180
4-BrC ₆ H ₄	CH ₃	2-(5,6,7,8-H ₄ -1-C ₁₀ H ₇ SO ₂ NHSO ₂)C ₆ H ₄	—	180
4-BrC ₆ H ₄	CH ₃	2-(5,6,7,8-H ₄ -2-C ₁₀ H ₇ SO ₂ NHSO ₂)C ₆ H ₄	—	180
4-BrC ₆ H ₄	CH ₃	2,4-(NO ₂)C ₆ H ₃	237°	125
4-BrC ₆ H ₄	H ₃ C ₂ OOCHC=CH	2,4-(NO ₂)C ₆ H ₃	264°	125
3-NO ₂ C ₆ H ₄	CH ₃	2-HO-5-ClC ₆ H ₃	—	1456
4-NO ₂ C ₆ H ₄	CH ₃	2-HO-5-H ₂ NO ₂ SC ₆ H ₃	—	1453, 1456
4-NO ₂ C ₆ H ₄	CH ₃	C ₆ H ₅	242°	690, 732
4-NO ₂ C ₆ H ₄	CH ₃	2-ClC ₆ H ₄	—	268
4-NO ₂ C ₆ H ₄	CH ₃	4-NO ₂ C ₆ H ₄	297°	732
4-NO ₂ C ₆ H ₄	CH ₃	2,5-Cl ₂ C ₆ H ₃	259°	591
4-NO ₂ C ₆ H ₄	CH ₃	2-HO-5-ClC ₆ H ₃	—	1456
4-NO ₂ C ₆ H ₄	CH ₃	2-HO-4-H ₂ NO ₂ SC ₆ H ₃	—	1456
4-NO ₂ C ₆ H ₄	CH ₃	2-Cl-5-(3,4-Cl ₂ C ₆ H ₃ SO ₂ NHSO ₂)C ₆ H ₃	—	180
2-HOOC ₆ H ₄	CH ₃	C ₆ H ₅	205°	1004

3-HOOCCH ₂ H ₄	CH ₃	C ₆ H ₅	245°	980
4-HOOCCH ₂ H ₄	CH ₃	C ₆ H ₅	277°	980
4-HOOCCH ₂ H ₄	CH ₃	4-H ₂ NO ₂ SC ₆ H ₄	291°	356
4-CH ₃ O ₂ SC ₆ H ₄	CH ₃	2-HO-5-NO ₂ C ₆ H ₃	—	1461
3-CH ₂ =CHO ₂ SC ₆ H ₄	CH ₃	4-HO ₂ SC ₆ H ₄	—	651
4-CH ₂ =CHO ₂ SC ₆ H ₄	CH ₃	2-HO ₂ SC ₆ H ₄	—	651
4-CHOCH ₂ CH ₂ O ₂ SC ₆ H ₄	CH ₃	2-CH ₃ O-5-HO ₂ SOCH ₂ CH ₂ O ₂ SC ₆ H ₄	—	651
4-HOCH ₂ CH ₂ O ₂ SC ₆ H ₄	CH ₃	2-HOOCCH ₂ H ₄	—	651
4-HOCH ₂ CH ₂ O ₂ SC ₆ H ₄	CH ₃	2-HO-4-HOCH ₂ CH ₂ O ₂ SC ₆ H ₃	—	648
4-HO ₂ SOCH ₂ CH ₂ O ₂ SC ₆ H ₄	CH ₃	2-HO-3,5-(NO ₂) ₂ C ₆ H ₂	—	651
4-HO ₂ SOCH ₂ CH ₂ O ₂ SC ₆ H ₄	CH ₃	2-HOOCCH ₂ H ₄	—	651
2-HO ₂ SC ₆ H ₄	CH ₃	2-HO-3,5-(NO ₂) ₂ C ₆ H ₂	—	651
3-HO ₂ SC ₆ H ₄	CH ₃	C ₆ H ₅	—	1293
3-HO ₂ SC ₆ H ₄	CH ₃	2-HO-5-CH ₃ COC ₆ H ₃	—	1619
3-HO ₂ SC ₆ H ₄	CH ₃	2-(C ₆ H ₅ SO ₂ HNO ₂)C ₆ H ₄	—	864
3-HO ₂ SC ₆ H ₄	CH ₃	2-(C ₆ H ₅ COHNO ₂)C ₆ H ₄	—	864
3-HO ₂ SC ₆ H ₄	CH ₃	3-(C ₆ H ₅ COHNO ₂)C ₆ H ₄	—	864
3-HO ₂ SC ₆ H ₄	CH ₃	2-HO-5-CH ₃ NHO ₂ SC ₆ H ₃	—	1460
3-HO ₂ SC ₆ H ₄	CH ₃	2-HOOC-4-(4-4-C ₆ H ₁₁ C ₆ H ₄ O ₂ SC ₆ H ₃	—	203
3-HO ₂ SC ₆ H ₄	CH ₃	2-HO-4-HO ₂ S-6-CH ₃ O-1-C ₁₀ H ₄	—	189
3-HO ₂ SC ₆ H ₄	CH ₃	2-CH ₃ O-4-HO ₂ S-6-CH ₃ O-1-C ₁₀ H ₄	—	189
3-HO ₂ SC ₆ H ₄	CH ₃	2,6-(CH ₃ O) ₂ -4-HO ₂ S-1-C ₁₀ H ₄	—	1616
3-H ₂ NO ₂ SC ₆ H ₄	CH ₃	2-Cl-5-(3,4-Cl ₂ C ₆ H ₃ SO ₂ NHSO ₂)C ₆ H ₃	—	180
3-H ₂ NO ₂ SC ₆ H ₄	CH ₃	2-HOOC-4-C ₆ H ₅ NHO ₂ SC ₆ H ₃	—	195, 1617
3-H ₂ NO ₂ SC ₆ H ₄	CH ₃	2-HOOC-4-iso-C ₆ H ₇ NHO ₂ SC ₆ H ₃	—	195
3-H ₂ NO ₂ SC ₆ H ₄	CH ₃	2-HO-3-Cl-5-NO ₂ C ₆ H ₃	—	207
3-H ₂ NO ₂ SC ₆ H ₄	CH ₃	2-HO-5-ClC ₆ H ₃	—	1680
3-H ₂ NO ₂ SC ₆ H ₄	CH ₃	2-HO-3-Cl-5-NO ₂ C ₆ H ₂	—	1680
3-H ₂ NO ₂ SC ₆ H ₄	CH ₃	2-HO-4-NO ₂ C ₆ H ₃	—	1444
3-H ₂ NO ₂ SC ₆ H ₄	CH ₃	2-HOOC-4-C ₆ H ₅ NO ₂ SC ₆ H ₃	—	1617
3-H ₂ NO ₂ SC ₆ H ₄	CH ₃	2-HOOC-4-C ₆ H ₅ NHO ₂ SC ₆ H ₄	—	1617
3-H ₂ NO ₂ SC ₆ H ₄	CH ₃	2-HO-4-NO ₂ C ₆ H ₃	—	1444

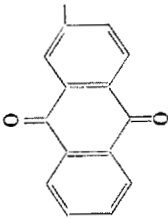
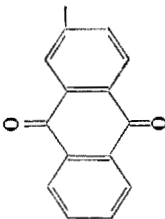
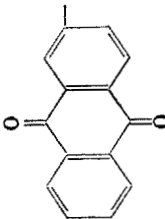
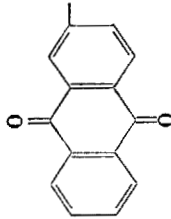
(Table continued)

4-H ₂ NO ₂ SC ₆ H ₄	CH ₃		211°	1629
2-(2-HOCCC ₆ H ₄ CO)C ₆ H ₄	CH ₃	2-HOCCC ₆ H ₄	—	160
2-CH ₃ -4-HO ₂ SOCH ₂ CH ₂ C ₆ H ₄	CH ₃	2-F ₃ C-4-ClC ₆ H ₄	—	651
4-CH ₃ -3-(CH ₃) ₂ NO ₂ SC ₆ H ₃	CH ₃	2-HO-5-OH ₂ NHO ₂ SC ₆ H ₃	—	1460
2-CH ₃ -O-5-CH ₂ =CHO ₂ SC ₆ H ₃	CH ₃	2-HO ₂ S-4-ClC ₆ H ₃	—	651
2-CH ₃ -O-5-HOCH ₂ CH ₂ O ₂ SC ₆ H ₃	CH ₃	2-ClC ₆ H ₄	—	651
2,4-Cl ₂ C ₆ H ₃	CH ₃	C ₆ H ₅	137°	296
2,5-Cl ₂ C ₆ H ₃	CH ₃	2,4-(CH ₃) ₂ C ₆ H ₃	—	1438
3,4-Cl ₂ C ₆ H ₃	CH ₃	2-Cl-5-(C ₆ H ₅ SO ₂ NHSO ₂)C ₆ H ₃	—	180
3,4-Cl ₂ C ₆ H ₃	CH ₃	2-HO-5-HO ₂ SC ₆ H ₃	—	80
3,4-Cl ₂ C ₆ H ₃	CH ₃	2-(2-CH ₃ -5-iso-C ₃ H ₇ C ₆ H ₃ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3,4-Cl ₂ C ₆ H ₃	CH ₃	2-(5-OH ₂ -2-iso-C ₃ H ₇ C ₆ H ₃ SO ₂ NHSO ₂)C ₆ H ₃	—	180
3,4-Cl ₂ C ₆ H ₃	CH ₃	2-HOOC-4-H ₂ NO ₂ SC ₆ H ₃	—	208
3,4-Cl ₂ C ₆ H ₃	CH ₃	2-HOOC-4-(2-HOCC ₆ H ₄ NHO ₂ S)C ₆ H ₃	—	208
3,4-Cl ₂ C ₆ H ₃	CH ₃	2-HO-3-NO ₂ -5-HO ₂ SC ₆ H ₂	—	80
3,4-Cl ₂ C ₆ H ₃	CH ₃	2-HO-3-HO ₂ S-5-CH ₃ C ₆ H ₂	—	80
3,4-Cl ₂ C ₆ H ₃	CH ₃	3-(4-CH ₃ C ₆ H ₄ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3,4-Cl ₂ C ₆ H ₃	CH ₃	3-(X,Y-(CH ₃) ₂ C ₆ H ₃ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3,4-Cl ₂ C ₆ H ₃	CH ₃	3-(4-CH ₃ C ₆ H ₄ SO ₂ NHSO ₂)-4-CH ₃ C ₆ H ₃	—	180
3,4-Cl ₂ C ₆ H ₃	CH ₃	2-CH ₃ -5-(4-CH ₃ C ₆ H ₄ SO ₂ NHSO ₂)C ₆ H ₃	—	180
3,4-Cl ₂ C ₆ H ₃	CH ₃	2-Cl-5-(4-CH ₃ C ₆ H ₄ SO ₂ NHSO ₂)C ₆ H ₃	—	180
3,4-Cl ₂ C ₆ H ₃	CH ₃	2-CH ₃ -5-(C ₆ H ₅ SO ₂ NHSO ₂)C ₆ H ₃	—	180
3,4-Cl ₂ C ₆ H ₃	CH ₃	2-(1-C ₁₀ H ₇ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3,4-Cl ₂ C ₆ H ₃	CH ₃	2-(2-C ₁₀ H ₇ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3,4-Cl ₂ C ₆ H ₃	CH ₃	2-(5,6,7,8-H ₄ -1-C ₁₀ H ₈ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3,4-Cl ₂ C ₆ H ₃	CH ₃	2-(5,6,7,8-H ₄ -2-C ₁₀ H ₈ SO ₂ NHSO ₂)C ₆ H ₄	—	180
3,4-Cl ₂ C ₆ H ₃	CH ₃	C ₆ H ₅	—	651
2-CH ₃ -4-HO ₂ SC ₆ H ₃	CH ₃	2-HO ₂ S-4,5-(CH ₃) ₂ C ₆ H ₃	—	523
3-HO ₂ S-4-(2-HO ₂ S-4-H ₂ NC ₆ H ₃ -CH=CH)C ₆ H ₃	CH ₃	2-HOOC-4-C ₆ H ₅ CONHC ₆ H ₃	—	176

(Table continued)

TABLE XXIII, Section B (continued)

R ¹	R ²	Ar	M.p.	Reference
3-HOOC-4-HOC ₆ H ₃	CH ₃	2-HO ₃ S-4-(4-H ₂ NC ₆ H ₅)C ₆ H ₅	—	1361
3-HOOC-4-C ₆ H ₄ OC ₆ H ₃	CH ₃	2-HOOC-6-ClC ₆ H ₃	—	160
2-Cl-5-HO ₃ SC ₆ H ₃	CH ₃	3-CF ₃ C ₆ H ₄	—	1486
2-Cl-5-HO ₃ SC ₆ H ₃	CH ₃	2-C ₁₀ H ₂₁ OOC ₆ H ₄	—	217
2-Cl-5-HO ₃ SC ₆ H ₃	CH ₃	2-HO-4-NH ₂ C ₆ H ₃	—	176
2-Cl-5-HO ₃ SC ₆ H ₃	CH ₃	2-HOOC-4-NH ₂ C ₆ H ₃	—	176
2-Cl-5-HO ₃ SC ₆ H ₃	CH ₃	3-C ₁₂ H ₂₅ CONHSO ₂ -4-CH ₃ C ₆ H ₃	—	173
2-Cl-5-HO ₃ SC ₆ H ₃	CH ₃	2-CF ₃ -4-ClC ₆ H ₃	—	1486
2-Cl-5-HO ₃ SC ₆ H ₃	CH ₃	2-CH ₃ O-5-C ₁₂ H ₂₅ NHSO ₂ C ₆ H ₄	—	1620
4-Cl-2-HO ₃ SC ₆ H ₃	CH ₃	3-C ₁₇ H ₃₅ CONHSO ₂ C ₆ H ₄	—	173
2,4-(NO ₂) ₂ C ₆ H ₃	CH ₃	C ₆ H ₅	216°	263
2,5-(HO ₃ S) ₂ C ₆ H ₃	CH ₃	2-CH ₃ O-5-C ₁₂ H ₂₅ NHSO ₂ C ₆ H ₃	—	1620
2-(3-HOOC-4-HOC ₆ H ₃ SO ₂)-5-HO ₃ SC ₆ H ₃	CH ₃	3-CF ₃ C ₆ H ₄	—	1486
2-Cl-4-HO ₃ SC ₆ H ₃	CH ₃	3-CH ₂ =CHSO ₂ C ₆ H ₄	—	652
2-CH ₃ -3-C ₁₇ H ₃₅ CONH-5-HO ₃ SC ₆ H ₂	CH ₃	4-(C ₂ H ₅) ₂ NC ₆ H ₄	—	1331
2-CH ₃ -4-CH ₂ =CHO ₂ S-6-ClC ₆ H ₂	CH ₃	2-HO ₃ SC ₆ H ₄	—	651
2,3-Cl ₂ -4-HO ₃ SC ₆ H ₂	CH ₃	4-HO ₃ SC ₆ H ₄	—	913
2,5-Cl ₂ -4-HO ₃ SC ₆ H ₂	CH ₃	4-HO ₃ SC ₆ H ₄	—	40
2,5-Cl ₂ -4-HO ₃ SC ₆ H ₂	CH ₃	3-C ₁₇ H ₃₅ CONHSO ₂ C ₆ H ₄	—	173
2,5-Cl ₂ -4-HO ₃ SC ₆ H ₂	CH ₃	3-C ₁₅ H ₃₁ CONHSO ₂ C ₆ H ₄	—	173
2,5-Cl ₂ -4-HO ₃ SC ₆ H ₂	CH ₃	3-C ₁₇ H ₃₅ CONHSO ₂ -4-CH ₃ OC ₆ H ₃	—	173
2-CH ₃ -4-HO ₃ S-6-ClC ₆ H ₂	CH ₃	3-CF ₃ C ₆ H ₄	—	1486
2,3,6-Cl ₃ -5-HO ₃ SC ₆ H	CH ₃	3-CF ₃ C ₆ H ₄	—	1486
2-C ₆ H ₅ C ₆ H ₄	CH ₃	2-HOOC ₆ H ₄	—	1382
2-C ₆ H ₅ C ₆ H ₄	CH ₃	2-HOOC-4(or 5)-HO ₃ SC ₆ H ₃	—	1382
2-C ₆ H ₅ C ₆ H ₄	CH ₃	2(or 6)-HO-3-HO ₃ S-5-NO ₂ C ₆ H ₂	—	1382
2-C ₆ H ₅ -4-HO ₃ SC ₆ H ₃	CH ₃	2-HOOC ₆ H ₄	—	1382
2-C ₆ H ₅ -4-HO ₃ SC ₆ H ₃	CH ₃	2-HO-4(or 5)-NO ₂ C ₆ H ₃	—	1382
2-C ₁₀ H ₇	CH ₃	2-Cl-5-(4-ClC ₆ H ₄ SO ₂ NHSO ₂)C ₆ H ₃	—	180

2-C ₁₀ H ₇	CH ₃		—	1251
6-HO ₃ S-2-C ₁₀ H ₆	CH ₃	2-C ₁₀ H ₂₁ OOCCH ₆ H ₄	—	217
	CH ₃	C ₆ H ₆	—	1251
	CH ₃	1-C ₁₀ H ₇	—	1251
	CH ₃	2-C ₁₀ H ₇	—	1251

(Table continued)

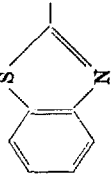
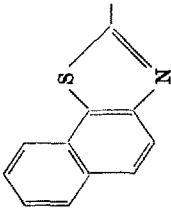
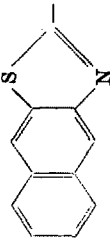
TABLE XXIII, Section B (continued)

R ¹	R ²	Ar	M.p.	Reference
	CH ₃		—	1251
	CH ₃	C ₆ H ₅	237°	413
	CH ₃	4-NaO ₃ SC ₃ H ₄	—	413
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	173°	129, 278, 372, 818, 1003, 1514, 1552, 1573
C ₆ H ₅	C ₆ H ₅	2-CH ₃ C ₆ H ₄	183°, 226°	278, 1552
C ₆ H ₅	C ₆ H ₅	3-CH ₃ C ₆ H ₄	179°	278
C ₆ H ₅	C ₆ H ₅	4-CH ₃ C ₆ H ₄	193°, 242°	278, 1552
C ₆ H ₅	C ₆ H ₅	2-CH ₃ OC ₆ H ₄	209°	278
C ₆ H ₅	C ₆ H ₅	4-CH ₃ OC ₆ H ₄	167°	278
C ₆ H ₅	C ₆ H ₅	2-C ₂ H ₅ OC ₆ H ₄	206°	278

C_6H_5	C_6H_5	$4-C_3H_5OC_6H_4$	177°	278
C_6H_5	C_6H_5	$4-H_2NC_6H_4$	208°	259
C_6H_5	C_6H_5	$4-CH_3CONHC_6H_4$	—	259
C_6H_5	C_6H_5	$2-ClC_6H_4$	177°	278
C_6H_5	C_6H_5	$3-ClC_6H_4$	193°	278
C_6H_5	C_6H_5	$4-ClC_6H_4$	216°	278
C_6H_5	C_6H_5	$4-BrC_6H_4$	231°	278
C_6H_5	C_6H_5	$2-NO_2C_6H_4$	204°	278
C_6H_5	C_6H_5	$3-NO_2C_6H_4$	203°	278
C_6H_5	C_6H_5	$4-NO_2C_6H_4$	245°	278
C_6H_5	C_6H_5	$4-CH_3COCH=N=NC_6H_4$	195°	259
		$\quad \quad \quad COOC_2H_5$		
		$4-C_6H_5COCHN=NC_6H_4$	203°	259
		$\quad \quad \quad COOC_2H_5$		
		$3-NaO_3SC_6H_4$	—	280
		$4-NaO_3SC_6H_4$	—	280
		$2-CH_3-4-ClC_6H_3$	204°	278
		$2-CH_3-5-ClC_6H_3$	220°	278
		$3-CH_3-4-NaO_3SC_6H_3$	—	280
		$2,5-Cl_2C_6H_3$	206°	278
		$2-NO_2-4-ClC_6H_3$	244°	278
		$3-NaO_3S-4-ClC_6H_3$	—	280
		$2-Cl-5-(4-ClC_6H_4SO_2NH_2SO_2)C_6H_3$	—	180
		$1-C_{10}H_7$	238°, 196°	278, 1552
		$2-C_{10}H_7$	175°, 225°	278, 1552
		$1-NaO_3S-2-C_{10}H_6$	—	280
			176°	281

(Table continued)

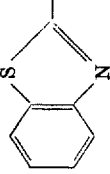
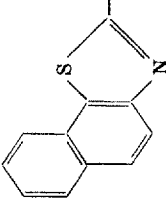
TABLE XXIII, Section B (continued)

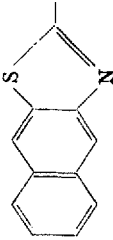
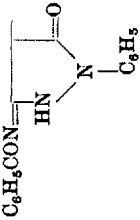
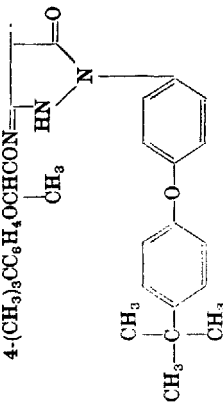
R ¹	R ²	Ar	M.p.	Reference
C ₆ H ₅	C ₆ H ₅		212°	281
C ₆ H ₅	C ₆ H ₅		271°	281
C ₆ H ₅	C ₆ H ₅		265°	281
C ₆ H ₅	3-CH ₃ C ₆ H ₄	C ₆ H ₅	141°	1145
C ₆ H ₅	2-HOC ₆ H ₄	C ₆ H ₅	189°	670
C ₆ H ₅	2-HOC ₆ H ₄	4-CH ₃ C ₆ H ₅	205°	670
C ₆ H ₅	2-HOC ₆ H ₄	4-NO ₂ C ₆ H ₄	285°	670
C ₆ H ₅	2-CH ₃ OC ₆ H ₄	C ₆ H ₅	139°, 149°	670, 1581
C ₆ H ₅	2-CH ₃ OC ₆ H ₄	4-NO ₂ C ₆ H ₄	267°	1581
C ₆ H ₅	3-CH ₃ OC ₆ H ₄	C ₆ H ₅	137°	1581
C ₆ H ₅	3-CH ₃ OC ₆ H ₄	4-NO ₂ C ₆ H ₄	235°	1581
C ₆ H ₅	4-CH ₃ OC ₆ H ₄	C ₆ H ₅	177°	129, 1581
C ₆ H ₅	4-CH ₃ OC ₆ H ₄	4-NO ₂ C ₆ H ₄	213°	1581

C ₆ H ₅	2-ClC ₆ H ₄	C ₆ H ₅	—	1580
C ₆ H ₅	3-ClC ₆ H ₄	C ₆ H ₅	—	1580
C ₆ H ₅	4-ClC ₆ H ₄	C ₆ H ₅	—	1580
3-ClC ₆ H ₄	C ₆ H ₅	2-Cl-5-(4-ClC ₆ H ₄ SO ₂ NHSO ₂)C ₆ H ₃	—	180
3-NO ₂ C ₆ H ₄	C ₆ H ₅	C ₆ H ₅	179°	1003
4-NO ₂ C ₆ H ₄	C ₆ H ₅	4-NO ₂ C ₆ H ₄	290°	1574
4-NO ₂ C ₆ H ₄	C ₆ H ₅	C ₆ H ₅	200°	1581
2-HOOCCH ₃	C ₆ H ₅	C ₆ H ₅	239°	1581
2-HOOCCH ₃	C ₆ H ₅	C ₆ H ₅	225°	1004
4-NO ₂ C ₆ H ₄	C ₆ H ₅	4-CH ₃ C ₆ H ₄	194°	1004
4-NO ₂ C ₆ H ₄	C ₆ H ₅	C ₆ H ₅	—	279
4-NO ₂ C ₆ H ₄	C ₆ H ₅	2-NO ₂ C ₆ H ₄	—	279
4-NO ₂ C ₆ H ₄	C ₆ H ₅	4-NO ₂ C ₆ H ₄	—	279
4-NO ₂ C ₆ H ₄	C ₆ H ₅	2-CH ₃ 4-ClC ₆ H ₃	—	279
4-NO ₂ C ₆ H ₄	C ₆ H ₅	2-CH ₃ -5-ClC ₆ H ₃	—	279
4-NO ₂ C ₆ H ₄	C ₆ H ₅	2-5-Cl ₂ C ₆ H ₃	—	77
4-NO ₂ C ₆ H ₄	C ₆ H ₅	2-HO-3-NO ₂ -5-HO ₃ SC ₆ H ₂	—	77
4-NO ₂ C ₆ H ₄	C ₆ H ₅	2-HO-3-Cl-5-HO ₃ SC ₆ H ₂	—	77
4-NO ₂ C ₆ H ₄	C ₆ H ₅	2-HO-3-NO ₂ -5-HO ₃ SC ₆ H ₂	—	77
4-NO ₂ C ₆ H ₄	C ₆ H ₅	C ₆ H ₅	165°	278, 1499
4-NO ₂ C ₆ H ₄	C ₆ H ₅	2-CH ₃ C ₆ H ₄	195°	278
4-NO ₂ C ₆ H ₄	C ₆ H ₅	3-CH ₃ C ₆ H ₄	187°	278
4-NO ₂ C ₆ H ₄	C ₆ H ₅	4-CH ₃ C ₆ H ₄	190°	278
4-NO ₂ C ₆ H ₄	C ₆ H ₅	2-CH ₃ OC ₆ H ₄	193°	278
4-NO ₂ C ₆ H ₄	C ₆ H ₅	4-CH ₃ OC ₆ H ₄	164°	278
4-NO ₂ C ₆ H ₄	C ₆ H ₅	2-C ₂ H ₅ OC ₆ H ₄	196°	278
4-NO ₂ C ₆ H ₄	C ₆ H ₅	4-C ₂ H ₅ OC ₆ H ₄	173°	278
4-NO ₂ C ₆ H ₄	C ₆ H ₅	2-ClC ₆ H ₄	200°	278
4-NO ₂ C ₆ H ₄	C ₆ H ₅	3-ClC ₆ H ₄	201°	278
4-NO ₂ C ₆ H ₄	C ₆ H ₅	4-ClC ₆ H ₄	227°	278
4-NO ₂ C ₆ H ₄	C ₆ H ₅	4-BrC ₆ H ₄	231°	278
4-NO ₂ C ₆ H ₄	C ₆ H ₅	2-NO ₂ C ₆ H ₄	223°	278
4-NO ₂ C ₆ H ₄	C ₆ H ₅	3-NO ₂ C ₆ H ₄	193°	278
4-NO ₂ C ₆ H ₄	C ₆ H ₅	4-NO ₂ C ₆ H ₄	260°	278

(Table continued)

TABLE XXIII, Section B (*continued*)

R ¹	R ²	Ar	M.p.	Reference
C ₆ H ₅	2-C ₄ H ₃ O	3-NaO ₃ SC ₆ H ₄	—	280
C ₆ H ₅	2-C ₄ H ₃ O	4-NaO ₃ SC ₆ H ₄	—	280
C ₆ H ₅	2-C ₄ H ₃ O	2-CH ₃ -4-ClC ₆ H ₃	217°	278
C ₆ H ₅	2-C ₄ H ₃ O	2-CH ₃ -5-ClC ₆ H ₃	214°	278
C ₆ H ₅	2-C ₄ H ₃ O	3-CH ₃ -4-NaO ₃ SC ₆ H ₃	—	280
C ₆ H ₅	2-C ₄ H ₃ O	2,5-Cl ₂ C ₆ H ₃	231°	278
C ₆ H ₅	2-C ₄ H ₃ O	2-NO ₂ -4-ClC ₆ H ₃	266°	278
C ₆ H ₅	2-C ₄ H ₃ O	3-NaO ₃ S-4-ClC ₆ H ₃	—	280
C ₆ H ₅	2-C ₄ H ₃ O	1-C ₁₀ H ₇	161°	278
C ₆ H ₅	2-C ₄ H ₃ O	2-C ₁₀ H ₇	202°	278, 1499
C ₆ H ₅	2-C ₄ H ₃ O	1-NaO ₃ S-2-C ₁₀ H ₉	—	280
C ₆ H ₅	2-C ₄ H ₃ O		198°	281
C ₆ H ₅	2-C ₄ H ₃ O		228°	281
C ₆ H ₅	2-C ₄ H ₃ O		261°	281

C_6H_5	$2-C_4H_9O$		287°	281
$4-NaO_3SC_6H_4$	$2-C_4H_9O$	C_6H_5	—	279
$4-NaO_3SC_6H_4$	$2-C_4H_9O$	$2-NO_2C_6H_4$	—	279
$4-NaO_3SC_6H_4$	$2-C_4H_9O$	$4-NO_2C_6H_4$	—	279
$4-NaO_3SC_6H_4$	$2-C_4H_9O$	$2-CH_3-4-ClC_6H_3$	—	279
$4-NaO_3SC_6H_4$	$2-C_4H_9O$	$2-CH_3-5-ClC_6H_3$	—	279
$4-NaO_3SC_6H_4$	$2-C_4H_9O$	$2,5-Cl_2C_6H_3$	—	279
$3-HO_3SC_6H_4$	CH_3		180°	593
$4-HO_3SC_6H_4$	CH_3		184°	593

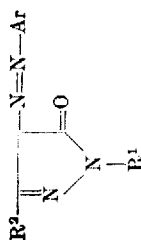


TABLE XXIII

Section C. Arylazo Substituted with Functional Groups

R ¹	R ²	Ar	M.p.	Reference
C ₆ H ₅	CH ₃ CO	C ₆ H ₅	182° (dec.)	768, 770
H	HOOC	C ₆ H ₅	> 250°	449, 1545
H	HOOC	3-CH ₃ C ₆ H ₄	—	449
H	HOOC	2-HOOC-C ₆ H ₄	227°	1552
C ₆ H ₅	HOOC	C ₆ H ₅	230°	292, 1082
C ₆ H ₅	HOOC	4-BrC ₆ H ₄	—	292
2-CH ₃ C ₆ H ₄	HOOC	2-CH ₃ C ₆ H ₄	229° (dec.)	293
4-CH ₃ C ₆ H ₄	HOOC	4-CH ₃ C ₆ H ₄	233° (dec.)	293
3-H ₂ NC ₆ H ₄	HOOC	4-[3-HO ₃ S-4-(4-HO ₃ SC ₆ H ₄ N=N)C ₆ H ₄ NHCO]C ₆ H ₄	—	215
3-ClC ₆ H ₄	HOOC	2-HO-3-NO ₂ -5-C ₆ H ₁₁ C ₆ H ₂	—	873
3-ClC ₆ H ₄	HOOC	2-HO-3-NO ₂ -5- <i>t</i> -C ₅ H ₁₁ C ₆ H ₂	—	873
3-ClC ₆ H ₄	HOOC	2-HO-3-NO ₂ -5-C ₆ H ₇ C ₆ H ₂	—	873
4-ClC ₆ H ₄	HOOC	4-ClC ₆ H ₄	254° (dec.)	291
4-BrC ₆ H ₄	HOOC	4-BrC ₆ H ₄	260° (dec.)	291
3-NO ₂ C ₆ H ₄	HOOC	2-HO-3,6-Cl ₂ -4-HO ₃ SC ₆ H	—	276
2-HO ₃ SC ₆ H ₄	HOOC	2-HO ₃ SC ₆ H ₄	—	1079
4-HO ₃ SC ₆ H ₄	HOOC	4-(4-NO ₂ C ₆ H ₄ SO ₂)C ₆ H ₄	—	571
4-HO ₃ SC ₆ H ₄	HOOC		323° (dec.)	1629

4-H ₂ NO ₂ SC ₆ H ₄	HOOC	4-H ₂ NO ₂ SC ₆ H ₄	—	1629, 1662
2-CH ₃ -4-HO ₃ SC ₆ H ₃	HOOC	2-HO ₃ S-4,5-(CH ₃) ₂ C ₆ H ₂	—	523
2,4-Cl ₂ C ₆ H ₃	HOOC	2,4-Cl ₂ C ₆ H ₄	252° (dec.)	291
3,4-Cl ₂ C ₆ H ₃	HOOC	2-HO-3-NO ₂ -5-C ₆ H ₁₁ C ₆ H ₂	—	873
3,4-Cl ₂ C ₆ H ₃	HOOC	2-HO-3-NO ₂ -5,4-C ₆ H ₁₁ C ₆ H ₂	—	873
3,6-Cl ₂ C ₆ H ₃	HOOC	2-HO-3-NO ₂ -5,4-C ₆ H ₁₁ C ₆ H ₂	—	873
3,6-Cl ₂ C ₆ H ₃	HOOC	2-HO-3-NO ₂ -5-C ₆ H ₁₇ C ₆ H ₂	—	873
2,4-Br ₂ C ₆ H ₃	HOOC	2,4-Br ₂ C ₆ H ₃	248°	291
2-CH ₃ -4-HO ₃ S-6-ClC ₆ H ₂	HOOC	3-CF ₃ C ₆ H ₄	—	1486
4-NaO ₃ SC ₆ H ₄	NaOOC	4-NaO ₃ SC ₆ H ₄	—	768, 770, 1066
5-HO-7-NaO ₃ S-2-C ₁₀ H ₈	NaOOC	5-HO-7-NaO ₃ S-2-C ₁₀ H ₈	—	71
H	H ₃ COOC	C ₆ H ₅	—	1549
H	H ₃ COOC	2-NO ₂ -4-CH ₃ OC ₆ H ₃	209°	369
H	H ₃ COOC	2-NO ₂ -4-C ₂ H ₅ OC ₆ H ₃	243°	369
H	H ₃ COOC	2-NO ₂ -4-ClC ₆ H ₃	244°	369
H	H ₃ COOC	2-NO ₂ -4-CH ₃ COC ₆ H ₃	225°	369
H	H ₃ COOC	2-NO ₂ -4-CH ₃ COC ₆ H ₃	254°	369
H	H ₃ COOC	2-NO ₂ -4-C ₄ H ₉ NHO ₂ SC ₆ H ₃	230°	369
4-BrC ₆ H ₄	H ₃ COOC	4-BrC ₆ H ₄	213°	291
2,4-Br ₂ C ₆ H ₃	H ₃ COOC	2,4-Br ₂ C ₆ H ₃	233°	291
H	C ₂ H ₅ COOC	2-HOOCOC ₆ H ₄	255°	1552
H	C ₂ H ₅ COOC	C ₆ H ₅	241°	1544, 1545
H	C ₂ H ₅ COOC	2-NO ₂ C ₆ H ₄	256°	369
H	C ₂ H ₅ COOC	2-NO ₂ -4-F ₃ CC ₆ H ₃	185°	369
H	C ₂ H ₅ COOC	2-NO ₂ -4-CH ₃ OC ₆ H ₃	246°	369
H	C ₂ H ₅ COOC	2-NO ₂ -4-ClC ₆ H ₃	228°	369
H	C ₂ H ₅ COOC	2-NO ₂ -4-C ₂ H ₅ COOC ₆ H ₃	205°	369
H	C ₂ H ₅ COOC	2-NO ₂ -4-HOCH ₂ CH ₂ NHCOC ₆ H ₃	154°	369
H	C ₂ H ₅ COOC	2-NO ₂ -4-CH ₃ CH ₂ CH ₂ NHCOC ₆ H ₃	226°	369
H	C ₂ H ₅ COOC	2-NO ₂ -4-C ₂ H ₅ NHSO ₂ C ₆ H ₃	251°	369
H	C ₂ H ₅ COOC	2-NO ₂ -4-C ₄ H ₉ NHSO ₂ C ₆ H ₃	230°	369
H	C ₂ H ₅ COOC	2-NO ₂ -4-SCNC ₆ H ₃	—	1357
CH ₃	C ₂ H ₅ COOC	4-CH ₃ OC ₆ H ₄	125°	594
C ₆ H ₅	C ₂ H ₅ COOC	C ₆ H ₅	152°	37, 44, 1240
2-CH ₃ C ₆ H ₄	C ₂ H ₅ COOC	2-CH ₃ C ₆ H ₄	145°	293, 445

(Table continued)

TABLE XXIII, Section C (continued)

R ¹	R ²	Ar	M.p.	Reference
3-CH ₃ C ₆ H ₄	C ₂ H ₅ OOCC	3-CH ₃ C ₆ H ₄	146°	445
4-CH ₃ C ₆ H ₄	C ₂ H ₅ OOCC	4-CH ₃ C ₆ H ₄	143°	293, 445
2-CH ₃ OC ₆ H ₄	C ₂ H ₅ OOCC	2-CH ₃ OC ₆ H ₄	177°	1661
2-C ₂ H ₅ OC ₆ H ₄	C ₂ H ₅ OOCC	2-C ₂ H ₅ OC ₆ H ₄	152°	1661
2-H ₂ NC ₆ H ₄	C ₂ H ₅ OOCC	2-H ₂ NC ₆ H ₄	195°	444
3-H ₂ NC ₆ H ₄	C ₂ H ₅ OOCC	3-H ₂ NC ₆ H ₄	146°	444
3-H ₂ NC ₆ H ₄	C ₂ H ₅ OOCC	2-CH ₃ -4-ClC ₆ H ₃	—	878
4-H ₂ NC ₆ H ₄	C ₂ H ₅ OOCC	4-H ₂ NC ₆ H ₄	143°	444
4-C ₆ H ₅ N=NC ₆ H ₄	C ₂ H ₅ OOCC	4-C ₆ H ₅ N=NC ₆ H ₄	198°	770
3-(3-HO-2-C ₁₀ H ₆ CONH)C ₆ H ₂	C ₂ H ₅ OOCC	2-CH ₃ -4-ClC ₆ H ₃	228°	877
2-ClC ₆ H ₄	C ₂ H ₅ OOCC	2-ClC ₆ H ₄	179°	1661
3-ClC ₆ H ₄	C ₂ H ₅ OOCC	2-Cl-5-(2,4,5-Cl ₃ C ₆ H ₂ SO ₂ NH)C ₆ H ₃	—	180
4-ClC ₆ H ₄	C ₂ H ₅ OOCC	4-ClC ₆ H ₄	190°	291, 1661
3-BrC ₆ H ₄	C ₂ H ₅ OOCC	3-BrC ₆ H ₄	160°	1661
4-BrC ₆ H ₄	C ₂ H ₅ OOCC	4-BrC ₆ H ₄	260°	291
4-NO ₂ C ₆ H ₄	C ₂ H ₅ OOCC	4-NO ₂ C ₆ H ₄	246°, 260°	444, 770
4-HOOC ₆ H ₄	C ₂ H ₅ OOCC	4-HOOC ₆ H ₄	224° (dec.)	768, 770
3-C ₂ H ₅ OOCC ₆ H ₄	C ₂ H ₅ OOCC	3-C ₂ H ₅ OOCC ₆ H ₄	132°	1661
4-(2-C ₁₀ H ₇ OCO)C ₆ H ₄	C ₂ H ₅ OOCC	4-(2-C ₁₀ H ₇ OCO)C ₆ H ₄	228°	1661
4-HO ₃ SC ₆ H ₄	C ₂ H ₅ OOCC	4-HO ₃ SC ₆ H ₄	—	444
4-HOCH ₂ CH ₂ SO ₂ C ₆ H ₄	C ₂ H ₅ OOCC	C ₆ H ₅	—	651
3-H ₂ NO ₂ SC ₆ H ₄	C ₂ H ₅ OOCC	2-HO-3-NO ₂ -5- <i>t</i> -C ₆ H ₁₁ C ₃ H ₂	—	874
3-H ₂ NO ₂ SC ₆ H ₄	C ₂ H ₅ OOCC	2-HO-3-NO ₂ -5- <i>t</i> -C ₆ H ₁₁ C ₃ H ₂	—	1450
3-HOCH ₂ CH ₂ NH)SO ₂ C ₆ H ₄	C ₂ H ₅ OOCC	2-HO-3-NO ₂ -5- <i>t</i> -C ₆ H ₁₁ C ₃ H ₂	—	1450
2,4-(CH ₃) ₂ C ₆ H ₃	C ₂ H ₅ OOCC	2,4-(CH ₃) ₂ C ₆ H ₃	165°	1661
2-CH ₃ -4-NO ₂ C ₆ H ₃	C ₂ H ₅ OOCC	2-CH ₃ -4-NO ₂ C ₆ H ₃	158°	1661
2,5-Cl ₂ C ₆ H ₃	C ₂ H ₅ OOCC	2,5-Cl ₂ C ₆ H ₃	213°	285
2,4-Br ₂ C ₆ H ₃	C ₂ H ₅ OOCC	2,4-Br ₂ C ₆ H ₃	229°	291
3-H ₂ NO ₂ -5-ClC ₆ H ₃	C ₂ H ₅ OOCC	2-HO-3-NO ₂ -5- <i>t</i> -C ₆ H ₁₁ C ₃ H ₂	—	874
1-C ₁₀ H ₇	C ₂ H ₅ OOCC	1-C ₁₀ H ₇	170° (dec.)	768, 770
2-C ₁₀ H ₇	C ₂ H ₅ OOCC	2-C ₁₀ H ₇	216° (dec.)	768, 770

1-NaO ₃ S ₂ -2-C ₁₀ H ₉	C ₆ H ₅ OOOC	1-NaO ₃ S ₂ -2-C ₁₀ H ₉	200° (dec.)	768, 770
4,8-(HO ₃ S) ₂ -2-C ₁₀ H ₆	C ₂ H ₅ OOOC	4,8-(HO ₃ S) ₂ -2-C ₁₀ H ₆	260°	770
2,4-Br ₂ C ₆ H ₃	C ₄ H ₉ OOOC	2,4-Br ₂ C ₆ H ₃	175°	291
H	H ₂ NOC	2-NO ₂ -4-ClC ₆ H ₃	218°	369
H	C ₄ H ₉ NHOC	2-HO-5-C ₆ H ₅ SC ₆ H ₅	—	225
C ₆ H ₅	H ₂ NOC	2-HO-4-(C ₆ H ₅ NHSO ₂)C ₆ H ₃	—	1218
C ₆ H ₅	H ₂ NOC	2-HO-3-(C ₆ H ₅ NHSO ₂)-5-ClC ₆ H ₂	—	1218
C ₆ H ₅	H ₂ NOC	2-HO-4-(C ₆ H ₅ NHSO ₂)-6-CH ₃ C ₆ H ₂	—	1218
2-Cl-5-OC ₆ H ₄	H ₂ NOC	2-HO-5-(C ₆ H ₅ NHSO ₂)C ₆ H ₃	—	1218
3-ClC ₆ H ₅	H ₂ NOC	2-Cl-5-(2,4,5-Cl ₃ C ₆ H ₂ NHSO ₂)C ₆ H ₃	—	180
3-H ₂ NO ₂ SC ₆ H ₄	H ₂ NOC	2-HO-3-NO ₂ -5-4-C ₆ H ₁₁ C ₆ H ₂	—	1450
2-Cl-5-H ₂ NO ₂ SC ₆ H ₃	H ₂ NOC	2-HO-3-NO ₂ -4-4-C ₆ H ₅ C ₆ H ₂	—	874
3-H ₂ NO ₂ S-4-ClC ₆ H ₃	H ₂ NOC	2-HO-3-NO ₂ -5-4-C ₆ H ₁₁ C ₆ H ₂	—	874
H	C ₄ H ₉ NHOC	2-HO-3-NO ₂ -5-5-ClC ₆ H ₂	—	1464
3-H ₂ NO ₂ SC ₆ H ₄	CH ₃ NHOC	2-HO-3-NO ₂ -5-4-C ₆ H ₁₁ C ₆ H ₂	—	1450
3-HOCH ₂ CH ₂ NHO ₂ SC ₆ H ₄	CH ₃ NHOC	2-HO-3-NO ₂ -5-4-C ₆ H ₁₁ C ₆ H ₂	—	1450
3-H ₂ NO ₂ SC ₆ H ₄	HOCH ₂ CH ₂ NHOC	2-HO-3-NO ₂ -5-4-C ₆ H ₁₁ C ₆ H ₂	—	1450
CH ₃	H ₂ NHNOOC	4-CH ₃ OC ₆ H ₄	212°	594
CH ₃	ONC	4-CH ₃ OC ₆ H ₄	253°	594
C ₆ H ₅	CN	C ₆ H ₅	152° (dec.), 126, 768	
			189°	
4-Br-C ₆ H ₄	CN	C ₆ H ₅	203°	126
CH ₃	N ₃ OC	4-CH ₃ OC ₆ H ₄	120° (exp.)	594
CH ₃ CO	C ₆ H ₅	C ₆ H ₅	199°	1560
C ₆ H ₅ CO	CH ₃	2-CH ₃ C ₆ H ₄	209°	264
C ₆ H ₅ CO	CH ₃	3-CH ₃ C ₆ H ₄	171°	264
C ₆ H ₅ CO	CH ₃	1-C ₁₀ H ₇	212°	264
C ₆ H ₅ CO	CH ₃	2-C ₁₀ H ₇	224°	264
H ₂ NCO	CH ₃	C ₆ H ₅	—	355
H ₂ NCS	CH ₃	C ₆ H ₅	217°	355

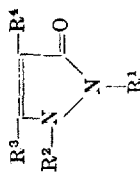


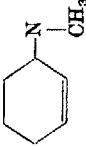
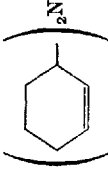
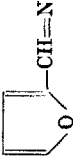
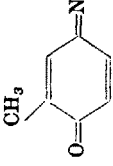
TABLE XXIV. 3-Pyrazolin-5-ones. Imino, Amino, Amido, Azo, Aminoazo, and Hydrazido Substituents

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	CH ₃	CH ₃	(CH ₃) ₂ N	—	860
C ₆ H ₅	CH ₃	C ₆ H ₅ CH ₂ N CH ₂ CH ₂ N(CH ₃) ₂	H	216°	1052
H	C ₆ H ₅	CH ₃	C ₆ H ₅ CH=N 4-CH ₃ OC ₆ H ₄ CH=N C ₆ H ₅ CH=CHCH=N CH ₃ C≡N COOH	248° 245° 232° 303°	984 984 984 984
H	C ₆ H ₅	CH ₃	C ₆ H ₅ CH=N 4-CH ₃ OC ₆ H ₄ CH=N C ₆ H ₅ CH=CHCH=N C ₆ H ₅ C≡N CH ₃	233° 235° 217° 302°	984 984 984 984
H	4-CH ₃ C ₆ H ₄	CH ₃	(C ₆ H ₅) ₂ C=N (CH ₃) ₂ N	305° 190°	984 1001

H	4-BrC ₆ H ₄	CH ₃	C ₆ H ₅ CH=N	249°	1001
H	4-BrC ₆ H ₄	CH ₃	4-CH ₂ OC ₆ H ₄ CH=N	303°	1001
H	4-BrC ₆ H ₄	CH ₃	4-(CH ₃) ₂ NC ₆ H ₄ CH=N	330°	1001
H	4-BrC ₆ H ₄	CH ₃	3-NO ₂ C ₆ H ₄ CH=N	274°	1001
H	4-BrC ₆ H ₄	CH ₃	H ₅ C ₂ OOCCH ₂ C=N CH ₃	199°	1001
H	4-BrC ₆ H ₄	CH ₃	OS=N	168°	1001
	CH ₃	CH ₃	(CH ₃) ₂ N	b ₃ 160°	101
	CH ₃	CH ₃	HO ₃ SCH ₂ N CH ₃	153° (dec.)	105
C ₆ H ₅ CH ₂	CH ₃	CH ₃	(CH ₃) ₂ N	74°	860
C ₆ H ₅	CH ₃	CH ₃	CH ₂ =N	—	134, 172
C ₆ H ₅	CH ₃	CH ₃	(CH ₃) ₂ N	106°	133, 144, 150, 172, 371, 463, 525, 527, 550, 551, 554, 603, 661, 691, 781, 915, 938, 941, 1198, 1256, 1356
CH ₃	C ₆ H ₅	CH ₃	(CH ₃) ₂ N	74°	984
CH ₃	CH ₃	C ₆ H ₅	(CH ₃) ₂ N	118°	992
CH ₃	CH ₃	C ₆ H ₅	(C ₂ H ₅) ₂ N	oil	992
C ₆ H ₅	CH ₃	CH ₃	iso-C ₃ H ₇ N CH ₃	102°	431
C ₆ H ₅	CH ₃	CH ₃	(C ₆ H ₅ CH ₂) ₂ N	101°	130, 743
C ₆ H ₅	CH ₃	CH ₃	(4-ClC ₆ H ₄ CH ₂) ₂ N	105°	130

(Table continued)

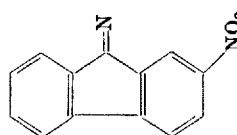
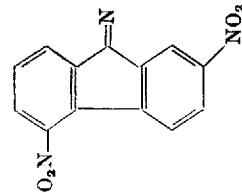
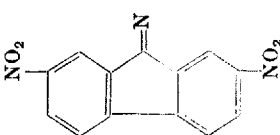
TABLE XXIV (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃		84°	101
C ₆ H ₅	CH ₃	CH ₃		94°	101
C ₆ H ₅	CH ₃	CH ₃	CH ₃ C≡N	158°	821
C ₆ H ₅	CH ₃	CH ₃	COOC ₂ H ₅	173°	821, 940, 1592
CH ₃	CH ₃	C ₆ H ₅	C ₆ H ₅ CH=N	151°	992
C ₆ H ₅	CH ₃	CH ₃	2-HOC ₆ H ₄ CH=N	198°	430, 954
CH ₃	CH ₃	C ₆ H ₅	2-HOC ₆ H ₄ CH=N	173°	992
CH ₃	CH ₃	C ₆ H ₅	4-CH ₃ OC ₆ H ₄ CH=N	177°	992
C ₆ H ₅	CH ₃	CH ₃	3-NO ₂ C ₆ H ₄ CH=N	213°	821
C ₆ H ₅	CH ₃	CH ₃	2,3-(OCH ₃)C ₆ H ₃ CH=N	230°	430
CH ₃	CH ₃	C ₆ H ₅	4-NO ₂ C ₆ H ₄ CH=N	155°	992
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ CH=CHCH=N	157°	430, 821
CH ₃	CH ₃	C ₆ H ₅	C ₆ H ₅ CH=CHCH=N	151°	992
C ₆ H ₅	CH ₃	CH ₃		206°	1184
C ₆ H ₅	CH ₃	CH ₃		—	426

12 + C ₆ H ₅	CH ₃	CH ₃	CH ₃	227° (dec.)	1217
CH ₃	CH ₃	CH ₃	CH ₃	167°	992
C ₆ H ₅	CH ₃	CH ₃	CH ₃	—	460
C ₆ H ₅	CH ₃	CH ₃	CH ₃	—	460
C ₆ H ₅	CH ₃	CH ₃	CH ₃	213° (HCl)	111, 1298
C ₆ H ₅	CH ₃	CH ₃	CH ₃	oil	111
C ₆ H ₅	CH ₃	CH ₃	CH ₃	182° (HCl)	111
C ₆ H ₅	CH ₃	CH ₃	CH ₃	—	524
C ₆ H ₅	CH ₃	CH ₃	CH ₃	75°	524
C ₆ H ₅	CH ₃	CH ₃	CH ₃	153°	524
CH ₃	CH ₃	CH ₃	CH ₃	141°	992

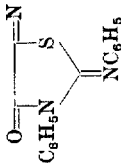
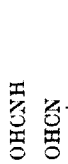
TABLE XXIV (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃	HO ₂ SCH ₂ N—CH ₃	131° (dec.)	105
C ₆ H ₅	CH ₃	CH ₃	HO ₂ SCH ₂ N—CH(CH ₃) ₂	—	104
C ₆ H ₅	CH ₃	CH ₃	HO ₂ SCH ₂ N—CH(CH ₃) ₂	—	104
C ₆ H ₅	CH ₃	CH ₃	HO ₂ SCH ₂ N—CH(CH ₃) ₂	166° (dec.)	104
C ₆ H ₅	CH ₃	CH ₃	HO ₂ SCH ₂ N—s-C ₄ H ₉	—	104
C ₆ H ₅	CH ₃	CH ₃	HO ₂ SCH ₂ N—s-C ₄ H ₉	170°	104
C ₆ H ₅	CH ₃	CH ₃	HO ₂ SCH ₂ N—iso-C ₄ H ₉	133° (dec.)	105
C ₆ H ₅	CH ₃	CH ₃	HO ₂ SCH ₂ N—CH ₂ C ₆ H ₅	—	417
C ₆ H ₅	CH ₃	CH ₃	$\left[\begin{array}{c} \text{H}_2\text{N}=\text{N} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{N}=\text{N} \end{array} \right]^+ \text{Cl}^-$	—	417
C ₆ H ₅	CH ₃	CH ₃	$\left[\begin{array}{c} \text{H}_2\text{N}=\text{N} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{N}=\text{N} \\ \\ \text{NH}_2 \end{array} \right]^+ \text{Cl}^-$	—	417

C_6H_5	CH_3	CH_3		153°	270
C_6H_5	CH_3	CH_3		280°	270
C_6H_5	CH_3	CH_3		280°	270

(Table continued)

TABLE XXIV (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃		144°	927
C ₆ H ₅	CH ₃	CH ₃		157°	927
C ₆ H ₅	CH ₃	CH ₃		148°	7
C ₆ H ₅	CH ₃	CH ₃		196°	1186
C ₆ H ₅	CH ₃	CH ₃		175°	424
C ₆ H ₅	CH ₃	CH ₃		189°	821
C ₆ H ₅	CH ₃	CH ₃		106°	618

C_6H_5	CH_3	CH_3	CH_3CONH	197°	821
C_6H_5	CH_3	CH_3	CH_3CON CH_3	152°	618
C_6H_5	CH_3	CH_3	iso- C_4H_9CON CH_3	—	537
C_6H_5	CH_3	CH_3	CH_3CHCON Br CH_3	128°	1471
C_6H_5	CH_3	CH_3	CH_3CHCON NH CH_3 CH_3	162°	1471
C_6H_5	CH_3	CH_3	CH_3CHCON $N(CH_3)_2$	181°	1471
C_6H_5	CH_3	CH_3	H_2NCONH	245°	821
C_6H_5	CH_3	CH_3	C_2H_5OOCNH S H_2NCN CH_3	206°	821
C_6H_5	CH_3	CH_3	$(CH_3)_2N$	115° (dec.)	1297
C_6H_5	C_2H_5	CH_3	$(CH_3)_2N$	107°	548
C_6H_5	CH_3		$(CH_3)_2N$	94°	1477

(Table continued)

TABLE XXIV (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
4-C ₃ H ₇ OC ₆ H ₅	CH ₃	CH ₃	(CH ₃) ₂ N	82°	1149
4-C ₃ H ₇ OC ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ CH=N	139°	1149
C ₆ H ₅	CH ₃	C ₆ H ₅ CH ₂	(CH ₃) ₂ N	111°	1320
4-H ₂ O ₃ AsC ₆ H ₄	CH ₃	CH ₃	3-HO-4-H ₂ O ₃ AsC ₆ H ₃ CH=N-	—	1365
H	C ₆ H ₅	CH ₃	CIN ₂	120°	984
H	4-BrC ₆ H ₄	CH ₃	CIN ₂	—	1001
C ₆ H ₅	CH ₃	CH ₃	CIN ₂	—	426, 1353
CH ₃	CH ₃	CH ₃	CIN ₂	—	992
H	C ₆ H ₅	C ₆ H ₅ N=N	CH ₃	99°	972
H	C ₆ H ₅	CH ₃	2,5-(C ₂ H ₅ O) ₂ -4-C ₆ H ₅ CONHC ₆ H ₃ N=N	236°	885
H	C ₆ H ₅	CH ₃	2-HO-1-C ₁₀ H ₆ N=N	215°	984
H	C ₆ H ₅	CH ₃	3,6-(HO ₃ S) ₂ -2-HO-1-C ₁₀ H ₄ N=N	—	1060
H	C ₆ H ₅	CH ₃	3,6-(HO ₃ S) ₂ -2-NH ₂ -1-C ₁₀ H ₄ N=N	—	1060
H	4-BrC ₆ H ₄	CH ₃	2-HO-1-C ₁₀ H ₆ N=N	253°	1001
H	2-HOOC ₆ H ₄	CH ₃	C ₆ H ₅ N=N	210°	1004
H	C ₆ H ₅	2-HOC ₆ H ₄	C ₆ H ₅ N=N	189°	670
H	C ₆ H ₅	2-HOC ₆ H ₄	4-CH ₃ C ₆ H ₄ N=N	205°	670
C ₆ H ₅	CH ₃	CH ₃	H ₃ C ₂ O ₂ CCHN=N	174°	426, 1017
			COCH ₃		
C ₆ H ₅	CH ₃	CH ₃	(CH ₃ CO) ₂ CHN=N	181°	1017
C ₆ H ₅	CH ₃	CH ₃	(CH ₃ CO) ₂ CN=N	199°	1017
			CH ₃		
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ COCHN=N	142°	1018
			COCH ₃		
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ N=N	174°	999
C ₆ H ₅	CH ₃	CH ₃	3-HOOC-4-HOC ₆ H ₃ N=N	256°	1323

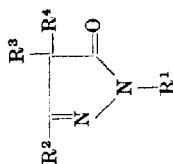


TABLE XXV. 2-Pyrazolin-5-ones. Halogen Substituted

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	CH ₃	Br	H	182°	1028, 1029
Br	CH ₃	H	H	78°	1309
CH ₃	CH ₃	Br	H	170° (HBr salt)	1309
H	CH ₃	Br	Br	132°	355, 1028, 1029
C ₆ H ₅ CH ₂	CH ₃	Cl	Cl	59°	333
C ₆ H ₅ CH ₂	CH ₃	Br	Br	81°	333
C ₆ H ₅	Cl	H	H	143°	981, 994
H	C ₆ H ₅	Br	Br	198°	1028, 1560
H	2-HOC ₆ H ₄	Br	Br	178°	353
H	3-NO ₂ C ₆ H ₄	Br	H	188°	335
C ₆ H ₅	CH ₃	Cl	H	153°	1513, 1514
C ₆ H ₅	CH ₃	Br	H	128°	809, 816, 1056, 1307, 1605
C ₆ H ₅	CH ₃	I	H	—	1605
C ₆ H ₅	CH ₃	Cl	Cl	65°	809, 816, 1605
C ₆ H ₅	CH ₃	Br	Br	80°	809, 816, 1605
C ₆ H ₅	CH ₃	I	I	—	1605
2-CH ₃ C ₆ H ₄	CH ₃	Br	H	116°	351
4-BrC ₆ H ₄	CH ₃	Br	H	171°	1513
2-HOOC ₆ H ₄	CH ₃	Br	H	202°	1004
3-HOOC ₆ H ₄	CH ₃	Cl	Cl	116°	980
4-HO ₂ SC ₆ H ₄	CH ₃	Br	H	—	1309
C ₆ H ₅	CH ₃	CH ₃	Cl	68°	1522, 1528, 1605
C ₆ H ₅	CH ₃	CH ₃	Br	83°	1605

C_6H_5	CH_3	I	70°	1605
C_6H_5	CH_3	CH_3	$b_{22}170^\circ$	994, 998
$\text{H}_2\text{N}^* \text{2-HOOC}\text{C}_6\text{H}_4$	Cl	H	210°	1004
$\text{2-CH}_3\text{C}_6\text{H}_4$	Br	H	110°	351
C_6H_5	Cl	$\text{C}_6\text{H}_5\text{CH}=\text{C}_6\text{H}_5$	108°	994
CH_3CO	CH_3	H	160°	1309
H_2NOC	CH_3	Br	225°	355
H_2NSC	CH_3	H	220°	355
H_2NSC	CH_3	Br	250°	355
H_2NOC	C_6H_5	Br	144°	357
H_2NSC	C_6H_5	Br	$130^\circ (\text{dec.})$	357
C_6H_5	Cl	H	146°	994

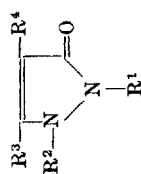


TABLE XXVI. 3-Pyrazolin-5-ones. Halogen and Halogen Combined with Carboxylic Acid and Derivatives

R^1	R^2	R^3	R^4	M.p.	Reference
H	CH_3	CH_3	Br	218°	1205
H	C_2H_5	CH_3	Br	39°	1205
C_6H_5	CH_3	Cl	H	67°	981
CH_3	C_6H_5	Cl	H	117°	981
H	C_6H_5	CH_3	Cl	261°	988
H	C_6H_5	CH_3	Br	$241^\circ (\text{dec.})$	988
H	$4\text{-BrC}_6\text{H}_4$	CH_3	Cl	220°	1001

(Table continued)

TABLE XXVI (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	4-BrC ₆ H ₄	CH ₃	Br	231°	1001
H	4-BrC ₆ H ₄	CH ₃	I	207° (dec.)	1001
H	3-NO ₂ C ₆ H ₄	CH ₃	Cl	253°	1001
H	3-NO ₂ C ₆ H ₄	CH ₃	Br	245°	1001
H	3-NO ₂ C ₆ H ₄	CH ₃	I	221°	1001
C ₆ H ₅	CH ₃	CH ₃	Cl	126°	795, 907, 908,
C ₆ H ₅	CH ₃	CH ₃	Br	115°	362, 793, 794, 809,
					1297, 1320, 1491,
					1605
CH ₃	C ₆ H ₅	CH ₃	Br	—	888
CH ₃	CH ₃	C ₆ H ₅	Br	179°	992
C ₆ H ₅	CH ₃	CH ₃	I	—	1155
C ₆ H ₅	CH ₃	C ₆ H ₅ CH ₂	Br	116°	1320
3-CH ₃ CONHC ₆ H ₄	CH ₃	CH ₃	Br	217°	978
4-CH ₃ CONHC ₆ H ₄	CH ₃	CH ₃	Br	240°	978
4-C ₆ H ₅ CONHC ₆ H ₄	CH ₃	CH ₃	Br	237°	978
4-C ₆ H ₅ SO ₂ NHC ₆ H ₄	CH ₃	CH ₃	Br	235°	978
4-BrC ₆ H ₅	CH ₃	CH ₃	I	163°	540, 1354
4-IC ₆ H ₄	CH ₃	CH ₃	Br	—	540
3-NO ₂ C ₆ H ₄	CH ₃	CH ₃	Br	184°	978
4-NO ₂ C ₆ H ₄	CH ₃	CH ₃	Br	173°	978
CH ₃	3-NO ₂ C ₆ H ₄	CH ₃	Br	200°	1001
C ₆ H ₅	CH ₃	HOCH ₂	Br	181°	362, 697, 698
C ₆ H ₅	CH ₃	CH ₃ NHCH ₂	Br	224° (dec.)	697
C ₆ H ₅	CH ₃	(CH ₃) ₂ NCH ₂	Br	143°	697
C ₆ H ₅	CH ₃	BrCH ₂	Br	135°	362, 697, 698, 899
H	C ₆ H ₅	Cl	Cl	249°	1201
CH ₃	C ₆ H ₅	Cl	Br	112°	981
C ₆ H ₅	CH ₃	HOOC	Br	186°	697, 698
C ₆ H ₅	CH ₃	CH ₃ COOC	Br	128°	697, 698
C ₆ H ₅	CH ₃	H ₂ NHNOC	Br	192°	697
C ₆ H ₅	CH ₃	N ₃ OC	Br	104° (exp.)	107

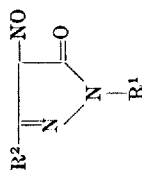
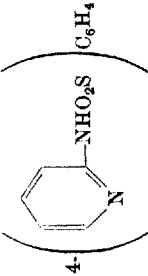
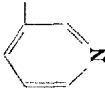


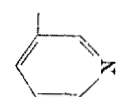
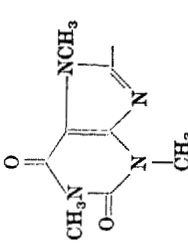
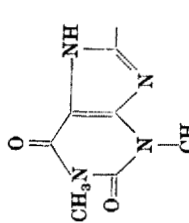
TABLE XXVII. 2-Pyrazolin-5-ones. 4-Nitroso Derivatives

R ¹	R ²	M.p.	Reference
H	H	87°	1544, 1546, 1549, 1550
H	CH ₃	237°, 232° (dec.)	258, 355, 406, 478, 480, 676, 1553
H	CH ₃ (also 4-CH ₃)	214°	1560
NO	CH ₃ (no 4-NO group)	135°	262
H	H ₆ C ₂ OOCCH ₂	114°	866
H	N ₃ COCH ₂	97°	866
H	C ₆ H ₅ NHCOCH ₂	165°	866
C ₆ H ₅ CH ₂	CH ₃	157° (dec.)	333
4-CH ₃ C ₆ H ₅ CH ₂	CH ₃	154° (dec.)	333
C ₆ H ₅	H	160° (dec.)	306
H	C ₆ H ₅	188°	406, 1028, 1552, 1553
H	4-CH ₃ C ₆ H ₄	191°	1125
H	3-NO ₂ C ₆ H ₄	217°	335
C ₆ H ₅	CH ₃	158°	240, 676, 809, 816
CH ₃	C ₆ H ₅	162°	992
C ₆ H ₅	C ₄ H ₉	131°	1536
C ₆ H ₅	C ₆ H ₅ CH ₃	172°	1534
2,4-(CH ₃) ₂ C ₆ H ₃ CH ₂	C ₆ H ₅	138°	334
3-CH ₃ C ₆ H ₄	CH ₃	162°	240
4-CH ₃ C ₆ H ₄	CH ₃	180°	240
2-ClC ₆ H ₄	CH ₃	174°	296

(Table continued)

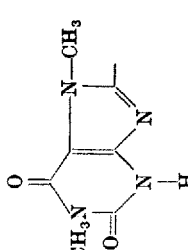
TABLE XXVII (continued)

R ¹	R ²	M.p.	Reference
3-ClC ₆ H ₄	CH ₃	173°	296
4-ClC ₆ H ₄	CH ₃	180°	296, 676
4-IC ₆ H ₄	CH ₃	189°	446
4-NO ₂ C ₆ H ₄	CH ₃	215°	9
2-HOOCOC ₆ H ₄	CH ₃	200°	1004
3-HOOCOC ₆ H ₄	CH ₃	242°	980
4-HOOCOC ₆ H ₄	CH ₃	253°	980
4- 	CH ₃	237°	25
2-CH ₃ -4-IC ₆ H ₃	CH ₃	181°	446
3,4-(OCH ₂ O)C ₆ H ₃	CH ₃	161°	334
2,4-Cl ₂ C ₆ H ₃	CH ₃	166°	296
3-HO ₃ SC ₆ H ₄	C ₆ H ₁₇	>250°	593
C ₆ H ₅	C ₆ H ₅	199°	9, 676, 818, 1125, 1153, 1552
C ₆ H ₅	4-CH ₃ C ₆ H ₄	202°	1125, 1152
C ₆ H ₅	3-CH ₃ OC ₆ H ₄	157°	1581
C ₆ H ₅	4-CH ₃ OC ₆ H ₄	244°	1581
4-CH ₃ C ₆ H ₄	C ₆ H ₅	241°	1125
2-HOOCOC ₆ H ₄	C ₆ H ₅	213°	1004
3,4-(OCH ₂ O)C ₆ H ₃	C ₆ H ₅	162°	334
H		253°	269

	CH_3	274°	240, 413
C_6H_5		183°	1499
C_6H_5		229°	269
	CH_3	248° (dec.)	1147
	CH_3	310° (dec.)	1147

(Table continued)

TABLE XXVII (continued)

R ¹	R ²	M.p.	Reference
	CH ₃	285° (dec.)	1147
H ₂ NOC	CH ₃	210°	355
H ₂ NSC	CH ₃	180°	355
H ₂ NSC	C ₆ H ₅	174°	357
H	HOOC	215° (dec.)	1544, 1545
H	H ₃ COOC	199°	1549
H	H ₃ C ₂ OOCC	182°	1545
H	H ₂ NOC	240°	337
H	C ₆ H ₅ HNOC	211° (dec.)	337
H	4-CH ₃ C ₆ H ₄ HNOC	222°	337
H	N ₃ OC	100° (exp.)	337

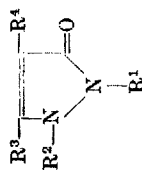
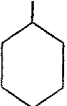


TABLE XXVIII. 3-Pyrazolin-5-ones. Nitroso and Nitro Substituted Derivatives

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	NO	CH ₃	H	—	1029
H	C ₆ H ₅	NO	CH ₃	159°	972
H	C ₆ H ₅	CH ₃	NO	159°	984
H	4-CH ₃ C ₆ H ₄	CH ₃	NO	167°	984
H	4-BrC ₆ H ₄	CH ₃	NO	185°	1001
	CH ₃	CH ₃	NO	—	103
C ₆ H ₅ CH ₂	CH ₃	CH ₃	NO	oil	333
C ₆ H ₅	CH ₃	CH ₃	NO	200° (exp.)	99, 461, 603, 781, 807, 809, 845, 854, 1174, 1175, 1257
CH ₃	C ₆ H ₅	CH ₃	NO	155° (exp.)	888
CH ₃	CH ₃	C ₆ H ₅	NO	—	992
C ₆ H ₅	CH ₃		NO	195°	1477
C ₆ H ₅	CH ₃		NO	185°	1499

(Table continued)

TABLE XXVIII (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	C ₆ H ₅	CH ₃	NO	—	647
4-CH ₃ C ₆ H ₄	C ₂ H ₅	CH ₃	NO	—	145
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	CH ₃	NO	—	541
4-C ₂ H ₅ OC ₆ H ₄	C ₂ H ₅	CH ₃	NO	—	145
4-C ₃ H ₇ OC ₆ H ₄	CH ₃	CH ₃	NO	163° (dec.)	1149
4-CH ₃ CONHC ₆ H ₄	CH ₃	CH ₃	NO	237°	978
4-C ₆ H ₅ CONHC ₆ H ₄	CH ₃	CH ₃	NO	214°	978
4-C ₆ H ₅ SO ₂ NHC ₆ H ₄	CH ₃	CH ₃	NO	211°	978
3-NO ₂ C ₆ H ₄	CH ₃	CH ₃	NO	188°	978
3-NO ₂ C ₆ H ₄	CH ₃	C ₆ H ₅	NO	225° (dec.)	1003
4-NO ₂ C ₆ H ₄	CH ₃	CH ₃	NO	188°	978
4-H ₂ O ₂ AsC ₆ H ₄	CH ₃	CH ₃	NO	—	546
H	CH ₃	CH ₃	NO ₂	217°	860
H	C ₆ H ₅	CH ₃	NO ₂	222°	984
H	4-CH ₃ C ₆ H ₄	CH ₃	NO ₂	190°	984
H	4-BrC ₆ H ₄	CH ₃	NO ₂	211°	1001
H	C ₆ H ₅	2-CH ₃ OC ₆ H ₄	NO ₂	164°	670
C ₆ H ₅ CH ₂	CH ₃	CH ₃	NO ₂	161°	333
C ₆ H ₅	CH ₃	CH ₃	NO ₂	273°	807, 809, 1491
CH ₃	C ₆ H ₅	CH ₃	NO ₂	210°	888
CH ₃	CH ₃	CH ₃	NO ₂	143° (dec.)	992
C ₆ H ₅	CH ₃	C ₆ H ₅ CH ₂	NO ₂	193°	1320
CH ₃	4-BrC ₆ H ₄	CH ₃	NO ₂	221°	1001
2-NO ₂ C ₆ H ₄	CH ₃	CH ₃	NO ₂	244°	978
3-NO ₂ C ₆ H ₄	CH ₃	CH ₃	NO ₂	203° (dec.)	978
CH ₃	3-NO ₂ C ₆ H ₄	CH ₃	NO ₂	271° (exp.)	1001
4-NO ₂ C ₆ H ₄	CH ₃	CH ₃	NO ₂	276°	978

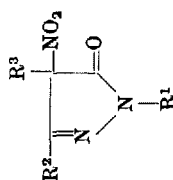


TABLE XXIX. 2-Pyrazolin-5-ones. 4-Nitro Derivatives

R ¹	R ²	R ³	M.p.	Reference
H	H	H	136°	653
H	CH ₃	H	276°	9, 61, 478, 480
CH ₃	CH ₃	CH ₃	127°	478
C ₆ H ₅ CH ₂	CH ₃	H	144° (dec.)	333
C ₆ H ₅	CH ₃	H	129° (dec.)	9, 809, 1607
C ₆ H ₅	CH ₃	K	250°	1642
4-NO ₂ C ₆ H ₄	CH ₃	H	—	672
3-Br-4-NO ₂ C ₆ H ₃	CH ₃	H	128°	1683
2-HOOCCH ₂ H ₄	C ₆ H ₅	H	288° (dec.)	1004
C ₆ H ₅	CH ₃	Br	84° (dec.)	1642
4-BrC ₆ H ₄	CH ₃	Br	85° (dec.)	1642
4-NO ₂ C ₆ H ₄	CH ₃	NO ₂	—	690
H ₃ C ₂ OOOC	CH ₃	H	172°	61
H ₇ C ₃ OOOC	CH ₃	H	157°	61

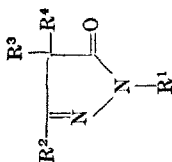
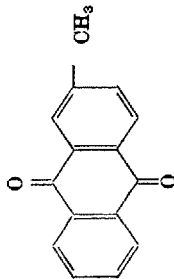


TABLE XXX. 2-Pyrazolin-5-ones. Aldehydes and Ketones

R¹	R²	R³	R⁴	M.p.	Reference
H	HCO	H	H	—	1546
H	H	CH₃CO	H	225°	1295
H	CH₃	C₆H₅CO	H	261°, 280° (dec.)	947, 1193
H	C₆H₅	HCO	H	215° (dec.)	1188
C₆H₅	CH₃CO	H	H	180°	767
C₆H₅	H	CH₃CO	H	191°	1295
H	C₆H₅	CH₃CO	H	204°	1188
C₆H₅	H₅C₂OCCCH₂CO	H	H	182°	837
3-CH₃C₆H₄	H₅C₂OCCCH₂CO	H	H	178°	837
4-CH₃C₆H₄	H₅C₂OCCCH₂CO	H	H	184°	837
4-CH₃OC₆H₄	H₅C₂OCCCH₂CO	H	H	189°	837
3-ClC₆H₄	H₅C₂OCCCH₂CO	H	H	180°	837
4-ClC₆H₄	H₅C₂OCCCH₂CO	H	H	109°	837
3-NO₂C₆H₄	H₅C₂OCCCH₂CO	H	H	183°	837
4-NO₂C₆H₄	H₅C₂OCCCH₂CO	H	H	227°	837
4-HO₃SC₆H₄	H₅C₂OCCCH₂CO	H	H	—	837
C₆H₅	CH₃	HCO	H	173°	586, 824, 1089, 1092, 1093
C₆H₅	CH₃	CH₃CO	H	66°	591, 1192
C₆H₅	CH₃	C₂H₅CO	H	68°	1193
C₆H₅	CH₃	C₃H₇CO	H	35°	1193
C₆H₅	CH₃	C₆H₅CH₂CH₂CO	H	131°	1532, 1533
C₆H₅	CH₃	(CH₃)₂NCH₂CH₂CO	H	220°	1098

C_6H_5	CH_3	$(C_2H_5)_2NCH_2CH_2CO$	H	212°	1098
C_6H_5	CH_3		H	220°	1098
C_6H_5	CH_3	HOOCOO	H	236° (dec.)	1641
C_6H_5	CH_3	C_2H_5OOCOO	H	81°	1641
C_6H_5	CH_3	C_6H_5CO	H	86°, 102°, 118°	973, 977, 1056
C_6H_5	CH_3	$4-NO_2C_6H_4CO$	H	203°	110
C_6H_5	CH_3	$2-HOOCOC_6H_4CO$	H	—	1202
C_6H_5	$C_{17}H_{35}$	$C_{17}H_{35}CO$	H	44°	1124
C_6H_5	$C_{21}H_{43}$	$C_{21}H_{43}CO$	H	52°	1124
C_6H_5	$C_{18}H_{33}CO$	$4-HOOC_6H_4CH=$	H	148°	315
C_6H_5	CH_3	HCO	H	166°	107
C_6H_5	CH_3	HOOCOO	H	218°	1641
C_6H_5	CH_3	H_2C_2OOCOO	H	108°	1641
C_6H_5	CH_3	HCO	H	152°	1186
C_6H_5	CH_3	CH_3CO	H	114°	1193
C_6H_5	CH_3	CH_3CO	H	198°	591
C_6H_5	$C_{18}H_{33}CO$	$4-HOOC_6H_4CH=$	H	197°	315
C_6H_5	$C_{18}H_{33}CO$	$4-HOOC_6H_4CH=$	H	222°	315
$2,4-(NO_2)_2C_6H_3$	$C_6H_5CH_2CH_2$	CH_3CO	H	178°	124
	CH_3	CH_3CO	H	237°	1009
C_6H_5	C_6H_5	HCO	H	149°	1186
C_6H_5	C_6H_5	H_5C_2OOCOO	H	108°	1641

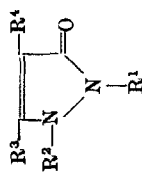


TABLE XXXI. 3-Pyrazolin-5-ones. Acyl Substituents on Carbon

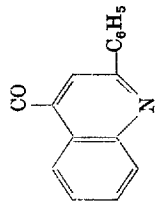
R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	C ₆ H ₅	H	CH ₃ CO	191°	1295
C ₆ H ₅	CH ₃	HCO	H	119°	698
C ₆ H ₅	CH ₃	H	CH ₃ CO	216°	108, 109, 331, 696, 901, 902, 1097
C ₆ H ₅	CH ₃	H	C ₂ H ₅ CO	169°	901
C ₆ H ₅	CH ₃	H	HOOCO	205°	108
C ₆ H ₅	CH ₃	H	C ₆ H ₅ CH=CHCO	190°, 234° (dec.)	696, 902
C ₆ H ₅	CH ₃	CH ₃	HCO	161°	196, 201, 204, 889, 892, 893, 896, 897, 1092, 1093, 1097, 1181, 1634
CH ₃	C ₆ H ₅	CH ₃	HCO	138°	1190
CH ₃	CH ₃	C ₆ H ₅	HCO	155°	1190
C ₆ H ₅	CH ₃	CH ₃	CH ₃ CO	156°	799
C ₆ H ₅	CH ₃	CH ₃	C ₂ H ₅ CO	146°	112, 740
C ₆ H ₅	CH ₃	CH ₃	C ₃ H ₇ CO	113°, 148°	88, 737
C ₆ H ₅	CH ₃	CH ₃	C ₄ H ₉ CO	104°	737
C ₆ H ₅	CH ₃	CH ₃	iso-C ₄ H ₉ CO	103°	88
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₁₁ CO	94°	737
C ₆ H ₅	CH ₃	CH ₃	(C ₂ H ₅) ₂ CHCO	133°	735, 740
C ₆ H ₅	CH ₃	CH ₃	HOCH ₂ CO	121°	362, 740
C ₆ H ₅	CH ₃	CH ₃	CH ₃ COOCH ₂ CO	173°	88, 740
C ₆ H ₅	CH ₃	CH ₃	2-HOC ₆ H ₄ COOCH ₂ CO	196°	740
C ₆ H ₅	CH ₃	CH ₃	CH ₃ CHCO	148°	112
C ₆ H ₅	CH ₃	CH ₃	CH ₃ COO		

C_6H_5	CH_3	CH_3	CH_3CH_2CHCO CH_3COO	141°	88
C_6H_5	CH_3	CH_3	H_2NCH_2CO	139°	88
C_6H_5	CH_3	CH_3	CH_3NHCH_2CO	242°	740
C_6H_5	CH_3	CH_3	$C_2H_5NHCH_2CO$	177°	740
C_6H_5	CH_3	CH_3	$(C_2H_5)_2NCH_2CO$	—	371
C_6H_5	CH_3	CH_3		125°	88
C_6H_5	CH_3	CH_3	$C_6H_5CH_2NHCH_2CO$	222°	740
C_6H_5	CH_3	CH_3	$C_6H_5NHCH_2CO$	152°	740
C_6H_5	CH_3	CH_3	$4-C_2H_5OC_6H_4NHCH_2CO$	185°	740
C_6H_5	CH_3	CH_3	CH_3CHCO NH_2	315°	23, 88
C_6H_5	CH_3	CH_3	CH_3COCO	224°	112
C_6H_5	CH_3	CH_3	CH_3CHCO C_2H_5NH	221°	112
C_6H_5	CH_3	CH_3	CH_3CHCO $iso-C_3H_7NH$	238°	112
C_6H_5	CH_3	CH_3	CH_3CHCO $(CH_3)_2N$	203°	112
C_6H_5	CH_3	CH_3	$H_2NCH_2CH_2CO$	162°	23
C_6H_5	CH_3	CH_3	CH_3CHCO CH_3NH	130°	23, 112

(Table continued)

TABLE XXXI (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃	CH ₃ CHCO 	125°	88
C ₆ H ₅	CH ₃	CH ₃	CHCH ₂ CO	170°	88, 737, 799
C ₆ H ₅	CH ₃	CH ₃	B-CH ₂ CO	135°	362
C ₆ H ₅	CH ₃	CH ₃	ICH ₂ CO	140°	88
C ₆ H ₅	CH ₃	CH ₃	Cl ₃ CCO	181°	88
C ₆ H ₅	CH ₃	CH ₃	CH ₃ CHBrCO	145°	88, 112
C ₆ H ₅	CH ₃	CH ₃	C ₂ H ₅ CHBrCO	127°	88
C ₆ H ₅	CH ₃	CH ₃	(CH ₃) ₂ CCO	152°	88
C ₆ H ₅	CH ₃	CH ₃	(CH ₃) ₂ CHCHCO Br	129°	88
C ₆ H ₅	CH ₃	CH ₃	CNCH ₂ CO	156°	740
C ₆ H ₅	CH ₃	CH ₃	HOOCO	206°	108
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ CO	149°	737, 740
C ₆ H ₅	CH ₃	CH ₃	4-C ₂ H ₅ OC ₆ H ₄ CO	194°	740
C ₆ H ₅	CH ₃	CH ₃	2-H ₂ NC ₆ H ₄ CO	144°	740
C ₆ H ₅	CH ₃	CH ₃	4-H ₂ NC ₆ H ₄ CO	260°	88, 740
C ₆ H ₅	CH ₃	CH ₃	4-(CH ₃) ₂ NC ₆ H ₄ CO	217°	740
C ₆ H ₅	CH ₃	CH ₃	4-CH ₃ CONHC ₆ H ₄ CO	216°	740
C ₆ H ₅	CH ₃	CH ₃	4-H ₂ NCONHC ₆ H ₄ CO	223°	740
C ₆ H ₅	CH ₃	CH ₃	4-C ₆ H ₅ NHCONHC ₆ H ₄ CO	210°	740
C ₆ H ₅	CH ₃	CH ₃	2-NO ₂ C ₆ H ₄ CO	172°	740
C ₆ H ₅	CH ₃	CH ₃	4-NO ₂ C ₆ H ₄ CO	166°, 209°	88, 110, 740

C_6H_5	CH_3	CH_3		198°	740
C_6H_5	CH_3	C_2H_5	HCO	78°	901
C_6H_5	C_2H_5	CH_3	$ClCH_2CO$	132°	737
C_6H_5	CH_3	CH_3S	CH_3CO	113°	89
C_6H_5	CH_3	C_6H_5	HCO	158°	107, 196, 201, 889, 902, 1097, 1180
C_6H_5	CH_3	HCO	HCO	216°	698
$4-CH_3C_6H_4$	CH_3	CH_3	HCO	166°	196, 889
$4-C_2H_5OC_6H_4$	CH_3	CH_3	HCO	—	1097
CH_3	$4-C_2H_5OC_6H_4$	CH_3	HCO	146°	902

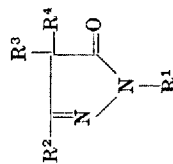


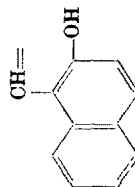
TABLE XXXII. 2-Pyrazolin-5-one-(3 or 4)-carboxylic Acids

R^1	R^2	R^3	R^4	M.p.	Reference
H	HOOC	H	H	$> 260^\circ$	337, 1229, 1544, 1547

(Table continued)

TABLE XXXII (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	H	HOOC	H	—	1228
H	HOOC	C ₁₄ H ₂₉	H	206°	43
H	HOOC		C ₆ H ₅ CH=	—	1546
C ₆ H ₅	HOOC	H	H	241°	626, 767, 837, 1304, 1635
C ₆ H ₅	H	HOOC	H	91° (dec.)	306, 1230
4-CH ₃ C ₆ H ₄	HOOC	H	H	188°	167, 1162, 1304
4-CH ₃ OC ₆ H ₄	HOOC	H	H	250°	87
3-H ₂ NC ₆ H ₄	HOOC	H	H	—	152, 347
3-ClC ₆ H ₄	HOOC	H	H	—	873
4-NO ₂ C ₆ H ₄	HOOC	H	H	233°	624
4-HO ₃ SC ₆ H ₄	HOOC	H	H	—	1162
4-H ₂ NO ₂ SC ₆ H ₄	HOOC	H	H	260° (dec.)	1628
3,4-Cl ₂ C ₆ H ₃	HOOC	H	H	—	873
3,6-Cl ₂ C ₆ H ₃	HOOC	H	H	—	873
2,4,6-Br ₃ C ₆ H ₃	HOOC	H	H	—	312
2-HO ₃ S-4,5-Cl ₂ C ₆ H ₃	HOOC	H	H	—	518
1-C ₁₀ H ₇	HOOC	H	H	264° (dec.)	767
2-C ₁₀ H ₇	HOOC	H	H	264° (dec.)	767
2-(C ₆ H ₅)-C ₆ H ₄	HOOC	H	H	—	1379
C ₆ H ₅	CH ₃	HOOC	H	189°	24
C ₆ H ₅	HOOC	s-C ₄ H ₉	H	96°	167
4-CH ₃ C ₆ H ₄	CH ₃	HOOC	H	187°	107
4-CH ₃ C ₆ H ₄	HOOC	iso-C ₃ H ₇	H	110°	167
C ₆ H ₅	HOOC	C ₆ H ₅ CH ₂	H	196°, 233°	167, 498
C ₆ H ₅	HOOC	C ₆ H ₅	H	144°	167, 506
C ₆ H ₅	HOOC				



H	CH ₃ OOC	H	C ₆ H ₅ CH ₂	H	226	1549
H	CH ₃ OOC		H		> 250°	1549
C ₆ H ₅	CH ₃ OOC		H		196°	767
4-CH ₃ OCCC ₆ H ₄	CH ₃ OOC		H		241° (dec.)	1274
4-HO ₃ SC ₆ H ₄	CH ₃ OOC		H		—	153
C ₆ H ₅	CH ₃ OOC		CH ₃		191°	1064
H	C ₂ H ₅ OOC		H		178°	2, 337, 358, 1220, 1229, 1357, 1544, 1547
H	H		C ₂ H ₅ OOC	H	180°	604, 1228, 1231, 1232, 1233
CH ₃	C ₂ H ₅ OOC		H		148°	594
H	CH ₃		C ₂ H ₅ OOC	H	195°	1081
H	H		CH ₃	C ₂ H ₅ OOC	—	1232
H	C ₂ H ₅ OOC		C ₇ H ₁₅	H	151°	43
H	C ₂ H ₅ OOC		C ₁₀ H ₂₁	H	142°	43
H	C ₂ H ₅ OOC		C ₁₂ H ₂₅	H	130°	43
H	C ₂ H ₅ OOC		C ₁₄ H ₂₉	H	130°	43
H	C ₂ H ₅ OOC		C ₁₆ H ₃₃	H	123°	43
H	C ₂ H ₅ OOC		C ₂ H ₅ OOCCH ₂	H	156°	962
H	C ₂ H ₅ OOC		C ₆ H ₅ CH=		> 250°	1545
CH ₃	C ₂ H ₅ OOC		CH ₃	H	150°	499
C ₆ H ₅	C ₂ H ₅ OOC		H	H	180°	365, 767, 1082, 1339, 1595
C ₆ H ₅	H		C ₂ H ₅ OOC	H	116°	306, 1230, 1231, 1556
H	C ₂ H ₅ OOC		C ₆ H ₅	H	233°	43
4-NO ₂ C ₆ H ₅	C ₂ H ₅ OOC		H	H	288°	767
4-HOCC ₆ H ₅	C ₂ H ₅ OOC		H	H	197°	767
4-HO ₃ SC ₆ H ₄	C ₂ H ₅ OOC		H	H	—	153
2-KO ₃ SC ₆ H ₄	C ₂ H ₅ OOC		H	H	—	414
4-H ₂ NO ₂ SC ₆ H ₄	C ₂ H ₅ OOC		H	H	197°	767, 1628
2-CH ₃ -6-Cl-4-HO ₃ SC ₆ H ₃	C ₂ H ₅ OOC		H	H	—	153

(Table continued)

TABLE XXXII (continued)

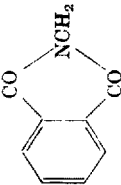
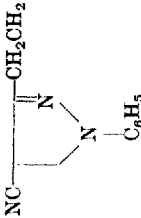
R ¹	R ²	R ³	R ⁴	M.p.	Reference
4-(4-CH ₃ CONHC ₆ H ₄)C ₆ H ₄	C ₂ H ₅ OOC	H	H	—	163
C ₆ H ₅	CH ₃	C ₂ H ₅ OOC	H	121°	1008
C ₆ H ₅	C ₂ H ₅ OOC	CH ₃	H	151°	37, 499
C ₆ H ₅	H	C ₂ H ₅ OOC	CH ₃	—	1232
C ₆ H ₅	C ₂ H ₅ OOC	C ₂ H ₅	H	199°	499
C ₆ H ₅	C ₂ H ₅ OOC	iso-C ₃ H ₇	H	100°	1339
C ₆ H ₅	HOOCCH ₂ CH ₂	C ₂ H ₅ OOC	H	—	1222
C ₆ H ₅	C ₂ H ₅ OOCCH ₂ CH ₂	C ₂ H ₅ OOC	H	61°	418
C ₆ H ₅	CH ₃ OOCCH=CH	C ₂ H ₅ OOC	H	147°	419
C ₆ H ₅	C ₂ H ₅ CHCOCH ₂ CH ₂ CN	C ₂ H ₅ OOC	H	106°	1223
C ₆ H ₅	C ₂ H ₅ OOC	C ₆ H ₅ CH ₂	H	194°	498
C ₆ H ₅	C ₂ H ₅ OOC	(C ₆ H ₅) ₂ CH	H	148°	1639
C ₆ H ₅		C ₂ H ₅ OOC	H	215°	138
C ₆ H ₅		C ₂ H ₅ OOC	H	167°	1223

TABLE XXXII (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	H ₂ NHNOC	H	H	235°	1595
C ₆ H ₅	H ₂ NHNOC	CH ₃	H	179°	499
C ₆ H ₅	H ₂ NHNOC	C ₂ H ₅	H	144°	499
C ₆ H ₅	H ₂ NHNOC	C ₆ H ₅ CH ₂	H	—	498
C ₆ H ₅	H ₂ NHNOC	C ₆ H ₅	H	213°	506
CH ₃	N ₃ OC	H	H	113° (def.)	594
C ₆ H ₅	N ₃ OC	H	H	134° (def.)	1595
C ₆ H ₅	N ₃ OC	C ₆ H ₅ CH ₂	H	134° (def.)	498
C ₆ H ₅	N ₃ OC	C ₆ H ₅	H	506	506
H	CH ₃	CN	H	281°	924
C ₆ H ₅	CH ₃	CN	H	>316°, 218°	24, 924, 925
C ₆ H ₅	C ₆ H ₅ CH ₂	CN	H	173°	1310
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	CN	H	198°	1186
C ₆ H ₅	C ₆ H ₅ CH ₂	CN	C ₂ H ₅	167°	1310
C ₆ H ₅	C ₆ H ₅	CN	H	232°	924
C ₆ H ₅	ClOC	C ₆ H ₅ CH ₂	H	liquid	498
CH ₃	C ₆ H ₅	CN	H	225°	1190

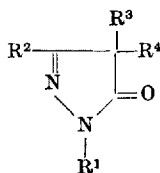


TABLE XXXIII. 2-Pyrazolin-5-ones. Carboxyl Derivatives Combined with Other Functional Substituents

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	C ₆ H ₅ CH=N	HOOC	H	> 280°	557
H	HOOC	NO	H	215° (dec.)	1545
C ₆ H ₅	HOOC	NO	H	—	1635
C ₆ H ₅	HOOC	H ₂ N	H	225°	292
4-HO ₃ SC ₆ H ₄	HOOC	H ₂ N	H	—	35
C ₆ H ₅	HOOC	CH ₃ CONH	H	216°	292
H	H ₃ COOC	NO	H	—	1549
H	C ₂ H ₅ OOC	C ₆ H ₅ O	H	213°	677
H	C ₂ H ₅ OOC	C ₆ H ₅ S	H	213°	677
H	C ₂ H ₅ OOC	NO	H	182°	1545
H ₂ NOC	C ₂ H ₅ OOC	HOOCCH ₂ CH ₂	H	170°	1222
H ₂ NOC	C ₂ H ₅ OOC	CN	H	—	366
C ₆ H ₅	C ₂ H ₅ OOC	C ₆ H ₅ CONH	H	195°	292
C ₆ H ₅	C ₂ H ₅ OOC	C ₆ H ₅ S	H	183.5°	677
C ₆ H ₅	C ₂ H ₅ OOC	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=		150°	519
C ₆ H ₅	C ₂ H ₅ OOC	2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=		161°	244
C ₆ H ₅ CO	C ₂ H ₅ OOC	C ₆ H ₅ CH ₂	H	217°	497
C ₆ H ₅	H ₂ NOC	2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=		210° (dec.)	244
H	H ₂ NHNOC	H ₂ NN=		178°	1549
CH ₃	H ₂ NHNOC	NO	H	112° (exp.)	594
C ₆ H ₅ CO	H ₂ NHNOC	C ₆ H ₅ CH ₂	H	203°	497
C ₆ H ₅ CO	N ₃ OC	C ₆ H ₅ CH ₂	H	135° (def.)	497
H	C ₆ H ₅ CONHNHCO	C ₆ H ₅ CO	H	214°	337

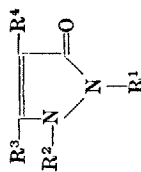


TABLE XXXIV. 3-Pyrazolin-5-ones. Carboxylic Acids and Thiocarboxylic Acids and Derivatives

R¹	R²	R³	R⁴	M.p.	Reference
H	C₆H₅	H	HOOC	216° (dec.)	993
C₆H₅	CH₃	HOOC	H	198°	108
C₆H₅	CH₃	H	HOOC	220°	108
C₆H₅	C₆H₅	HOOC	H	205°	370
C₆H₅	CH₃	CH₃	HOOC	(dec.)	17, 107, 741, 896
C₆H₅	CH₃	HOOC	C₂H₅	72°	167
C₆H₅	C₂H₅	CH₃	HOOC	178°	741
C₆H₅	CH₃	HOOC	iso-C₃H₇	73°	167
C₆H₅	CH₃	HOOC	C₆H₅CH₂	110°	167
C₆H₅	CH₃	C₆H₅	HOOC	186°	107, 196
C₆H₅	CH₃	HOOC	C₆H₅	107°	167
4-CH₃C₆H₄	CH₃	CH₃	HOOC	187°	196
C₆H₅	CH₃	CH₃	HSOC	189°	107, 109
C₆H₅	CH₃	CH₃	HSSC	189°	109, 831
C₆H₅	CH₃	CH₃OOC	H	(dec.)	698
C₆H₅	C₆H₅	CH₃OOC	H	121°	370
C₆H₅	CH₃	CH₃	CH₃OOC	138°	18, 741
C₆H₅	CH₃	CH₃	CH₃S₂C	154°	109
H	C₆H₅	H	C₂H₅OOC	187°	993
CH₃	CH₃	H	C₂H₅OOC	oil	1228

C_6H_5	CH_3	C_2H_5OOC	71°	1230
C_6H_5	C_6H_5	H	—	370
C_6H_5	CH_3	C_2H_5OOC	152°	107, 741
C_6H_5	CH_3	CH_3	96°	167
C_6H_5	CH_3	C_2H_5OOC	73°	1339
$4\cdot CH_3C_6H_4$	CH_3	iso- C_3H_7	101°	167
C_6H_5	CH_3	iso- C_4H_9OOC	111°	741
C_6H_5	CH_3	iso- $C_5H_{11}OOC$	99°	741
C_6H_5	CH_3	$ClCH_2CH_2OOC$	144°	741
C_6H_5	CH_3	$NCOCH_2CH_2OOC$	230°	741
C_6H_5	CH_3	$H_2NCH_2CH_2OOC$	(dec.)	
C_6H_5	CH_3	$CH_3NHCH_2CH_2OOC$	$>260^\circ$	741
C_6H_5	CH_3	$(CH_3)_2NCH_2CH_2OOC$	208°	741
C_6H_5	CH_3	$C_6H_5NHCH_2CH_2OOC$	202°	741
C_6H_5	CH_3	$4\cdot C_2H_5OC_6H_4NHCH_2CH_2OOC$	(dec.)	
C_6H_5	CH_3	$4\cdot C_2H_5OC_6H_4NHCH_2CH_2OOC$	242°	741
C_6H_5	CH_3	$4\cdot C_2H_5OC_6H_4NHCH_2CH_2OOC$	(dec.)	
C_6H_5	CH_3	$4\cdot C_2H_5OC_6H_4NHCH_2CH_2OOC$	186°	741
C_6H_5	CH_3	$(C_6H_5)_2NCH_2CH_2OOC$	175°	741
C_6H_5	CH_3	$4\cdot C_2H_5OC_6H_4NHCH_2CH_2OOC$	134°	741
C_6H_5	CH_3	$4\cdot C_2H_5OC_6H_4NHCH_2CH_2OOC$	160°	741
C_6H_5	CH_3	$H_2NCNHC(=O)CH_2OOC$		
C_6H_5	CH_3	$C_6H_5CH_2OOC$	130°	741
C_6H_5	CH_3	$C_6H_5CH_2OOC$	126°	741
C_6H_5	CH_3	$2\cdot CH_3OC_6H_4OOC$	198°	741
C_6H_5	CH_3	$2\cdot CH_3OC_6H_4OOC$	183°	741
C_6H_5	CH_3	$2\cdot C_6H_5OOCOC_6H_4OOC$	138°	741
C_6H_5	CH_3	$1\cdot C_{10}H_7OOC$	179°	741
C_6H_5	CH_3	$2\cdot C_{10}H_7OOC$	175°	741
C_6H_5	CH_3	$2\cdot C_{10}H_7OOC$	186°	741

(Table continued)

TABLE XXXIV (continued)

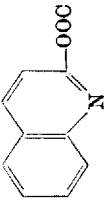
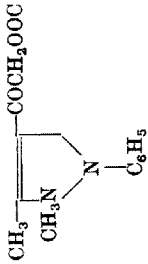
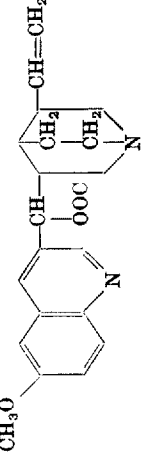
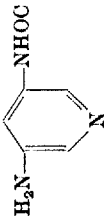
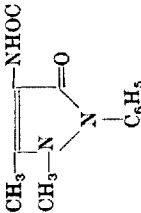
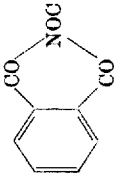
R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃		217°	741
C ₆ H ₅	CH ₃	CH ₃		256°	741
C ₆ H ₅	CH ₃	CH ₃		265°	741
H	C ₆ H ₅	CH ₃	C ₂ H ₅ SSC	114°	89
C ₆ H ₅	CH ₃	CH ₃	C ₂ H ₅ SSC	178°	89, 831
CH ₃	C ₆ H ₅	CH ₃	C ₂ H ₅ SSC	161°	829
C ₆ H ₅	CH ₃	H ₂ NOC	H	197°	167, 697, 1339
C ₆ H ₅	CH ₃	C ₆ H ₅ NHOC	C ₆ H ₅	291°	167
H	C ₆ H ₅	CH ₃	C ₆ H ₅ NHOC	258°	826
H	C ₆ H ₅	CH ₃	1-C ₁₀ H ₇ NHOC	231°	826
C ₆ H ₅	CH ₃	CH ₃	H ₂ NOC	246°	741, 831, 925
C ₆ H ₅	CH ₃	CH ₃	CH ₃ NHOC	207°	741
C ₆ H ₅	CH ₃	CH ₃	(CH ₃) ₂ NOC	211°	741
C ₆ H ₅	CH ₃	CH ₃	(C ₂ H ₅) ₂ NOC	106°	23, 107, 741
C ₆ H ₅	CH ₃	CH ₃	H ₂ NCH ₂ CH ₂ NHOC	234°	741
C ₆ H ₅	CH ₃	CH ₃	C ₂ H ₅ O ₂ CH ₂ NHOC	—	741

TABLE XXXIV (continued)

R ¹	R ²	R ³	R ⁴	M.P.	Reference
C ₆ H ₅	CH ₃	CH ₃		298°	741
C ₆ H ₅	CH ₃	CH ₃		246°	741
C ₆ H ₅	CH ₃	CH ₃	(C ₆ H ₅) ₂ NOC	208°	741
C ₆ H ₅	CH ₃	CH ₃		186° (dec.)	741
CH ₃	C ₆ H ₅	CH ₃	H ₂ NOC	215°	830
CH ₃	C ₆ H ₅	CH ₃	C ₆ H ₅ NHOC	164°	829
CH ₃	C ₆ H ₅	CH ₃	3-NO ₂ C ₆ H ₄ NHOC	—	829
C ₆ H ₅	CH ₃	H ₂ NOC	iso-C ₃ H ₇	130°	1339
CH ₃	C ₆ H ₅	CH ₃	1-C ₁₀ H ₇ NHOC	185°	829
H	C ₆ H ₅	CH ₃	C ₆ H ₅ NHSC	238°	826
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ NHSC	184°, 199°	826, 831
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ N=C	148°, 200°	826, 831
				186°	830

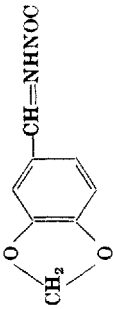
CH ₃	C ₆ H ₅	CH ₃	HN=C SH	197°	830
CH ₃	C ₆ H ₅	CH ₃	C ₆ H ₅ NHSC	152°	830
CH ₃	C ₆ H ₅	CH ₃	C ₆ H ₅ N=C SH	206°	829
CH ₃	C ₆ H ₅	CH ₃	1-C ₁₀ H ₇ N=C SH	195°	829
CH ₃	CH ₃	H ₂ NHNOC	H	204°	167
C ₆ H ₅	CH ₃	H ₂ NHNOC	H	233°, 147°	167, 698, 1387
C ₆ H ₅	CH ₃		H	247°	698
C ₆ H ₅	CH ₃	C ₆ H ₅ SO ₂ NHNHOC	H	229°	698
C ₆ H ₅	C ₂ H ₅	H ₂ NHNOC	H	(dec.)	167
C ₆ H ₅	CH ₃	CH ₃	H ₂ NHNOC	200°, 270°	696, 892, 1634
C ₆ H ₅	CH ₃	H ₂ NHNOC	CH ₃	158°	167
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ SO ₂ NHNHOC	262°	892, 204, 1634
C ₆ H ₅	CH ₃	H ₂ NHNOC	C ₂ H ₅	175°	167
C ₆ H ₅	CH ₃	H ₂ NHNOC	iso-C ₃ H ₇	113°	167, 1387
C ₆ H ₅	CH ₃	H ₂ NHNOC	s-C ₄ H ₉	145°	167
C ₆ H ₅	CH ₃	H ₂ NHNOC	C ₆ H ₅ CH ₂	191°	167
C ₆ H ₅	CH ₃	H ₂ NHNOC	C ₆ H ₅	75°	167
C ₆ H ₅	CH ₃	H ₂ NHNOC	Br	(C ₂ H ₅ OH)	167
C ₆ H ₅	CH ₃	H ₂ NHNOC		183°	

Table continued)

TABLE XXXIV (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
4-CH ₃ C ₆ H ₄	CH ₃	H ₂ NHNOC	iso-C ₃ H ₇	96°	167
CH ₃	C ₆ H ₅	CH ₃	H ₂ NHNSC	166°	830
CH ₃	C ₆ H ₅	CH ₃	C ₆ H ₅ HNHNSC	186°	830
CH ₃	C ₆ H ₅	CH ₃	H ₂ NN=C	165°	830
			SH		
CH ₃	CH ₃	N ₃ OC	H	110°	167
				(exp.)	
C ₆ H ₅	CH ₃	N ₃ OC	H	95° (dec.)	167, 1387
C ₆ H ₅	C ₂ H ₅	N ₃ OC	H	117°	167
				(dec.)	
C ₆ H ₅	CH ₃	N ₃ OC	iso-C ₃ H ₇	88° (dec.)	167, 1387
C ₆ H ₅	CH ₃	N ₃ OC	s-C ₄ H ₉	90° (dec.)	167
C ₆ H ₅	CH ₃	N ₃ OC	C ₆ H ₅ CH ₂	110°	167
				(exp.)	
C ₆ H ₅	CH ₃	N ₃ OC	C ₆ H ₅	97° (dec.)	167
4-CH ₃ C ₆ H ₄	CH ₃	N ₃ OC	iso-C ₃ H ₇	92° (dec.)	167
C ₆ H ₅	CH ₃	CH ₃	CN	224°	741, 925, 1181
C ₆ H ₅	CH ₃	C ₆ H ₅	CN	188°	1183
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	CH ₃	CN	186°	1180
C ₆ H ₅	CH ₃	CH ₃	ClOC	171°	18, 107, 741
C ₆ H ₅	CH ₃	CH ₃	NOOC	174°	741
C ₆ H ₅	CH ₃	CH ₃	CH ₃ COOOC	154°	741
C ₆ H ₅	CH ₃	CH ₃	(C ₂ H ₅) ₂ CHCOOOC	218°	741
				(dec.)	
C ₆ H ₅	CH ₃	CH ₃	ClCH ₂ COOOC	122°	23
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ COOOC	185°	741
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ SO ₃ OC	103°	741
C ₆ H ₅	CH ₃	CH ₃	4-CH ₃ C ₆ H ₄ SO ₃ OC	102°	741

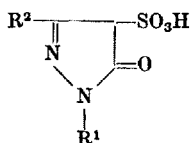


TABLE XXXV. 2-Pyrazolin-5-ones. Sulfonic Acids

R ¹	R ²	M.p.	Reference
H	CH ₃	—	1671
C ₆ H ₅	CH ₃	218°	684, 685, 738, 745, 1671, 1672
3-H ₂ NC ₆ H ₄	CH ₃	—	1674
4-H ₂ NC ₆ H ₄	CH ₃	—	1671, 1672, 1674
3-NO ₂ C ₆ H ₄	CH ₃	—	1674
4-NO ₂ C ₆ H ₄	CH ₃	—	1671
4-HO ₃ SC ₆ H ₄	CH ₃	—	684, 685
3-NO ₂ C ₆ H ₄	HOOC	—	1671

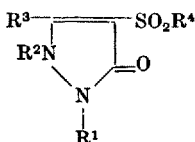


TABLE XXXVI. 3-Pyrazolin-5-ones. Sulfonic Acids

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃	HO	276° (dec.)	738, 745, 1249
C ₆ H ₅	C ₂ H ₅	CH ₃	HO	—	738
C ₆ H ₅	CH ₃	CH ₃	Cl	191°	745, 1248, 1249
C ₆ H ₅	CH ₃	CH ₃	H ₂ N	228°	745, 1248, 1249
C ₆ H ₅	CH ₃	CH ₃	CH ₃ HN	193°	745, 1248
C ₆ H ₅	CH ₃	CH ₃	(C ₂ H ₅) ₂ N	153°	745, 1248
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ NH	203°	745
C ₆ H ₅	CH ₃	CH ₃	4-C ₂ H ₅ OC ₆ H ₄ NH	93°	745
C ₆ H ₅	CH ₃	CH ₃	4-H ₂ NO ₂ SC ₆ H ₄ NH	213°	1248
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ CONH	242°	745
C ₆ H ₅	CH ₃	CH ₃		244° (dec.)	745, 1249

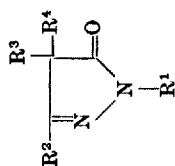
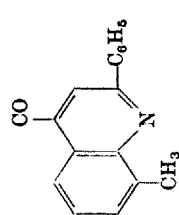
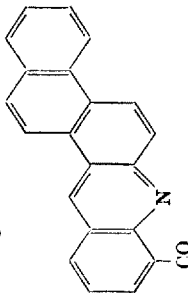
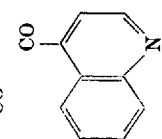
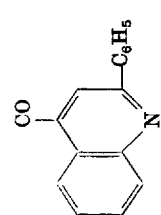
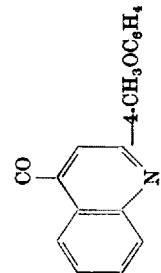


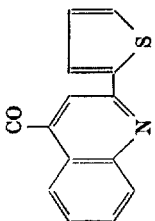
TABLE XXXVII. 2-Pyrazolin-5-ones. Acyl and Carboxyl Derivatives and Sulfonyl Substituents on N-1

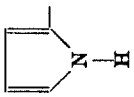
R ¹	R ²	R ³	R ⁴	M.p.	Reference
CH ₃ CO	C ₂ H ₅ OOCCCH ₂	H	H	116°	866
CH ₃ CO	CH ₃	CH ₃	H	126°	1531
CH ₃ CO	CH ₃	CH ₃	CH ₃	168°	1557, 1560
CH ₃ CO	CH ₃	C ₆ H ₅ CH ₃	H	128°	302
CH ₃ CO	C ₆ H ₅	H	H	127°	1598
CH ₃ CO		H	H	153°	1498, 1499
C ₆ H ₅ CH ₂ CO	CH ₃	H	H	134°	6
C ₆ H ₅ CO	CH ₃	H	H	—	6
	CH ₃	H	H	237°	718
	CH ₃	H	H	> 300°	719

	CH ₃	H	H	—	719
	CH ₃	H	H	—	720
	C ₆ H ₅	H	H	—	1050
	C ₆ H ₅	H	H	190°	1050
	C ₆ H ₅	H	H	183°	1050

(Table continued)

TABLE XXXVII (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
	C ₆ H ₅	H	H	182°	1050
	CH ₃	H	H	152°, 166°	716, 1197, 1199
4-H ₂ NC ₆ H ₄ SO ₂	CH ₃	H	H	167°	356
4-CH ₃ CONHC ₆ H ₄ SO ₂	CH ₃	H	H	158°	1199
4-NO ₂ C ₆ H ₄ SO ₂	CH ₃	H	H	—	1627
CH ₃ OOOC	CH ₃	C ₂ H ₅	H	—	61
C ₆ H ₅ OOOC	CH ₃	H	H	203°	61
C ₂ H ₅ OOOC	CH ₃	CH ₃	H	184°	61
C ₂ H ₅ OOOC	CH ₃	C ₂ H ₅	H	170°	61
C ₃ H ₇ OOOC	CH ₃	H	H	120°	61
C ₃ H ₇ OOOC	CH ₃	CH ₃	H	149°	61
C ₃ H ₇ OOOC	CH ₃	C ₂ H ₅	H	126°	61
H ₂ NOC	CH ₃	H	H	170°, 192°	61, 275, 355
H ₂ NOC	iso-C ₄ H ₉	H	H	165°	97
H ₂ NOC	H	HOOCCH ₂	H	185°	275
H ₂ NOC	HOOCCH ₂ CH ₂	H	H	195° (dec.)	1221
H ₂ NOC	CH ₃ OOCCCH ₂ CH ₂	H	H	172°	1221
H ₂ NOC	CH ₃	CH ₃	H	180°, 194°	61, 358, 692
H ₂ NOC	CH ₃	C ₂ H ₅	H	168°	61, 358, 1012
H ₂ NOC	C ₆ H ₇	C ₂ H ₅	H	145°	1013
H ₂ NOC	CH ₃	iso-C ₂ H ₁₁	H	157°	65
H ₂ NOC	CH ₃	2-CH ₃ C ₄ H ₉	H	156°	65
H ₂ NOC	C ₆ H ₅	H	H	179°	357

$\begin{array}{c} \text{H}_2\text{NOC} \\ \text{H}_2\text{NOC} \\ \text{H}_2\text{NOC} \end{array}$	$\begin{array}{c} \text{C}_6\text{H}_5 \\ \text{iso-C}_3\text{H}_7 \\ \text{C}_6\text{H}_5 \end{array}$	$\begin{array}{c} \text{H} \\ \text{H} \\ \text{H} \end{array}$	$\begin{array}{c} 181^\circ \\ 318^\circ \\ 131^\circ \end{array}$	$\begin{array}{c} 1012 \\ 1640 \\ 1345 \end{array}$
H_2NOC		H	192°	1067
$\text{C}_6\text{H}_5\text{NHOC}$	CH_3	H	237°	643
$\text{C}_6\text{H}_5\text{NHOC}$		H	192°	1498, 1500
$\text{C}_6\text{H}_5\text{NHOC}$		$\text{C}_6\text{H}_5\text{CH=}$	$> 300^\circ$	1498, 1500
$\begin{array}{c} 4\text{-CH}_3\text{C}_6\text{H}_4\text{NHOC} \\ 4\text{-(1-C}_{10}\text{H}_7\text{)NHOC} \\ \text{NH} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{H} \\ \text{H} \end{array}$	$\begin{array}{c} 234^\circ \\ 195^\circ \end{array}$	$\begin{array}{c} 643 \\ 643 \end{array}$
$\begin{array}{c} \text{H}_2\text{NC} \\ \text{NH} \end{array}$	CH_3	H	235° (dec.)	359, 1568
$\begin{array}{c} \text{H}_2\text{NC} \\ \text{NH} \end{array}$	CH_3	CH_3	202°	359
$\begin{array}{c} \text{H}_2\text{NC} \\ \text{NH} \end{array}$	CH_3	C_2H_5	262°	359
$\begin{array}{c} \text{H}_2\text{NC} \\ \text{NH} \end{array}$	CH_3	C_3H_7	260°	359

(Table continued)

TABLE XXXVII (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
$\begin{array}{c} \text{NH} \\ \parallel \\ \text{H}_2\text{NC} \end{array} \text{ (HNO}_3 \text{ salt)}$	CH ₃	CH ₃	CH ₃	151°	359
$\begin{array}{c} \text{NH} \\ \parallel \\ \text{H}_2\text{NC} \end{array} \text{ (HNO}_3 \text{ salt)}$	CH ₃	C ₂ H ₅ OOC	H	290°	359
$\begin{array}{c} \text{NH} \\ \parallel \\ \text{H}_2\text{NC} \end{array}$	C ₆ H ₅	H	H	102°	359, 1563
$\begin{array}{c} \text{CH}_3 \\ \\ \text{NH} \\ \parallel \\ \text{H}_2\text{NC} \end{array}$	CH ₃	C ₆ H ₅ CH=		210° (dec.)	1296
$\begin{array}{c} \text{CH}_3 \\ \\ \text{NH} \\ \parallel \\ \text{C}_2\text{H}_5\text{OOCCH}_2\text{C}=\text{NC} \end{array}$	CH ₃	H	H	180° (dec.)	1568
$\begin{array}{c} \text{NH} \\ \parallel \\ \text{C}_2\text{H}_5\text{OOCCH}_2\text{C}=\text{NC} \end{array}$	CH ₃	H	H	185°	1568
$\begin{array}{c} \text{NC}_6\text{H}_5 \\ \parallel \\ \text{C}_6\text{H}_5\text{NHC} \end{array}$	CH ₃	H	H	198°	359
$\begin{array}{c} \text{N-4-CH}_3\text{C}_6\text{H}_4 \\ \parallel \\ \text{4-CH}_3\text{C}_6\text{H}_4\text{C} \end{array}$	CH ₃	H	H	210°	359
$\begin{array}{c} \text{N-2-C}_{10}\text{H}_7 \\ \parallel \\ \text{2-C}_{10}\text{H}_7\text{NHC} \end{array}$	CH ₃	H	H	290°	359
$\begin{array}{c} \text{NC}_6\text{H}_5 \\ \parallel \\ \text{C}_6\text{H}_5\text{NHC} \end{array}$	C ₆ H ₅	H	H	206°	359

$\text{N}-4\text{-CH}_3\text{C}_6\text{H}_4$ $\text{4-CH}_3\text{C}_6\text{H}_4\text{NHC}=\text{N}$	C_6H_5	H	H	249°	359
$\text{N}-2\text{-C}_{10}\text{H}_7$ $\text{2-C}_{10}\text{H}_7\text{NHC}=\text{N}$	C_6H_5	H	H	180°	359
CH_3 $\text{C}_2\text{H}_5\text{OOCCH}_2\text{C}=\text{N}-\text{NNHCO}$	CH_3	H	H	230° (dec.)	1037, 1632
H_2NCS	CH_3	H	H	180°	355, 358, 421
H_2NCS	C_6H_5	H	H	161°	357
CH_3NHCs	CH_3	H	H	84°	357
$\text{C}_2\text{H}_5\text{NHCs}$	C_6H_5	H	H	179°	357
CH_3 $\text{C}_2\text{H}_5\text{OOCCH}=\text{CNHCs}$	CH_3	H	H	175°	355
$\text{C}_6\text{H}_5\text{NHCs}$	CH_3	H	H	117°	357
$\text{C}_6\text{H}_5\text{NHCs}$	C_6H_5	H	H	127°	357
$\text{4-CH}_3\text{C}_6\text{H}_4\text{NHCs}$	CH_3	H	H	121°	357
$\text{4-CH}_3\text{C}_6\text{H}_4\text{NHCs}$	C_6H_5	H	H	106°	357
$\text{C}_6\text{H}_5\text{NHNHCs}$	CH_3	H	H	—	602

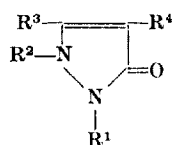
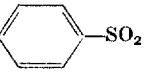


TABLE XXXVIII. 3-Pyrazolin-5-ones. Acyl Substituents on Nitrogen

R ¹	R ²	R ³	R ⁴	M.p.	Reference
H	CH ₃ CO	C ₆ H ₅	H	144°	1598
H	4-H ₂ N-  -SO ₂	CH ₃	H	169°	356
H	4-CH ₃ CONH-  -SO ₂	CH ₃	H	195°	356
C ₆ H ₅	C ₆ H ₅ CO	CH ₃	H	75°	1056
C ₆ H ₅	C ₆ H ₅ NHCO	CH ₃	H	142°	643
C ₆ H ₅	CH ₃ CO		H	69°	1499
CH ₃ CO	CH ₃ CO	CH ₃	H	54°	729
CH ₃ CO	CH ₃ CO		H	102°	1498, 1499
C ₆ H ₅	C ₆ H ₅ CO	CH ₃	CH ₃	99°	1056
C ₆ H ₅	C ₆ H ₅ CO	CH ₃	Br	82.5°	1056
CH ₃ CO	C ₆ H ₅ N=N	CH ₃	CH ₃	—	1531
CH ₃ CO	CH ₃ CO	CH ₃	CH ₃	44°, 56°	1531, 1557
CH ₃ CO	CH ₃ CO	CH ₃	C ₂ H ₅	57°	729
CH ₃ CO	CH ₃ CO	CH ₃	C ₃ H ₇	40°	729
CH ₃ CO	CH ₃ CO	CH ₃	C ₆ H ₅ CH ₂	69°	729
C ₆ H ₅	C ₆ H ₅ CO	CH ₃	C ₆ H ₅ CO	157°	973, 1056

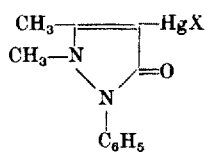


TABLE XXXIX. Mercurated 3-Pyrazolin-5-ones

X	M.p.	Reference
Cl	95°	1155
Br	130°	1155
I	—	1155
OH	—	1155
CH_3COO	—	1155

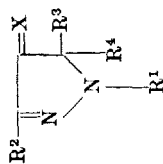
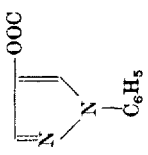


TABLE XL. 2-Pyrazolin-4-ones and 4-Imino-2-pyrazolines

X=O				
R ¹	R ²	R ³	R ⁴	M.p. Reference
H	H	H	H	118° 1644
CH ₃	H	H	H	— 1644
H	(CH ₃) ₂ CHCH ₂ CH ₂	H	H	185° 92
H	C ₆ H ₅ CH ₂	H	H	157° 92
C ₆ H ₅	H	H	H	— 425
H	HOOC	H	H	208° 425, 1644
H	H	HOOC	H	204° 92
C ₆ H ₅	H	C ₆ H ₅ N=N	H	122° 1644
C ₆ H ₅	H	NO	H	190° 1644
2-NO ₂ C ₆ H ₄	C ₆ H ₅ CO	H	H	121° 288
4-NO ₂ C ₆ H ₄	C ₆ H ₅ CO	H	H	211° 288
H	(CH ₃) ₂ CHCH ₂ CH ₂	HOOC	H	186° 92
H	C ₆ H ₅ CH ₂	HOOC	H	183° 92
C ₆ H ₅	HOOC	H	H	153° 425, 1644
H	(CH ₃) ₂ CHCH ₂ CH ₂	C ₂ H ₅ COOC	H	115° 92
H	C ₆ H ₅ CH ₂	C ₂ H ₅ COOC	H	169° 92
H	C ₆ H ₅	C ₂ H ₅ COOC	H	162° 92
C ₆ H ₅	C ₂ H ₅ COOC	H	H	84° 1644
2-NO ₂ C ₆ H ₄	C ₂ H ₅ COOC	H	H	153° 286
4-NO ₂ C ₆ H ₄	C ₂ H ₅ COOC	H	H	220° 286
4-H ₂ O ₃ AsC ₆ H ₄	C ₂ H ₅ COOC	H	H	— 1292
2-CH ₃ -4-NO ₂ C ₆ H ₃	C ₂ H ₅ COOC	H	H	177° 290

2-CH ₃ -5-NO ₂ C ₆ H ₃	C ₂ H ₅ OOC	H	114°	290
3,5-Cl ₂ C ₆ H ₃	C ₂ H ₅ OOC	H	154°	295
3,5-Br ₂ C ₆ H ₃	C ₂ H ₅ OOC	H	154°	295
2-Br-4-NO ₂ C ₆ H ₃	C ₂ H ₅ OOC	H	189°	286
2,4-(NO ₂) ₂ C ₆ H ₃	C ₂ H ₅ OOC	H	150°	289
2-CH ₃ -6-NO ₂ C ₆ H ₃	C ₂ H ₅ OOC	H	99°	290
2-NO ₂ -4-CH ₃ C ₆ H ₃	C ₂ H ₅ OOC	H	119°	290
3-NO ₂ -4-CH ₃ C ₆ H ₃	C ₂ H ₅ OOC	H	182°	290
2-CH ₃ -4-Br-6-NO ₂ C ₆ H ₂	C ₂ H ₅ OOC	H	182°	290
2-CH ₃ -4-NO ₂ -6-BrC ₆ H ₂	C ₂ H ₅ OOC	H	183°	290
2-NO ₂ -4-CH ₃ -6-BrC ₆ H ₂	C ₂ H ₅ OOC	H	165°	290
2,6-Br ₂ -3-NO ₂ -4-CH ₃ C ₆ H	C ₂ H ₅ OOC	H	184°	290
2,4,6-Cl ₃ C ₆ H ₂	C ₂ H ₅ OOC	H	158°	294
2,4,6-Br ₃ C ₆ H ₂	C ₂ H ₅ OOC	H	160°	294
2,4-Cl ₂ -4-NO ₂ C ₆ H ₂	C ₂ H ₅ OOC	H	—	287
2,6-Br ₂ -4-NO ₂ C ₆ H ₂	C ₂ H ₅ OOC	H	170°	286
C ₆ H ₅	H	H	177°	1644

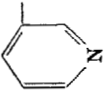
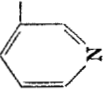
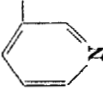
				
H	CH ₃ OOC	H	232°	92
H	C ₂ H ₅ OOC	H	151°	92
2-NO ₂ C ₆ H ₄	C ₆ H ₅ CO	H	120°	288
4-NO ₂ C ₆ H ₄	C ₆ H ₅ CO	H	177°	288
C ₆ H ₅	HOOC	H	209° (dec.)	1644
2-NO ₂ C ₆ H ₄	C ₂ H ₅ OOC	H	142°	287
3-NO ₂ C ₆ H ₄	C ₂ H ₅ OOC	H	109°	287
4-NO ₂ C ₆ H ₄	C ₂ H ₅ OOC	H	146°	287
4-NO ₂ C ₆ H ₄	C ₂ H ₅ OOC	H (4-NOH)	222°	287
2-CH ₃ -4-NO ₂ C ₆ H ₃	C ₂ H ₅ OOC	H	181°	290
2-CH ₃ -5-NO ₂ C ₆ H ₃	C ₂ H ₅ OOC	H	101°	290

(Table continued)

TABLE XL (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
2-CH ₃ -6-NO ₂ C ₆ H ₃	C ₂ H ₅ OOC	Cl	H	135°	290
3-NO ₂ -4-CH ₃ C ₆ H ₃	C ₂ H ₅ OOC	Cl	H	128°	290
2-Cl-4-NO ₂ C ₆ H ₃	C ₂ H ₅ OOC	Cl	H	191°	287
2-CH ₃ -4-Br-6-NO ₂ C ₆ H ₂	C ₂ H ₅ OOC	Cl	H	164°	290
2-CH ₃ -4-NO ₂ -6-BrC ₆ H ₂	C ₂ H ₅ OOC	Cl	H	202°	290
2-NO ₂ -4-CH ₃ -6-BrC ₆ H ₂	C ₂ H ₅ OOC	Cl	H	168°	290
2,4,6-Cl ₃ C ₆ H ₂	C ₂ H ₅ OOC	Cl	H	178°, 195°	294
2,6-Cl ₂ -4-NO ₂ C ₆ H ₂	C ₂ H ₅ OOC	Cl	H	200°	287
2-CH ₃ -4,6-Br ₂ -5-NO ₂ C ₆ H	C ₂ H ₅ OOC	Cl	H	165°	290
2,6-Br ₂ -3-NO ₂ -4-CH ₃ C ₆ H	C ₂ H ₅ OOC	Cl	H	169°	290
2-NO ₂ C ₆ H ₄	C ₂ H ₅ OOC	Br	H	161°	286
3-NO ₂ C ₆ H ₄	C ₂ H ₅ OOC	Br	H	167°	286
4-NO ₂ C ₆ H ₄	C ₂ H ₅ OOC	Br	H	163°	286
4-H ₂ O ₃ AsC ₆ H ₄	C ₂ H ₅ OOC	Br	H	—	1292
2-CH ₃ -5-NO ₂ C ₆ H ₃	C ₂ H ₅ OOC	Br	H	133°	290
2-CH ₃ -6-NO ₂ C ₆ H ₃	C ₂ H ₅ OOC	Br	H	146°	290
3-NO ₂ -4-CH ₃ C ₆ H ₃	C ₂ H ₅ OOC	Br	H	143°	290
3,5-Cl ₂ C ₆ H ₃	C ₂ H ₅ OOC	Br	H	156°	295
2-Br-4-NO ₂ C ₆ H ₃	C ₂ H ₅ OOC	Br	H	218°	286
2,4,6-Cl ₃ C ₆ H ₂	C ₂ H ₅ OOC	Br	H	190°	294
2,4,6-Br ₃ C ₆ H ₂	C ₂ H ₅ OOC	Br	H	208°	294
2,6-Br ₂ -4-NO ₂ C ₆ H ₂	C ₂ H ₅ OOC	Br	H	209°	286
C ₆ H ₅	HOOC	NO	H	190°	1644
2-NO ₂ C ₆ H ₄	C ₂ H ₅ CO	Cl	Cl	166°	288
4-NO ₂ C ₆ H ₄	C ₆ H ₅ CO	Cl	Cl	145°	288
2-NO ₂ C ₆ H ₄	C ₂ H ₅ OOC	Cl	Cl	98°	287
3-NO ₂ C ₆ H ₄	C ₂ H ₅ OOC	Cl	Cl	135°	287
4-NO ₂ C ₆ H ₄	C ₂ H ₅ OOC	Cl	Cl	—	287
2-CH ₃ -4-NO ₂ C ₆ H ₃	C ₂ H ₅ OOC	Cl	Cl	124°	290
2-Cl-4-NO ₂ C ₆ H ₃	C ₂ H ₅ OOC	Cl	Cl	131°	287

TABLE XL (continued)

X=NR ⁵						Reference
R ¹	R ²	R ³	R ⁴	R ⁵	M.p.	
H	H	H	H	H	80°, 195°	92, 368, 819
H	H	H	H	C ₆ H ₅ CO	173°	1646
H	H	H	H	4-H ₂ NC ₆ H ₄ SO ₂	185°	368, 1157
H	H	H	H	H	97°	368, 680
H	CH ₃	H	H	C ₆ H ₅ CO	205°	1045
H	CH ₃	H	H	4-H ₂ NC ₆ H ₄ SO ₂	176°	368
H	CH ₃	H	H	H	104°	671
C ₆ H ₅	H	H	H	H	—	1529
H		H	H	H	—	1529
H		H	H	4-H ₂ NC ₆ H ₄ SO ₂	210° (H ₂ O)	1529
H		H	H	4-CH ₃ CONHC ₆ H ₄ SO ₂	234°	1529
H	CH ₃	CH ₃	H	H	—	680, 1015, 1019
H	CH ₃	CH ₃	H	C ₆ H ₅ CO	290° (dec.)	1019

(Table continued)

TABLE XL (continued)

X = NR ⁵					
R ¹	R ²	R ³	R ⁴	R ⁵	M.p. Reference
H	CH ₃	CH ₃	H	4-H ₂ NC ₆ H ₄ SO ₂	233° 1157
C ₆ H ₅	CH ₃	H	H	H	88° 995
C ₆ H ₅	CH ₃	H	H	4-H ₂ NC ₆ H ₄	188° 995
C ₆ H ₅	CH ₃	H	H	4-CH ₃ CONHC ₆ H ₄	239° 995
C ₆ H ₅	CH ₃	H	H	HCO	81° 995
C ₆ H ₅	CH ₃	H	H	CH ₃ CO	120° 995
C ₆ H ₅	CH ₃	H	H	H ₂ NCO	198° 995
C ₆ H ₅	CH ₃	H	H	C ₆ H ₅ NHCO	193° 995
C ₆ H ₅	CH ₃	H	H	C ₆ H ₅ NHCS	173° 995
CH ₃	CH ₃	H	H	H	102° 812
C ₆ H ₅	CH ₃	CH ₃	H	H	38° 1043
C ₆ H ₅	CH ₃	CH ₃	H	CH ₃ CO	130° 1043
C ₆ H ₅	CH ₃	CH ₃	H	C ₆ H ₅ CO	153° 1165
H	CH ₃	Cl	H	H	182° 1045
H	CH ₃	Br	H	CH ₃ CO	185° 1045
C ₆ H ₅	CH ₃	Cl	H	H	227° 974, 995
C ₆ H ₅	CH ₃	Cl	H	HCO	137° 974
C ₆ H ₅	CH ₃	Cl	H	CH ₃ CO	123° 974
C ₆ H ₅	CH ₃	Cl	H	C ₆ H ₅ CO	148° 974
C ₆ H ₅	CH ₃	Cl	H	C ₆ H ₅ SO ₂	154° 974
C ₆ H ₅	CH ₃	Cl	H	H ₂ NCO	230° 974
C ₆ H ₅	CH ₃	Cl	H	C ₆ H ₅ NHCO	216° 974
C ₆ H ₅	CH ₃	Cl	H	C ₆ H ₅ NHCS	182° 974
H	H	HOOC	H	H	212° 92, 1210
H	CH ₃	HOOC	H	H	208° 1049
H	C ₂ H ₅ OOC	C ₂ H ₅ OOC	H	H	144° 92
CH ₃ CO	C ₆ H ₅	CH ₃	H	CH ₃ CO	186° 1044
CH ₃ CO	CH ₃	Cl	H	CH ₃ CO	176° 1045

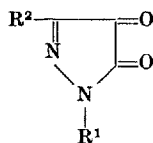


TABLE XLI. 2-Pyrazolin-4,5-diones

R ¹	R ²	M.p.	Reference
C ₆ H ₅	CH ₃	118°	52, 424, 809, 1242
4-BrC ₆ H ₄	CH ₃	171°	1642
4-NO ₂ C ₆ H ₄	CH ₃	185°	690
4-CH ₃ OC ₆ H ₄	C ₂ H ₅ OOCCH=CHCH=CH	164°	125
4-BrC ₆ H ₄	C ₂ H ₅ OOCCH=CH	91°	125
4-BrC ₆ H ₄	C ₂ H ₅ OOCCH=CHCH=CH	159°	125
C ₆ H ₅	C ₆ H ₅	—	1243

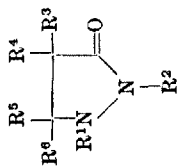
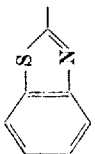


TABLE XLII. 3-Pyrazolidinones

Section A. All Substituents Except Mercury

R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	M.p.	Reference
H	H	H	H	H	H	b ₇₆₀ 132°	1209, 1550
H	H	CH ₃	H	H	H	b ₁₂ 162°	911, 1209
C ₃ H ₅	H	H	H	H	H	120°	57, 396, 750, 756, 758, 1122, 1177, 1550, 1630
H	C ₆ H ₅	H	H	H	H	78°	1351, 1491
H	H	H	H	C ₆ H ₅	H	101°	581, 1028
2-CH ₃ C ₆ H ₄	H	H	H	H	H	195°	1177
3-CH ₃ C ₆ H ₄	H	H	H	H	H	178°	1177
4-CH ₃ C ₆ H ₄	H	H	H	H	H	163°	396, 750, 756, 758, 1177, 1631
4-CH ₃ OC ₆ H ₄	H	H	H	H	H	146°	758
4-ClC ₆ H ₄	H	H	H	H	H	117°	396, 750, 756, 758
4-NO ₂ C ₆ H ₄	H	H	H	H	H	212°	1177
H	H	H	H	3-NO ₂ C ₆ H ₄	H	139°	335, 581
4-NCC ₆ H ₄	H	H	H	H	H	195°	1177
4-HOCH ₂ CH ₂ C ₆ H ₄	H	H	H	H	H	109°	1177, 1630

4-CH ₃ SO ₂ NHCH ₂ CH ₂ C ₆ H ₄	H	H	H	H	142°	1177
	H	H	H	H	215°	1177
C ₆ H ₅	H	CH ₃	H	H	135°	396, 701, 758, 762, 1569
C ₆ H ₅	H	CH ₃	H	CH ₃	127°	758, 762, 888
H	C ₆ H ₅	CH ₃	H	H	110°	911, 1569
H	C ₆ H ₅	H	H	CH ₃	84°	68, 816, 1569
H	4-CH ₃ C ₆ H ₄	H	H	CH ₃	—	68
H	4-ClC ₆ H ₄	CH ₃	H	H	117°	758
H	3-HO ₃ SC ₆ H ₄	H	H	CH ₃	—	1388
4-HOCH ₂ CH ₂ C ₆ H ₄	H	CH ₃	H	H	—	1631
H	2-Cl-3-HO ₃ SC ₆ H ₃	H	H	CH ₃	—	1388
H	2-C ₁₀ H ₇	H	H	CH ₃	107°	849
C ₆ H ₅	H	H	H	C ₆ H ₅	159°	396, 758, 762, 1327
C ₆ H ₅ CH ₂	H	H	H	C ₆ H ₅	114°	581
NO	H	CH ₃	H	H	116°	911
NO	H	H	H	CH ₃	131° (dec.), 173°	479, 1028, 1029
NO	H	H	H	C ₆ H ₅	127° (dec.)	1028
NO	H	H	H	2-HOC ₆ H ₄	126°	353
NO	H	H	H	3-NO ₂ C ₆ H ₄	108°	335
H	H	C ₆ H ₅ CONH	H	C ₆ H ₅	228°	319, 1342
C ₆ H ₅	CH ₃	H	H	CH ₃	160°	888
C ₆ H ₅	H	CH ₃	H	H	164°	15, 701
C ₆ H ₅	H	H	H	CH ₃	166°	758, 762
CH ₃	C ₆ H ₅	H	H	CH ₃	107°	26, 816, 1491, 1592
2-CH ₃ C ₆ H ₄	H	CH ₃	CH ₃	H	143°	15, 1630

(Table continued)

TABLE XLII, Section A (continued)

R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	M.p.	Reference
3-CH ₃ C ₆ H ₄	H	CH ₃	CH ₃	H	H	105°	15
4-CH ₃ C ₆ H ₄	H	CH ₃	CH ₃	H	H	105°	15, 1176, 1630
4-HOC ₆ H ₄	H	CH ₃	CH ₃	H	H	—	15
4-HOCH ₂ CH ₂ C ₆ H ₄	H	CH ₃	CH ₃	H	H	140°	15, 1176, 1630
4-CH ₃ COOCH ₂ CH ₂ C ₆ H ₄	H	CH ₃	CH ₃	H	H	81.5°	15
4-ClC ₆ H ₄	H	CH ₃	C ₂ H ₅	H	H	—	15
4-H ₂ NC ₆ H ₄	H	CH ₃	C ₃ H ₇	H	H	—	15
4-CH ₃ OC ₆ H ₄	H	C ₂ H ₅	C ₂ H ₅	H	H	—	15
4-CH ₃ CONHC ₆ H ₄	H	C ₂ H ₅	C ₂ H ₅	H	H	—	15
2-(7-HOC ₁₀ H ₆)	H	CH ₃	C ₃ H ₇	H	H	—	15
C ₆ H ₅	C ₆ H ₅	H	H	CH ₃	H	—	647
C ₆ H ₅	H	CH ₃	H	C ₆ H ₅	H	164°	1327
C ₆ H ₅	H	H	H	C ₆ H ₅	C ₆ H ₅	170°	1327
H	4-H ₂ NC ₆ H ₄	H ₂ N	H	CH ₃	H	—	12
H	3-HO ₃ SC ₆ H ₄	H ₂ N	H	CH ₃	H	—	12
H	4-(4-H ₂ NC ₆ H ₄)C ₆ H ₄	H ₂ N	H	CH ₃	H	—	12
H	H	C ₆ H ₅ CONH	H	CH ₃	CH ₃	106°	319
NO	H	C ₆ H ₅ CONH	H	C ₆ H ₅	H	107° (dec.)	1342
NO	C ₆ H ₅	H	H	CH ₃	H	54°	1491
NO	C ₂ H ₅	H	H	CH ₃	H	83°	1029
NO	CH ₃ CO	H	H	CH ₃	H	168°	335
C ₆ H ₅	C ₆ H ₅	H	H	3-NO ₂ C ₆ H ₄	H	79°	888
CH ₃ (^o)	C ₆ H ₅	H	H	CH ₃	H	61°	1569
H	C ₆ H ₅	H	CH ₃	H	HOOC	139°	446
H	4-CH ₃ C ₆ H ₄	H	H	CH ₃	HOOC	148°	446
H	C ₆ H ₅	H	H	CH ₃	C ₆ H ₅ NNHCO	144°	446
H	4-CH ₃ C ₆ H ₄	H	H	CH ₃	4-BrC ₆ H ₄ NNHCO	204°	446
C ₆ H ₅	H	CH ₃	H	C ₆ H ₅	CH ₃	220°	1327
H	C ₆ H ₅	HO	H	CH ₃	CH ₃	182°	156, 1260, 1261
CH ₃	C ₆ H ₅	HO	H	CH ₃	CH ₃	109°	1261

C_6H_5	HO	H	HO	H	160°	1501
C_6H_5	H	H	CH_3	$HOOC$	122° (dec.)	647
C_6H_5	H	H	CH_3	H_3COOC	130°	647
H	NO	H	CH_3	$HOOC$	—	446
H	NO	H	CH_3	$HOOC$	—	446
CH_3	HO	Br	CH_3	Br	218°	820

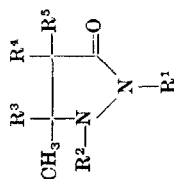


TABLE XLII (continued)

Section B. Mercury Substituents

R^1	R^2	R^3	R^4	R^5	M.p.	Reference
$X,Y-(CH_3COOHg)_2C_6H_3$	CH_3	CH_3COOHg	CH_3O	CH_3COOHg	200° (dec.)	1275
$X,Y-(CH_3COOHg)_2C_6H_3$	CH_3	CH_3O	CH_3O	H	—	1275
$X,Y-(CH_3COOHg)_2C_6H_3$	CH_3	CH_3O	CH_3O	CH_3COOHg	—	1275
$X,Y-(CH_3COOHg)_2C_6H_3$	CH_3	CH_3O	C_2H_5O	H	—	1275
$X,Y-(CH_3COOHg)_2C_6H_3$	C_2H_5	CH_3COOHg	CH_3O	CH_3COOHg	$>200^\circ$ (dec.)	1275

(Table continued)

TABLE XLII, Section B (*continued*)

R ¹	R ²	R ³	R ⁴	R ⁵	M.p.	Reference
X,Y-(CH ₂) ₂ C ₆ H ₃	C ₂ H ₅	CH ₃	CH ₃ O	H	—	1275
4-CH ₃ -X,Y-(CH ₃ COO) ₂ C ₆ H ₂	CH ₃	CH ₃ COOHg	CH ₃ O	CH ₃ COOHg	—	1275
2-CH ₃ -X,Y-(CH ₃ COO) ₂ C ₆ H ₂	C ₂ H ₅	CH ₃ COOHg	CH ₃ O	CH ₃ COOHg	—	1275
2-CH ₃ -X,Y-(CH ₃) ₂ C ₆ H ₃	C ₂ H ₅	CH ₃	CH ₃ O	H	—	1275
X-CH ₃ COOHgC ₆ H ₄	H	CH ₃ COOHg	CH ₃ O	CH ₃ COOHg	167°	1275
X-CH ₃ C ₆ H ₄	H	CH ₃	CH ₃ O	H	—	1275
X,Y-(CH ₃ COOHg) ₂ C ₆ H ₃	H	CH ₃ COOHg	CH ₃ O	CH ₃ COOHg	225°	1275
X,Y-(CH ₃ COOHg) ₂ C ₆ H ₃	CH ₃	CH ₃ COOHg	HO	Br	225° (dec.)	1275
X,Y-(CH ₃ COOHg) ₂ C ₆ H ₃	CH ₃	CH ₃ COOHg	HO	CH ₃	237° (dec.)	1275
X,Y-(CH ₃) ₂ C ₆ H ₃	CH ₃	CH ₃	HO	CH ₃	245° (dec.)	1275

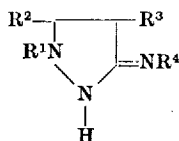


TABLE XLIII. 3-Iminopyrazolidines

R¹	R²	R³	R⁴	M.p.	Reference
H	H	H	H	196° (HCl)	757
C₆H₅	H	H	H	167°	396, 757, 1122
2-CH₃C₆H₄	H	H	H	74°	396, 757
3-CH₃C₆H₄	H	H	H	110°	396, 757
4-CH₃C₆H₄	H	H	H	143°	396, 757
4-CH₃OC₆H₄	H	H	H	179°	757
4-C₂H₅OC₆H₄	H	H	H	192°	760
4-CH₃CONHC₆H₄	H	H	H	204°	757
4-(4-CH₃C₆H₄S)C₆H₄	H	H	H	123°	760
3-ClC₆H₄	H	H	H	142°	760
4-ClC₆H₄	H	H	H	132°	396, 760
4-BrC₆H₄	H	H	H	121°	760
2,5-(CH₃)₂C₆H₃	H	CH₃	H	99°	760
C₆H₅	H	CH₃	H	82°	396, 757
C₆H₅	CH₃	H	H	106°	396, 757
C₆H₅	CH₃	CH₃	H	172°	760
3-CH₃C₆H₄	C₆H₅	H	H	152°	396, 757
4-CH₃C₆H₄	C₆H₅	H	H	195°	396, 757
4-ClC₆H₄	C₆H₅	H	H	129°	396, 760
C₆H₅	H	H	C₂H₅	74°	396
C₆H₅	H	H	CH₃CO	192°	396
C₆H₅	H	H	C₆H₅NHSC	196°	396
H	H₂N	H₂N	H	—	336
H	C₂H₅OOCHN	C₂H₅OOCHN	C₂H₅OOC	—	336

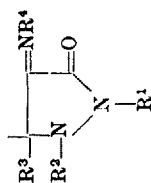
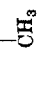
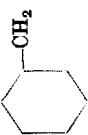


TABLE XLIV. 4-Imino-3-pyrazolidinones

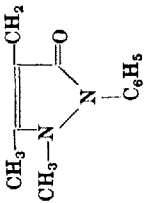
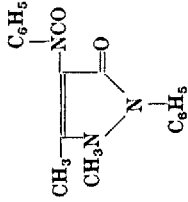
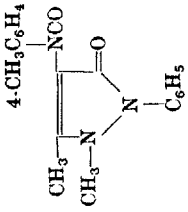
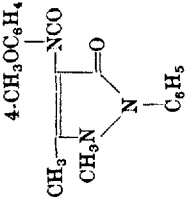
R ³	R ²	R ³	R ⁴	M.p.	Reference
H	C ₆ H ₅	CH ₃	H	—	1168
H	4-BrC ₆ H ₄	CH ₃	H	238°	1001
H	4-BrC ₆ H ₄	CH ₃	HCO	240°	1001
H	4-BrC ₆ H ₄	CH ₃	CH ₃ CO	259°	1001
H	4-BrC ₆ H ₄	CH ₃	H ₂ NCO	> 350°	1001
H	4-BrC ₆ H ₄	H	C ₆ H ₅ NHCS	262°	1001
H	C ₆ H ₅	CH ₃	H	182°	984
H	C ₆ H ₅	CH ₃	HCO	197°	984
H	C ₆ H ₅	CH ₃	CH ₃ CO	233°	984
H	C ₆ H ₅	CH ₃	C ₆ H ₅ NHCS	221°	984
H	4-CH ₃ C ₆ H ₄	CH ₃	H	249°	984
H	4-CH ₃ C ₆ H ₄	CH ₃	CH ₃ CO	244°	984
H	4-CH ₃ C ₆ H ₄	CH ₃	C ₆ H ₅ NHCS	220°	984
H	3-NO ₂ C ₆ H ₄	CH ₃	H	155°	1001
H	3-NO ₂ C ₆ H ₄	CH ₃	CH ₃ CO	199°	1001
H	C ₆ H ₅	2-HOC ₆ H ₄	H	255°	670
	CH ₃	CH ₃	H	b ₄ 178°	101
	CH ₃	CH ₃	CH ₃	102°	101

		CH ₃	H·HCl	205°	101
		CH ₃	CH ₃	—	101
C ₆ H ₅	CH ₃	CH ₃	H	108°	99, 426, 461, 527, 617, 1174, 1175, 1491
C ₆ H ₅	CH ₃	CH ₃	CH ₃	63°	172, 431, 537, 940, 1303
C ₆ H ₅	CH ₃	CH ₃	C ₂ H ₅	61°	1303
C ₆ H ₅	CH ₃	CH ₃	C ₃ H ₇	82°	1303
C ₆ H ₅	CH ₃	CH ₃	iso-C ₃ H ₇	80°	164, 431, 1303
C ₆ H ₅	CH ₃	CH ₃	iso-C ₄ H ₉	67°	1303
C ₆ H ₅	CH ₃	CH ₃	s-C ₄ H ₉	78°	104, 431, 1303
C ₆ H ₅	CH ₃	CH ₃	iso-C ₃ H ₁₁	53.5°	1303
C ₆ H ₅	CH ₃	CH ₃	(C ₂ H ₅) ₂ CH	61°	1303
C ₆ H ₅	CH ₃	CH ₃	(iso-C ₃ H ₇) ₂ CH	100°	1303
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₁₁ CH	37°	1303
C ₆ H ₅	CH ₃	CH ₃		44°	1303
C ₆ H ₅	CH ₃	CH ₃		159°	1303

(Table continued)

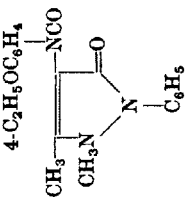
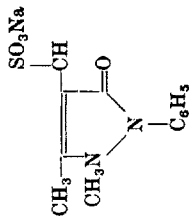
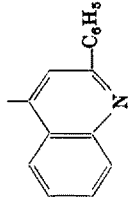
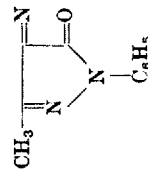
TABLE XLIV (continued)

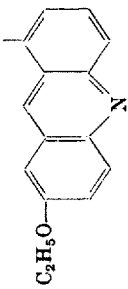
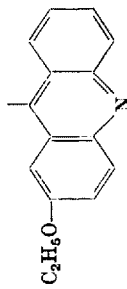
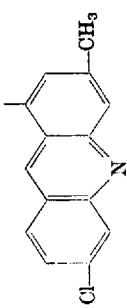
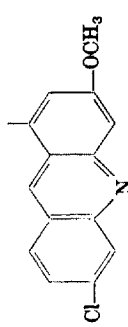
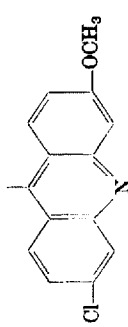
R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃		93°	101
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ CH ₂	73°	111, 1303
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ CH	95.2°	1303
C ₆ H ₅	CH ₃	CH ₃		196°	1303
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ CH ₂ CH ₂	84°	1303
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ CH ₂ CH ₂ CH ₂	—	1303
C ₆ H ₅	CH ₃	CH ₃	HOOCCH ₂	> 300°	524
C ₆ H ₅	CH ₃	CH ₃	NCCH ₂	112°	524
C ₆ H ₅	CH ₃	CH ₃	H ₂ NOCCH ₂	194°	524, 930
C ₆ H ₅	CH ₃	CH ₃	(CH ₃) ₂ C(OH)CH	151°	1261
				—	1076
C ₆ H ₅	CH ₃	CH ₃	HO ₂ SCH ₂	231°(dec.)	164, 541
C ₆ H ₅	CH ₃	CH ₃	HO ₃ SCH ₂	—	542
C ₆ H ₅	CH ₃	CH ₃	HO ₃ SCH	124°	542
				—	542
C ₆ H ₅	CH ₃	CH ₃	HO ₃ SCH	124°	542
				—	542
C ₆ H ₅	CH ₃	CH ₃	4-H ₂ NCSNH=CHC ₆ H ₄	251°	1265
C ₆ H ₅	CH ₃	CH ₃	4-(C ₆ H ₅ NH)C ₆ H ₄	220.5°	417
C ₆ H ₅	CH ₃	CH ₃	2,4(H ₂ N) ₂ C ₆ H ₃	265°	417
C ₆ H ₅	CH ₃	CH ₃	2,4(NO ₂)C ₆ H ₃	213°	417

C_6H_5	CH_3	CH_3		151°	111
C_6H_5	CH_3	CH_3		240° (dec.)	589
C_6H_5	CH_3	CH_3		235°	589
C_6H_5	CH_3	CH_3		200°	589

(Table continued)

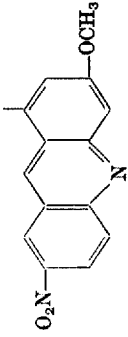
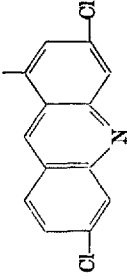
TABLE XLIV (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃		234°	589
C ₆ H ₅	CH ₃	CH ₃		190° (dec.)	891
C ₆ H ₅	CH ₃	CH ₃		247°	717
C ₆ H ₅	CH ₃	CH ₃		200°	821

C_6H_5	CH_3	CH_3		257°	547
C_6H_5	CH_3	CH_3		—	951
C_6H_5	CH_3	CH_3		257°	69
C_6H_5	CH_3	CH_3		248°	69
C_6H_5	CH_3	CH_3		250°	390

(Table continued)

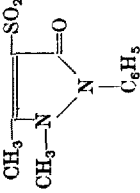
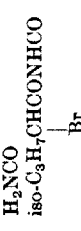
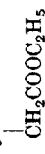
TABLE XLIV (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃		278°	69
C ₆ H ₅	CH ₃	CH ₃		276°	69
C ₆ H ₅	CH ₃	CH ₃	HCO	189°	618
C ₆ H ₅	CH ₃	CH ₃	CH ₃ CO	198°	617, 618
C ₆ H ₅	CH ₃	CH ₃	iso-C ₃ H ₇ CO	—	536
C ₆ H ₅	CH ₃	CH ₃	iso-C ₄ H ₉ CO	—	58, 533
C ₆ H ₅	CH ₃	CH ₃	H ₂ NCH ₂ CO(HCl)	260°	58, 731
C ₆ H ₅	CH ₃	CH ₃	(CH ₃) ₂ NCH ₂ CO	151°	1470, 1473
C ₆ H ₅	CH ₃	CH ₃	(C ₂ H ₅) ₂ NCH ₂ CO	111°	371, 1470, 1473
C ₆ H ₅	CH ₃	CH ₃	CH ₃ CHCO	175°	1471
C ₆ H ₅	CH ₃	CH ₃		181°	1470, 1471, 1473
C ₆ H ₅	CH ₃	CH ₃	CH ₃ CHCO	79°	1470, 1473
C ₆ H ₅	CH ₃	CH ₃		168°	1470, 1473

C_6H_5 14 + c.h.c.	CH_3	CH_3	CH_3	C_2H_5CHCO $N(C_2H_5)_2$ C_3H_7CHCO	119°	1470, 1473
C_6H_5 20	CH_3	CH_3	CH_3	C_3H_7CHCO $N(CH_3)_2$ C_3H_7CHCO	130°	1470, 1473
C_6H_5	CH_3	CH_3	CH_3	$iso-C_3H_7CHCO$ $N(C_2H_5)_2$ $iso-C_3H_7CHCO$	80°	1470, 1473
C_6H_5	CH_3	CH_3	CH_3	$iso-C_3H_7CHCO$ $N(CH_3)_2$ $iso-C_3H_7CHCO$	186°	1470, 1473
C_6H_5	CH_3	CH_3	CH_3	$ClCH_2CO$ $N(C_2H_5)_2$	177°	1470, 1473
C_6H_5	CH_3	CH_3	CH_3	CH_3CHCO Cl	187°, 198°	50, 1156, 1470, 1473 1471
C_6H_5	CH_3	CH_3	CH_3	CH_3CHCO Br	218°	
C_6H_5	CH_3	CH_3	CH_3	C_2H_5CHCO Br	206° (dec.)	1470, 1471, 1473
C_6H_5	CH_3	CH_3	CH_3	C_3H_7CHCO Br	208°	1470, 1473
C_6H_5	CH_3	CH_3	CH_3	$iso-C_3H_7CHCO$ Br	185°	1470, 1473
C_6H_5	CH_3	CH_3	CH_3	$2-CH_3COOC_6H_4CO$ Br	205°	533, 1470, 1473
C_6H_5	CH_3	CH_3	CH_3	$3,5-Br_2C_6H_3CO$ $COCH=NOH$	219°	1346
C_6H_5	CH_3	CH_3	CH_3	$HOOC$	252°	1414
C_6H_5	CH_3	CH_3	CH_3		190°	731
					—	549

(Table continued)

TABLE XLIV (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	CH ₃	CH ₃	C ₂ H ₅ OOC	206°	589
C ₆ H ₅	CH ₃	CH ₃	ClCO	oil	589
C ₆ H ₅	CH ₃	CH ₃	CH ₃ COOCO	—	371
C ₆ H ₅	CH ₃	CH ₃	HCS	175°	472, 556, 1374
C ₆ H ₅	CH ₃	CH ₃	4-H ₂ NC ₆ H ₄ SO ₂	249°, 260°	70, 98, 356, 1105, 1197, 1504, 1633
C ₆ H ₅	CH ₃	CH ₃	(CH ₃) ₂ NSO ₂	198°	489
C ₆ H ₅	CH ₃	CH ₃	(C ₂ H ₅) ₂ NSO ₂	184°	489
C ₆ H ₅	CH ₃	CH ₃	4-(CH ₃) ₂ NC ₆ H ₄ SO ₂	208°	98
C ₆ H ₅	CH ₃	CH ₃	4-CH ₃ CONHC ₆ H ₄ SO ₂	213°, 269°	98, 356, 1105, 1249, 1504
C ₆ H ₅	CH ₃	CH ₃		242°	745
C ₆ H ₅	CH ₃	CH ₃	H ₂ NCO	—	929
C ₆ H ₅	CH ₃	CH ₃	iso-C ₃ H ₇ -CHCONHCO	70°	1300
C ₆ H ₅	CH ₃	CH ₃		—	1367
C ₆ H ₅	CH ₃	CH ₃	3-HO-4-CH ₃ OOC-C ₆ H ₃ NHCS	200° (dec.)	49
C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅ HNCO	236°	929
C ₆ H ₅	CH ₃	CH ₃	H ₂ NHNCO	135°	929
C ₆ H ₅	CH ₃	CH ₃	C ₂ H ₅ CH=NNHCO	209°	929
C ₆ H ₅	CH ₃	CH ₃		207°	929

C_6H_5	CH_3	CH_3	CH_3	$C_6H_5CH=NNHCO$	225°	929
C_6H_5	CH_3	CH_3	CH_3	$CH_3CONHCO$	214°	929
C_6H_5	CH_3	CH_3	CH_3	$\begin{array}{c} NH \quad NH \\ \parallel \quad \parallel \\ H_2NCNHC \end{array}$	—	928
C_6H_5	CH_3	CH_3	CH_3	$(CH_3O)_2OP$	186°	1496
C_6H_5	CH_3	CH_3	CH_3	$(C_6H_5)_2OP$	—	1496
C_6H_5	CH_3	CH_3	CH_3	$(C_3H_7O)_2OP$	102°	1496
C_6H_5	CH_3	CH_3	CH_3	$(iso-C_3H_7O)_2OP$	156°	1496
C_6H_5	CH_3	CH_3	CH_3	$(C_4H_9O)_2OP$	105°	1496
C_6H_5	CH_3	CH_3	CH_3	$(iso-C_4H_9O)_2OP$	113°	1496
C_6H_5	CH_3	CH_3	CH_3	$(iso-C_5H_{11}O)_2OP$	85°	1496
C_6H_5	CH_3	CH_3	CH_3	$(ClCH_2CH_2O)_2OP$	—	1496
C_6H_5	CH_3	CH_3	CH_3	$(C_6H_5CH_2O)_2OP$	—	1496
C_6H_5	CH_3	CH_3	C_6H_5	H	176°	509
CH_3	CH_3	CH_3	C_6H_5	HCO	109°	992
CH_3	CH_3	CH_3	C_6H_5	CH_3CO	209°	992
CH_3	CH_3	CH_3	C_6H_5	C_6H_5CO	233°	992
CH_3	CH_3	CH_3	C_6H_5	C_2H_5OOC	234°	992
CH_3	CH_3	CH_3	C_6H_5	$C_6H_5SO_2$	190°	992
CH_3	CH_3	CH_3	C_6H_5	C_6H_5NHCS	245°	992
C_6H_5	CH_3	CH_3	CH_3	H	210°	992
C_6H_5	CH_3	CH_3	CH_3	$H_2NCH_2CO(HBr)$	117°	520
C_6H_5	CH_3	CH_3	CH_3	$ClCH_2CO$	150°	50
C_6H_5	CH_3	CH_3	CH_3	H	186°	50
C_6H_5	CH_3	CH_3		H	125°	1477
$2-CH_3C_6H_4$	CH_3	CH_3	CH_3	H	117°	521
$2-CH_3C_6H_4$	C_2H_5	CH_3	CH_3	H	129°	521
$4-CH_3C_6H_4$	CH_3	CH_3	CH_3	H	118°	521
$4-CH_3C_6H_4$	CH_3	CH_3	CH_3	HO_3SCH_2	125° (dec.)	541
$4-CH_3C_6H_4$	C_2H_5	CH_3	CH_3	H	—	145, 521

(Table continued)

TABLE XLIV (continued)

	R ²	R ³	R ⁴	M.p.	Reference
4-CH ₃ C ₆ H ₄	C ₂ H ₅	CH ₃	HO ₃ SCH ₂	—	145
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	CH ₃	H	132°	541
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	CH ₃	HO ₃ SCH ₂	113°	541
4-C ₂ H ₅ OC ₆ H ₄	C ₂ H ₅	CH ₃	H	—	145
4-C ₂ H ₅ OC ₆ H ₄	C ₂ H ₅	CH ₃	HO ₃ SCH ₂	—	145
4-C ₃ H ₇ OC ₆ H ₄	CH ₃	CH ₃	H	99°	1149
3-H ₂ NC ₆ H ₄	CH ₃	CH ₃	H	170°	978
4-H ₂ NC ₆ H ₄	3-H ₂ NC ₆ H ₄	CH ₃	H	185°	1001
4-H ₂ NC ₆ H ₄	CH ₃	CH ₃	H	239°	978
4-H ₂ NC ₆ H ₄	CH ₃	CH ₃	(CH ₃) ₂ CHCHCONHCO	74°	1300
4-(CH ₃) ₂ NC ₆ H ₄	CH ₃	CH ₃	Br (CH ₃) ₂ CHCHCONHCO	94°	1300
4-CH ₃ CONHC ₆ H ₄	CH ₃	CH ₃	Br CH ₃ CO	291°	978
4-H ₂ O ₃ AsC ₆ H ₄	CH ₃	CH ₃	CH ₃ CH=CHCO	—	1363
C ₆ H ₅	C ₆ H ₅	CH ₃	H	165°	647

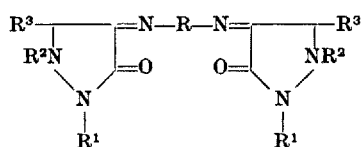


TABLE XLV. 4,4'-Bis(4-imino-3-pyrazolidinones)

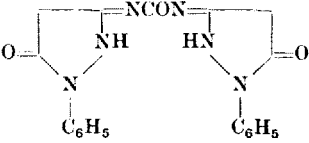
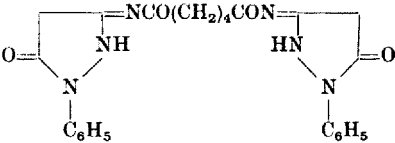
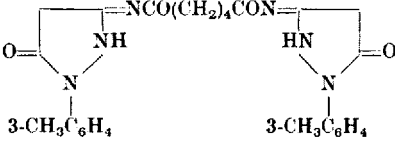
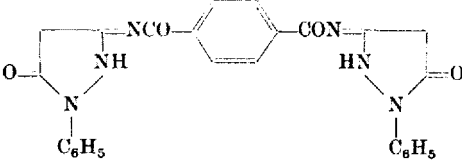
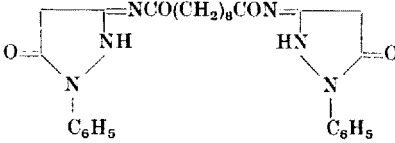
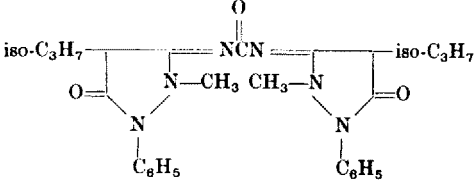
R	R¹	R²	R³	M.p.	Reference
	H	C₆H₅	CH₃	299°	984
	H	C₆H₅	CH₃	296°	984
(C₆H₅)₂C<	H	C₆H₅	CH₃	301°	984
—CH₂CH₂—	C₆H₅	CH₃	CH₃	54°	927
—CH₂CH₂—	CH₃	CH₃	C₆H₅	132°	992
—CH₂CH₂OCH₂CH₂—	C₆H₅	CH₃	CH₃	—	460
C=S	H	4-BrC₆H₄	CH₃	289°	1001
C=O	C₆H₅	CH₃	CH₃	259°	589
C=S	H	C₆H₅	CH₃	265°	984
C=S	CH₃	CH₃	C₆H₅	225°	992
C=S	C₆H₅	CH₃	CH₃	248°	821

TABLE XLVI. Miscellaneous Bis(3,5-pyrazolidinediones), Bis(5-imino-3-pyrazolidinones), and Bis(4-imino-3-pyrazolidinones)

Compound	M.p.	Reference
	310°(dec.)	1190
	290°	1538
	> 300°	1538
	—	1362
	—	546
	—	546

(Table continued)

TABLE XLVI (*continued*)

Compound	M.p.	Reference
	260° (dec.)	797
	281°	797
	—	797
	—	797
	251°	797
	165°	1387

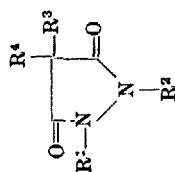


TABLE XLVII. 3,5-Pyrazolidinediones

Section A. Alkyl and Aryl Substituents

R ¹	R ²	R ³	R ⁴	M.p.	Reference
CH ₃	H	H	H	—	769
C ₆ H ₁₃	H	H	H	250°	504
H	H	C ₂ H ₅	C ₂ H ₅	270°	248, 388, 1234
H	H	C ₂ H ₅	C ₃ H ₇	232°	1234
H	H	C ₃ H ₇	C ₃ H ₇	254°	388, 1234
H	H	C ₃ H ₅	C ₃ H ₅	280°	1234
H	H	C ₃ H ₅	s-C ₄ H ₉	186°	388
H	H	C ₄ H ₉	C ₄ H ₉	220°	248, 388
H	H	C ₂ H ₅	iso-C ₅ H ₁₁	228°	388
H	H	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	289°	388
H	H	C ₆ H ₅ CH ₂	C ₆ H ₅ CH ₂	301°	497
C ₆ H ₁₃	H	CH ₃	H	—	504
C ₆ H ₁₃	H	C ₂ H ₅	H	—	504
H	H	C ₂ H ₅	C ₂ H ₁₃	182°	388
C ₆ H ₁₃	H	C ₃ H ₇	H	83°	504
C ₆ H ₁₃	H	C ₄ H ₉	H	94°	504
C ₆ H ₁₃	H	C ₆ H ₁₁	H	93°	504
C ₆ H ₁₃	H	C ₆ H ₁₃	H	93°	504
C ₆ H ₁₃	H	C ₇ H ₁₅	H	81°	504

C_6H_{13}	H	$\text{C}_6\text{H}_5\text{CH}_2$	H	155°	504
$\text{C}_6\text{H}_5\text{CH}_2$	H	C_2H_5	C_2H_5	134°	248
$\text{C}_6\text{H}_5\text{CH}_2$	H	C_4H_9	C_4H_9	128°	248
$\text{C}_6\text{H}_5\text{CH}_2$	$\text{C}_6\text{H}_5\text{CH}_2$	C_2H_5	C_2H_5	74°	248, 734

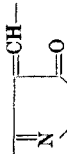
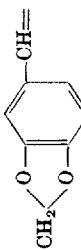
TABLE XLVII (continued)

Section B. Alkyl, Aryl, Heterocycalkyl, Aryl and Acyl on Carbon Substituents

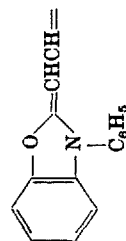
R^1	R^2	R^3	R^4	M.P.	Reference
C_6H_5	H	H	H	192°	248, 317, 496, 681, 976, 994, 997, 1512, 1596
2-ClC ₆ H ₄	H	H	H	181°	504
3-ClC ₆ H ₄	H	H	H	174°	504
4-ClC ₆ H ₄	H	H	H	207°	504
4-BrC ₆ H ₄	H	H	H	217°	997
4-NO ₂ C ₆ H ₄	H	H	H	—	997
C_6H_5	CH ₃	H	H	84°	1339
C_6H_5	H	CH ₃	H	177°	496
C_6H_5	H	C_2H_5	H	108°	388, 496, 998
H	H	C_6H_5	C_2H_5	198°	381, 388, 1234

(Table continued)

TABLE XLVII, Section B (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	H	C ₃ H ₇	H	186°	496
C ₆ H ₅	H	C ₂ H ₅	H	99°, 149°	248, 496
C ₆ H ₅	H	s-C ₄ H ₉	H	94°	388
C ₆ H ₅	H	C ₃ H ₉	H	139°	496
C ₆ H ₅	H	C ₃ H ₁₇	H	154°	496
C ₆ H ₅	H	C ₃ H ₅ CH ₂	H	188°	496
H	H	C ₆ H ₅	C ₆ H ₅ CH ₂ CH ₂	—	612
C ₆ H ₅	H	C ₆ H ₅ CH=CH	H	b ₃ , 7 372°	681
C ₆ H ₅	H		H	262°	1190
C ₆ H ₅	H	(CH ₃) ₂ C=			
C ₆ H ₅	H	C ₆ H ₅ CH=		164°	976
C ₆ H ₅	H	2-HOC ₆ H ₄ CH=		—	681, 976
C ₆ H ₅	H	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH=		—	681
C ₆ H ₅	H			—	681
C ₆ H ₅	H			—	681
2-ClC ₆ H ₄	H	CH ₃	H	181°	504
2-ClC ₆ H ₄	H	C ₂ H ₅	H	160°	504
2-ClC ₆ H ₄	H	C ₃ H ₇	H	161°	504

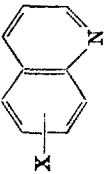
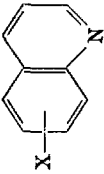
2-ClC ₆ H ₄	H	C ₄ H ₉	H	169°	504
2-ClC ₂ H ₄	H	C ₂ H ₁₁	H	150°	504
2-ClC ₆ H ₄	H	C ₆ H ₁₃	H	154°	504
2-ClC ₂ H ₄	H	C ₇ H ₁₅	H	131°	504
2-ClC ₆ H ₄	H	C ₆ H ₅ CH ₂	H	197°	504
3-ClC ₂ H ₄	H	CH ₃	H	210°	504
3-ClC ₆ H ₄	H	C ₂ H ₅	H	196°	504
3-ClC ₂ H ₄	H	C ₃ H ₇	H	239°	504
3-ClC ₆ H ₄	H	C ₄ H ₉	H	155°	504
3-ClC ₂ H ₄	H	C ₃ H ₁₁	H	132°	504
3-ClC ₆ H ₄	H	C ₆ H ₁₃	H	110°	504
3-ClC ₂ H ₄	H	C ₇ H ₁₅	H	106°	504
3-ClC ₆ H ₄	H	C ₆ H ₅ CH ₂	H	187°	504
4-ClC ₂ H ₄	H	CH ₃	H	220°	504
4-ClC ₆ H ₄	H	C ₂ H ₅	H	202°	504
4-ClC ₂ H ₄	H	C ₃ H ₇	H	193°	504
4-ClC ₆ H ₄	H	C ₄ H ₉	H	193°	504
4-ClC ₂ H ₄	H	C ₆ H ₁₁	H	174°	504
4-ClC ₆ H ₄	H	C ₆ H ₁₃	H	147°	504
4-ClC ₂ H ₄	H	C ₇ H ₁₅	H	160°	504
4-ClC ₆ H ₄	H	C ₆ H ₅ CH ₂	H	181°	504
1-C ₁₀ H ₇	H	C ₈ H ₁₇	H	184°	506
1-C ₁₀ H ₇	H	C ₆ H ₅ CH ₂	H	169°	506
2-C ₁₀ H ₇	H	C ₄ H ₉	H	172°	506
2-C ₁₀ H ₇	H	C ₆ H ₁₁	H	157°	506
2-C ₁₀ H ₇	H	C ₆ H ₁₃	H	155°	506
2-C ₁₀ H ₇	H	C ₆ H ₁₇	H	147°	506
2-C ₁₀ H ₇	H	C ₆ H ₅ CH ₂	H	189°	506



313° 1330

(Table continued)

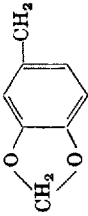
TABLE XLVII, Section B (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	C ₆ H ₅	H	H	178°	248, 681, 766, 969, 1150, 1234, 1501
C ₆ H ₅	H	C ₆ H ₅	H	172°, 233°	222, 506, 612
C ₆ H ₅	H	3,4-(CH ₃ O) ₂ C ₆ H ₃	H	—	612
X-CH ₂ C ₆ H ₄	X-CH ₂ C ₆ H ₄	H	H	—	769
4-CH ₃ OC ₆ H ₄	4-CH ₃ OC ₆ H ₄	H	H	—	769
H	H	4-H ₂ NC ₆ H ₄	4-H ₂ NC ₆ H ₄	298° (dec.)	339
H	H	4-(C ₆ H ₅ CH=N)C ₆ H ₄	4-(C ₆ H ₅ CH=N)C ₆ H ₄	271°	339
4-ClC ₆ H ₄	4-ClC ₆ H ₄	H	H	177°	766
3-NO ₂ C ₆ H ₄	3-NO ₂ C ₆ H ₄	H	H	—	769
4-(C ₆ H ₅)C ₆ H ₄	4-(C ₆ H ₅)C ₆ H ₄	H	H	—	769
		H	H	—	769
C ₆ H ₅	H	CH ₃	CH ₃	176°	997
C ₆ H ₅	H	C ₂ H ₅	C ₂ H ₅	113°	248, 388, 496
C ₆ H ₅	CH ₃	iso-C ₃ H ₇	H	116°	1339
C ₆ H ₅	H	C ₃ H ₇	C ₃ H ₇	105°	317, 496
C ₆ H ₅	H	iso-C ₃ H ₇	C ₃ H ₅	b _{0.1} 148°	248
C ₆ H ₅	H	C ₂ H ₅	iso-C ₆ H ₁₁	b _{0.3} 182°	248
C ₆ H ₅	H	C ₆ H ₁₁	C ₆ H ₁₁	211°	496
C ₆ H ₅	H	C ₇ H ₁₅	C ₇ H ₁₅	136°	496
C ₆ H ₅	C ₆ H ₅ CH ₂	C ₄ H ₉	H	98°	248

C_6H_5	H	$C_6H_5CH_2$	C_4H_9	171°	248
C_6H_5	H	$C_6H_5CH_2$	$C_6H_5CH_2$	258°	496
$2-C_{10}H_7$	H	$C_6H_5CH_2$	$C_6H_5CH_2$	243°	506
C_6H_5	C_6H_5	CH_3	H	114°	1338
C_6H_5	H	C_6H_5	CH_3	168°	222, 612
C_6H_5	CH_3	C_6H_5	H	114°	222
$6-H_5$	C_6H_5	C_6H_5	H	108°	1033, 1150, 1338
C_6H_5	H	C_6H_5	C_2H_5	172°	222, 612
C_6H_5	C_6H_5	C_3H_7	H	108°	188, 619, 1440
C_6H_5	C_6H_5	iso- C_3H_7	H	143°	188, 1338, 1437, 1439, 1440
C_6H_5	C_6H_5	C_6H_5	H	135°	619, 1338
C_6H_5	C_6H_5	C_4H_9	H	105°	63, 188, 612, 952, 1032, 1150, 1312, 1324, 1325, 1430, 1439
C_6H_5	H	C_6H_5	C_4H_9	168°	222
C_6H_5	C_6H_5	a- C_4H_9	H	118°	1338, 1440
C_6H_5	C_6H_5	iso- C_4H_9	H	127°	1338
C_6H_5	C_6H_5	2- C_4H_7	H	128°	1338
C_6H_5	C_6H_5	C_6H_{11}	H	104°	1338
C_6H_5	C_6H_5	iso- C_6H_{11}	H	137°	1338
C_6H_5	C_6H_5	$(CH_3)_2CHCH_2CH$ CH_3	H	107°	1338

(Table continued)

TABLE XLVII, Section B (*continued*)

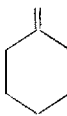
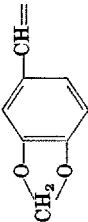
R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	C ₆ H ₅	C ₇ H ₁₅	H	95°	1338
C ₆ H ₅	C ₆ H ₅		H	172°	188, 1338
C ₆ H ₅	C ₆ H ₅		H	177°	188, 619, 1338, 1430, 1440
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ CH ₂	H	136°	188, 619, 1338, 1437, 1439, 1440
C ₆ H ₅	H	C ₆ H ₅	C ₆ H ₅ CH ₂	176°	222, 612
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ CH CH ₃	H	—	188
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	H	184°	222
C ₆ H ₅	C ₆ H ₅	4-CH ₃ C ₆ H ₄ CH ₂	H	—	188
C ₆ H ₅	C ₆ H ₅		H	—	188
C ₆ H ₅	C ₆ H ₅	4-ClC ₆ H ₄ CH ₂	H	—	188, 1338
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ CH ₂ CH ₂ CH ₂	H	—	188
C ₆ H ₅	C ₆ H ₅	C ₃ H ₇ CO	H	77°	919
C ₆ H ₅	C ₆ H ₅	iso-C ₃ H ₇ CO	H	85°	919

C ₆ H ₅	C ₆ H ₅	CH ₃ COOCH ₂ CO	H	173°	919
C ₆ H ₅	C ₆ H ₅	ClCH ₂ CO	H	149°	919
C ₆ H ₅	C ₆ H ₅	CH ₃ SCH ₂ CO	H	154°	919
C ₆ H ₅	C ₆ H ₅	C ₄ H ₉ SOCH ₂ CO	H	149°	919
C ₆ H ₅	C ₆ H ₅	3-HOC ₄ H ₉	H	—	267
C ₆ H ₅	C ₆ H ₅	C ₃ H ₅ OCH ₂ CH ₂	H	—	615
C ₆ H ₅	C ₆ H ₅	C ₃ H ₇ OCH ₂ CH ₂	H	90°	615
C ₆ H ₅	C ₆ H ₅	iso-C ₃ H ₇ OCH ₂ CH ₂	H	104°	615
C ₆ H ₅	C ₆ H ₅	C ₄ H ₉ OCH ₂ CH ₂	H	93°	615
C ₆ H ₅	C ₆ H ₅	C ₃ H ₅ OCH ₂ CH ₂ CH ₂ CH ₂	H	—	615
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ OCH ₂ CH ₂	H	147°	615
C ₆ H ₅	C ₆ H ₅	C ₃ H ₅ OCH ₂ CH ₂ CH ₂ CH ₂ CH ₂	H	—	615
C ₆ H ₅	C ₆ H ₅	C ₃ H ₅ CH ₂ OCH ₂ CH ₂ CH ₂ CH ₂ CH ₂	H	—	615
C ₆ H ₅	C ₆ H ₅	NaO ₂ SOCH ₂	H	250°	919
C ₆ H ₅	C ₆ H ₅	CH ₃ SOCH ₂ CH ₂	H	120°	1454
C ₆ H ₅	C ₆ H ₅	C ₂ H ₅ SOCH ₂ CH ₂	H	92°	615
C ₆ H ₅	C ₆ H ₅	C ₃ H ₇ SOCH ₂ CH ₂	H	94°	615
C ₆ H ₅	C ₆ H ₅	iso-C ₃ H ₇ SOCH ₂ CH ₂	H	105°	615
C ₆ H ₅	C ₆ H ₅	C ₃ H ₅ SOCH ₂ CH ₂ CH ₂	H	—	615
C ₆ H ₅	C ₆ H ₅	C ₃ H ₅ SOCH ₂ CH ₂ CH ₂ CH ₂	H	—	233
C ₆ H ₅	C ₆ H ₅	4-CH ₃ C ₆ H ₄ SOCH ₂ CH ₂	H	101°	615
C ₆ H ₅	C ₆ H ₅	2,4-(CH ₃) ₂ C ₆ H ₃ SOCH ₂ CH ₂	H	104°	615
C ₆ H ₅	C ₆ H ₅	4-ClC ₆ H ₄ SOCH ₂ CH ₂	H	117°	615
C ₆ H ₅	C ₆ H ₅	4-BrC ₆ H ₄ SOCH ₂ CH ₂	H	—	615
C ₆ H ₅	C ₆ H ₅	4-CH ₃ OC ₆ H ₄ SOCH ₂ CH ₂	H	—	615
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ CH ₂ SOCH ₂ CH ₂	H	—	615
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ SOCH ₂ CH ₂ CH ₂	H	112°	615
C ₆ H ₅	C ₆ H ₅	C ₃ H ₅ SOCH ₂ CH ₂ CH ₂ CH ₂	H	121°	615
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ CH ₂ SOCH ₂ CH ₂ CH ₂ CH ₂	H	—	615
C ₆ H ₅	C ₆ H ₅	C ₃ H ₅ SOCH ₂ CH ₂	H	181°	615
C ₆ H ₅	C ₆ H ₅	C ₂ H ₅ SO ₂ CH ₂ CH ₂	H	—	615
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ SOCH ₂ CH ₂	H	—	615
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ SO ₂ CH ₂ CH ₂	H	—	615
C ₆ H ₅	C ₆ H ₅	4-CH ₃ OC ₆ H ₄ SO ₂ CH ₂ CH ₂	H	—	615

(Table continued)

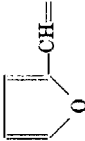
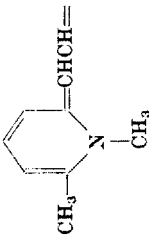
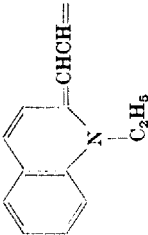
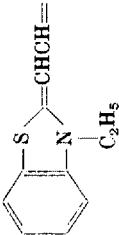
TABLE XLVII, Section B (continued)

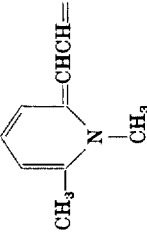
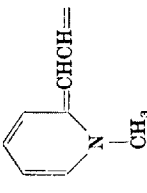
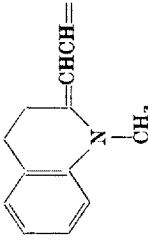
R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	C ₆ H ₅	4-ClC ₆ H ₄ SOCH ₂ CH ₂	H	—	615
C ₆ H ₅	C ₆ H ₅	4-ClC ₆ H ₄ SO ₂ CH ₂ CH ₂	H	—	615
C ₆ H ₅	C ₆ H ₅	NOCH ₂	H	140°	919
C ₆ H ₅	C ₆ H ₅	CH ₃ NHCH ₂	H	214°	919
C ₆ H ₅	C ₆ H ₅	(CH ₃) ₂ NCH ₂	H	208°	919
C ₆ H ₅	C ₆ H ₅		H	112°	919
C ₆ H ₅	C ₆ H ₅	H ₂ NCH ₂ CH ₂	H	195°	919
C ₆ H ₅	C ₆ H ₅	(CH ₃) ₂ NCH ₂ CH ₂	H	—	614
C ₆ H ₅	C ₆ H ₅	(C ₂ H ₅) ₂ NCH ₂ CH ₂	H	228°	614
C ₆ H ₅	C ₆ H ₅		H	—	614
C ₆ H ₅	C ₆ H ₅	(C ₂ H ₅) ₂ NCH ₂ CH ₂ CH ₂	H	—	614
C ₆ H ₅	C ₆ H ₅	C ₃ H ₇ CH NH ₂	H	195°	919
C ₆ H ₅	C ₆ H ₅	COOC ₂ H ₅ CH ₃ CONHCH ₂	H	133°	919
C ₆ H ₅	C ₆ H ₅	COOC ₂ H ₅ HOOCCHCH ₂	H	290° (HCl)	919
C ₆ H ₅	C ₆ H ₅	NH ₂ CH ₃ CH ₂ CH=		260° (dec.)	681
C ₆ H ₅	C ₆ H ₅	CH ₃ C=		113°	681, 1501
		 CH ₃			

C_6H_5	C_6H_5		153°	188, 1338
C_6H_5	C_6H_5		173°	188, 1338, 1430
C_6H_5	C_6H_5	$C_6H_5CH=$	164°	188, 681, 1501
C_6H_5	C_6H_5	$2-HOC_3H_4CH=$	193°	681, 1502
C_6H_5	C_6H_5	$3-HOC_3H_4CH=$	194°	681, 1502
C_6H_5	C_6H_5	$4-HOC_3H_4CH=$	231°	681, 1502
C_6H_5	C_6H_5	$4-CH_3OC_6H_4CH=$	199°	681, 1502
C_6H_5	C_6H_5	$4-CH_3C_6H_4CH=$	175°	681, 1502
C_6H_5	C_6H_5	$4-(CH_3)_2NC_6H_4CH=$	256°	681, 1502
C_6H_5	C_6H_5	$2-NO_2C_6H_4CH=$	174°	1502
C_6H_5	C_6H_5	$3-NO_2C_6H_4CH=$	185°	1502
C_6H_5	C_6H_5	$4-NO_2C_6H_4CH=$	243°	681, 1502
C_6H_5	C_6H_5	$3,4-(HO)_2C_6H_3CH=$	255° (dec.)	681, 1502
C_6H_5	C_6H_5	$3,4-(CH_3O)_2C_6H_3CH=$	156°	681, 1502
C_6H_5	C_6H_5		234°	681, 1502
C_6H_5	C_6H_5	$C_6H_5CH=CHCH=$	190°	188, 1501
C_6H_5	C_6H_5	$C_6H_5C=$ $\quad \quad \quad $ $\quad \quad \quad CH_3$	148°	681, 1501
C_6H_5	C_6H_5	$C_6H_5C=$ $\quad \quad \quad $ $\quad \quad \quad C_6H_5$	269°	1501

(Table continued)

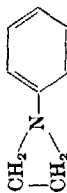
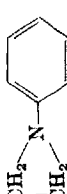
TABLE XLVII, Section B (*continued*)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ COC=	C ₆ H ₅	—	1503
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ CHOHC=	C ₆ H ₅	—	1503
C ₆ H ₅	C ₆ H ₅			157°	681, 1501
C ₆ H ₅	C ₆ H ₅			295° (dec.)	1670
C ₆ H ₅	C ₆ H ₅			296° (dec.)	1670
C ₆ H ₅	C ₆ H ₅			291° (dec.)	1670

C_6H_5	C_6H_5	C_6H_5	H	184°	222, 619, 1031, 1032
C_6H_5 C_6H_5	C_6H_5 C_6H_5	4- $CH_3OC_6H_4$ 4- ClC_6H_4	H H	196°	188 1031, 1032
C_6H_5	4- $CH_3C_6H_4$			225° (dec.)	1670
C_6H_5	2- $CH_3SC_6H_4$	C_4H_9	H	124°	613
4- $CH_3C_6H_4$	4- $CH_3C_6H_4$			202°	1670
4- $CH_3C_6H_4$	4- $CH_3C_6H_4$			292° (dec.)	1670
4- $CH_3OC_6H_4$ 4- $CH_3OC_6H_4$ 4- $C_2H_5OC_6H_4$ 4- $C_2H_5OC_6H_4$	4- $CH_3OC_6H_4$ 4- $CH_3OC_6H_4$ 4- $C_2H_5OC_6H_4$ 4- $C_2H_5OC_6H_4$	4- $CH_3C_6H_4CH_2OCH_2$ $CH_3OCH_2CH_2$ $CH_3OCH_2CH_2$ $C_2H_5OCH_2CH_2$	H H H H	— — — —	615 615 615 615

(Table continued)

TABLE XLVII, Section B (continued)

R ¹	R ²	R ³	R ⁴	M.p.	Reference
2-CH ₃ SC ₆ H ₄	2-CH ₃ SC ₆ H ₄	iso-C ₄ H ₉ SCH ₂ CH ₂	H	—	615
4-CH ₃ SC ₆ H ₄	4-CH ₃ SC ₆ H ₄	CH ₃ SCHCH ₂ CH ₃	H	—	615
4-CH ₃ SC ₆ H ₄	4-CH ₃ SC ₆ H ₄	CH ₃ CHCH ₂ OC ₂ H ₅	H	—	615
4-CH ₃ SC ₆ H ₄	4-CH ₃ SC ₆ H ₄	C ₆ H ₅ SCH ₂ CH ₃	H	—	615
4-HO ₂ CC ₆ H ₄	4-HO ₂ CC ₆ H ₄	C ₂ H ₅	H	270° (dec.)	252
4-HO ₂ CC ₆ H ₄	4-HO ₂ CC ₆ H ₄	C ₃ H ₇	H	228° (dec.)	252
4-HO ₂ CC ₆ H ₄	4-HO ₂ CC ₆ H ₄	iso-C ₃ H ₇	H	275° (dec.)	252
4-HO ₂ CC ₆ H ₄	4-HO ₂ CC ₆ H ₄	C ₄ H ₉	H	222° (dec.)	252
4-HO ₂ CC ₆ H ₄	4-HO ₂ CC ₆ H ₄	C ₆ H ₁₃	H	245° (dec.)	252
4-C ₂ H ₅ O ₂ CC ₆ H ₄	4-C ₂ H ₅ O ₂ CC ₆ H ₄	C ₂ H ₅	H	200°	252
4-C ₂ H ₅ O ₂ CC ₆ H ₄	4-C ₂ H ₅ O ₂ CC ₆ H ₄	C ₃ H ₇	H	198°	252
4-C ₂ H ₅ O ₂ CC ₆ H ₄	4-C ₂ H ₅ O ₂ CC ₆ H ₄	iso-C ₃ H ₇	H	180°	252
		C ₄ H ₉	H	—	1289
4-C ₂ H ₅ O ₂ CC ₆ H ₄	4-C ₂ H ₅ O ₂ CC ₆ H ₄	C ₄ H ₉	H	158°	252
4-C ₂ H ₅ O ₂ CC ₆ H ₄	4-C ₂ H ₅ O ₂ CC ₆ H ₄	C ₆ H ₁₃	H	132°	252
3-HO-4-HO ₂ CC ₆ H ₃	3-HO-4-HO ₂ CC ₆ H ₃	CH ₃	H	272° (dec.)	252
3-HO-4-HO ₂ CC ₆ H ₃	3-HO-4-HO ₂ CC ₆ H ₃	C ₂ H ₅	H	280° (dec.)	252
3-HO-4-HO ₂ CC ₆ H ₃	3-HO-4-HO ₂ CC ₆ H ₃	C ₃ H ₇	H	256° (dec.)	252
3-HO-4-HO ₂ CC ₆ H ₃	3-HO-4-HO ₂ CC ₆ H ₃	iso-C ₃ H ₇	H	270° (dec.)	252
3-HO-4-HO ₂ CC ₆ H ₃	3-HO-4-HO ₂ CC ₆ H ₃	C ₄ H ₉	H	220° (dec.)	252
3-HO-4-HO ₂ CC ₆ H ₃	3-HO-4-HO ₂ CC ₆ H ₃	iso-C ₃ H ₁₁	H	255° (dec.)	252
3-HO-4-HO ₂ CC ₆ H ₃	3-HO-4-HO ₂ CC ₆ H ₃	C ₆ H ₁₃	H	225° (dec.)	252
3-HO-4-CH ₃ O ₂ CC ₆ H ₃	3-HO-4-CH ₃ O ₂ CC ₆ H ₃	CH ₃	H	283°	252
3-HO-4-CH ₃ O ₂ CC ₆ H ₃	3-HO-4-CH ₃ O ₂ CC ₆ H ₃	C ₂ H ₅	H	244°	252

3-HO-4-CH ₃ O ₂ CC ₆ H ₃	3-HO-4-CH ₃ O ₂ CC ₆ H ₃	C ₃ H ₇	H	164°	252
3-HO-4-CH ₃ O ₂ CC ₆ H ₃	3-HO-4-CH ₃ O ₂ CC ₆ H ₃	iso-C ₃ H ₇	H	186°	252
3-HO-4-CH ₃ O ₂ CC ₆ H ₃	3-HO-4-CH ₃ O ₂ CC ₆ H ₃	C ₄ H ₉	H	154°	252
3-HO-4-CH ₃ O ₂ CC ₆ H ₃	3-HO-4-CH ₃ O ₂ CC ₆ H ₃	iso-C ₅ H ₁₁	H	180°	252
3-HO-4-CH ₃ O ₂ CC ₆ H ₃	3-HO-4-CH ₃ O ₂ CC ₆ H ₃	C ₆ H ₁₃	H	123°	252
3-CH ₃ CO ₂ -4-CH ₃ O ₂ CC ₆ H ₃	3-CH ₃ CO ₂ -4-CH ₃ O ₂ CC ₆ H ₃	C ₄ H ₉	H	143°	252
2-C ₁₀ H ₇	H	C ₆ H ₅ CH ₂	C ₆ H ₅ CH ₂	243°	506
C ₆ H ₅	CH ₃	CH ₃	CH ₃	70°	248, 998
C ₆ H ₅	CH ₃	CH ₃	C ₂ H ₅	62°	998
C ₆ H ₅	CH ₃	C ₂ H ₅	C ₂ H ₅	94°	41, 248
C ₆ H ₅	CH ₃	C ₂ H ₅	iso-C ₅ H ₁₁	b _{0.15} 123°	248
C ₆ H ₅	CH ₃	C ₂ H ₅	C ₃ H ₅	b _{0.03} 124°	248
C ₆ H ₅	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	57°	248
C ₆ H ₅	C ₃ H ₇	C ₂ H ₅	C ₂ H ₅	b _{0.2} 130°	248
C ₆ H ₅	iso-C ₃ H ₇	C ₂ H ₅	C ₂ H ₅	b _{0.02} 106°	248
C ₆ H ₅	C ₃ H ₅	C ₂ H ₅	C ₂ H ₅	42°	248, 734
C ₆ H ₅	C ₆ H ₅ CH ₂	C ₂ H ₅	C ₂ H ₅	93°	248
C ₆ H ₅	C ₆ H ₅ CH ₂	C ₃ H ₅	C ₂ H ₅	b _{0.06} 155°	248
C ₆ H ₅	C ₆ H ₅ CH ₂	C ₂ H ₅	iso-C ₃ H ₇	99°	248
C ₆ H ₅	(C ₂ H ₅) ₂ NCH ₂ CH ₂	C ₄ H ₉	iso-C ₃ H ₇	b _{0.01} 175°	248
C ₆ H ₅	(CH ₃) ₂ NCH ₂ CH ₂	C ₂ H ₅	C ₂ H ₅	b _{0.01} 144°	248
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ CH ₂	C ₄ H ₉	b _{0.05} 180°	248
C ₆ H ₅	C ₆ H ₅	C ₄ H ₉	C ₄ H ₉	121°	304
C ₆ H ₅	C ₆ H ₅ CH ₂	CH ₃	CH ₃	115°	222
C ₆ H ₅	C ₆ H ₅ CH ₂	C ₆ H ₅ CH ₂	C ₆ H ₅ CH ₂	110°	222
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	CH ₃	159°	222

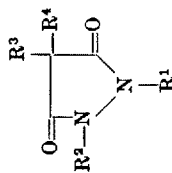
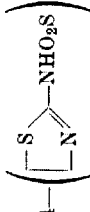


TABLE XLVIII. 3,5-Pyrazolidinediones. Acyl on Nitrogen and Oxygen, Nitrogen, and Halogen Substituents

R ¹	R ²	R ³	R ⁴	M.p.	Reference
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	HO	132°	1312
C ₆ H ₅	C ₆ H ₅	(CH ₃) ₂ NCH ₂ CH ₂ O	H	227°	1048
C ₆ H ₅	H	H ₂ N	H	320° (dec.)	317
C ₆ H ₅	CH ₃	H ₂ N	H	180°	1339
C ₆ H ₅	C ₆ H ₅	H ₂ N	H	—	1048
C ₆ H ₅	H	HON=		182°	976
C ₆ H ₅	CH ₃	HON=		193° (dec.)	981, 1339
C ₆ H ₅	C ₆ H ₅	HON=		163°	1501
C ₆ H ₅	C ₆ H ₅	4-C ₂ H ₅ O ₂ CC ₆ H ₄ NH	H	260°	1048
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ N=N	H	232°	976
C ₆ H ₅	H	C ₆ H ₅ N=N	H	266°	257
H	H	4-H ₃ NO ₂ SC ₆ H ₄ N=N	H	268°	1048
C ₆ H ₅	C ₆ H ₅				
C ₆ H ₅	C ₆ H ₅	4-()C ₆ H ₄ N=N	H	261°	1048

4-O ₂ NC ₆ H ₄	H	4-O ₂ NC ₆ H ₄ N=N	H	—	1340
C ₆ H ₅	C ₆ H ₅	Br	H	51°	1048
C ₆ H ₅	C ₆ H ₅	C ₄ H ₉	Cl	106°	458
C ₆ H ₅	C ₆ H ₅	C ₂ H ₅	Br	98°	1033
C ₆ H ₅	C ₆ H ₅	iso-C ₃ H ₇	Br	100°	1033
C ₆ H ₅	C ₆ H ₅	C ₄ H ₉	Br	116°	458, 1032, 1033
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	Br	160°	1031, 1033
C ₆ H ₅	C ₆ H ₅ NHCO	4-ClC ₆ H ₄	Br	119°	1031
C ₆ H ₅	HCO	H	H	166°	976
C ₆ H ₅	CH ₃ CO	C ₂ H ₅	C ₂ H ₅	110°	734
C ₆ H ₅	C ₆ H ₅ CO	C ₂ H ₅	C ₂ H ₅	96°	734
C ₆ H ₅ NHCO	H	C ₆ H ₅ CO	H	111°	976
C ₆ H ₅ NHCO	H	C ₆ H ₁₃	H	170° (dec.)	506
C ₆ H ₅ NHCO	H	C ₇ H ₁₅	H	160° (dec.)	506
C ₆ H ₅ NHCO	H	C ₆ H ₁₇	H	150°	506
C ₆ H ₅ NHCO	H	C ₄ H ₉	C ₄ H ₉	217°	506
C ₆ H ₅ NHCO	H	C ₆ H ₁₃	C ₆ H ₁₃	198°	506
C ₆ H ₅ NHCO	H	C ₇ H ₁₅	C ₇ H ₁₅	199°	506
C ₆ H ₅ NHCO	H	C ₆ H ₁₇	C ₆ H ₁₇	194°	506
C ₆ H ₅ NHCO	H	C ₆ H ₅ CH ₂	C ₆ H ₅ CH ₂	243°	506
C ₆ H ₅	CH ₃	CH ₃ CO	H	81°	89, 109
(3-Thiono)					

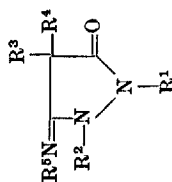
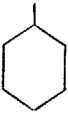
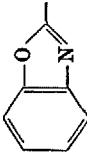


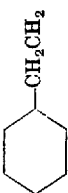
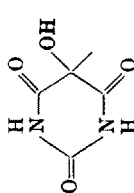
TABLE XLIX. 5-Imino-3-pyrazolidinones

Section A. Alkyl, Alicyclic, Aromatic, Heterocyclic, and Aryl Substituents					
R ¹	R ²	R ³	R ⁴	R ⁵	M.p. Reference
H	H	H	H	H	214° 594, 644, 1083
H	H	H	H	C ₆ H ₅	255° 1597, 1649
H	H	H	H	2-CH ₃ C ₆ H ₄	223° (dec.) 1651
H	H	H	H	3-CH ₃ C ₆ H ₄	250° (dec.) 1651
H	H	H	H	4-CH ₃ C ₆ H ₄	246° (dec.) 1649
H	H	H	H	2-CH ₃ OC ₆ H ₄	200° 1651
H	H	H	H	3-CH ₃ OC ₆ H ₄	212° 1651
H	H	H	H	4-CH ₃ OC ₆ H ₄	205° (dec.) 1651
H	H	H	H	4-C ₂ H ₅ OC ₆ H ₄	198° (dec.) 1651
H	H	H	H	3-BrC ₆ H ₄	271° (dec.) 1651
H	H	H	H	4-BrC ₆ H ₄	234° 1649
H	H	H	H	4-IC ₆ H ₄	242° (dec.) 1651
H	H	H	H	2,4-Br ₂ C ₆ H ₃	249° (dec.) 1651
H	H	H	H	1-C ₁₀ H ₇	214° 1651
H	H	H	H	2-C ₁₀ H ₇	239° (dec.) 1651
H	H	H	H	CH ₃ CO	227° 594
H	H	H	H	C ₆ H ₅ CO	227° 594
H	H	H	H	H	192° 594
CH ₃	H	H	H	C ₆ H ₅	220° 1597
CH ₃	H	H	H	C ₆ H ₅ CO	215° 594

H	CH ₃	H	CH ₃	H	H	H	182°	H	594
H	CH ₃	H	CH ₃	H	H	H	208°	C ₆ H ₅	1597
H	CH ₃	H	CH ₃	H	H	H	243°	C ₆ H ₅ CO	594
H	H	H	H	CH ₃	H	H	242°	H	501
H	H	H	H	C ₂ H ₅	H	H	247°	H	501
H	H	H	H	C ₄ H ₉	H	H	128°	H	508
H	H	H	H	s-C ₄ H ₉	H	H	145°	H	508
H	H	H	H	C ₆ H ₁₃	H	H	133°	H	507
H	H	H	H	(C ₂ H ₅) ₂ CHCH ₂	H	H	190°	H	507
H	H	H	H	C ₇ H ₁₅	H	H	136°	H	507
H	H	H	H	C ₄ H ₉ CHCH ₂	H	H	131°	H	507
				C ₂ H ₅					
H	H	H	H	C ₉ H ₁₉	H	H	222°	H	498
H	H	H	H	C ₁₀ H ₂₁	H	H	234°	H	507
H	H	H	H	C ₁₂ H ₂₅	H	H	152°	H	500
H	H	H	H	C ₁₈ H ₃₇	H	H	200°	H	498
									
H	H	H	H	H	H	H	239°	H	507
C ₆ H ₁₁ CH	H	H	H	H	H	H	—	H	705
COOH									
C ₆ H ₁₁ CH	H	H	H	H	H	H	—		705
COOH									
									
H	H	H	H	H	H	H	202°	H	497, 501
H	H	H	H	H	H	H	80°	H	120
H	H	H	H	C ₆ H ₅ CH ₂			244°	H	644, 1085
H	H	H	H	C ₆ H ₅ CH			> 280°	HOOC	557
				CH ₃					
				C ₆ H ₅ CH=					
				C ₆ H ₅ CH=					

(Table continued)

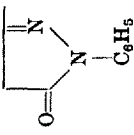
TABLE XLIX, Section A (continued)

R ¹	R ²	R ³	R ⁴	R ⁵	M.P.	Reference
H	H	2-ClC ₆ H ₄ CH ₂		H	199°	1083
H	H	1-C ₁₀ H ₇ CH ₂	H	H	170°	500
H	H	H ₂ NHNOCH ₂	H	H	—	507
H	H	C ₆ H ₅ N=CH	H	H	212°	507
H	H		H	H	—	1085
H	H		H	H	203°	498
H	H	C ₆ H ₅ CH=CH	H	H	198°	498
H	H	CH ₃ SCH ₂ CH ₂	H	H	121°	508
H	H	C ₆ H ₅ CH ₂ SCH ₂ CH ₂	H	H	109°	508
H	H	C ₆ H ₅ OCH ₂ CH ₂	H	H	186°	501
H	H	4-CH ₃ C ₆ H ₄ OCH ₂ CH ₂	H	H	184°	500
H	H	4-C ₂ H ₅ C ₆ H ₄ OCH ₂ CH ₂	H	H	170°	500
H	H	4-ClC ₆ H ₄ OCH ₂ CH ₂	H	H	203°	500
H	H	3-C ₂ H ₅ C ₆ H ₄ OCH ₂ CH ₂	H	H	135°	120
H	H	C ₆ H ₅ OCH ₂ CH ₂ CH ₂	H	H	110°	501
H	H	4-CH ₃ C ₆ H ₄ OCH ₂ CH ₂ CH ₂	H	H	159°	500
H	H	4-ClC ₆ H ₄ OCH ₂ CH ₂ CH ₂	H	H	203°	500
H	H	2-BrC ₆ H ₄ OCH ₂ CH ₂ CH ₂	H	H	152°	120
H	H	4-BrC ₆ H ₄ OCH ₂ CH ₂ CH ₂	H	H	214°	500
H	H	2,4-Cl ₂ C ₆ H ₃ OCH ₂ CH ₂ CH ₂	H	H	183°	120
H	H	3-C ₂ H ₅ C ₆ H ₄ OCH ₂ CH ₂	3-C ₂ H ₅ C ₆ H ₄ OCH ₂ CH ₂	H	215°	120
H	H	3-CH ₃ C ₆ H ₄ OCH ₂ CH ₂ CH ₂	3-CH ₃ C ₆ H ₄ OCH ₂ CH ₂ CH ₂	H	215°	120
H	H		H	H	—	1083

C_6H_5	H	H	H	H	219°	67, 317, 693, 870, 1141, 1595, 1601
C_6H_5 C_6H_5 C_6H_5	H H H	H H H	H H H	H H H	153° 219° > 400°	595, 596 595, 1595 595
C_6H_5	H	H	H	H	227°	704
C_6H_5	H	H	H	H	257°	705
C_6H_5	H	H	H	H	190°	704
C_6H_5	H	H	H	H	> 290°	704
C_6H_5	H	H	H	H	224°	704

(Table continued)

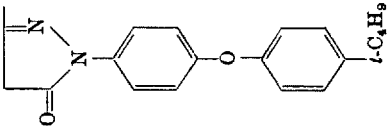
TABLE XLIX, Section A (continued)

R ¹	R ²	R ³	R ⁴	R ⁵	M.p.	Reference
C ₆ H ₅	H	H	H		290°	595, 596
C ₆ H ₅	H	H	H	CH ₃ CO	218°	693, 1139, 1595
C ₆ H ₅	H	H	H	HSCH ₂ CO	—	1594
C ₆ H ₅	H	H	H	BrCH ₂ CO	—	1602
C ₆ H ₅	H	H	H	CH ₃ CH ₂ CHCO C ₆ H ₅	170°	1255
C ₆ H ₅	H	H	H	CH ₃ COSCH ₂ CO	195°	776
C ₆ H ₅	H	H	H	C ₆ H ₅ HNCH ₂ CO	—	1602
C ₆ H ₅	H	H	H	C ₆ H ₅ CO	220°	693, 1595
C ₆ H ₅	H	H	H	3-H ₂ NC ₆ H ₄ CO	220°	67, 1139, 1247
C ₆ H ₅	H	H	H	3-O ₂ NC ₆ H ₅ CO	215°	67, 1247
C ₆ H ₅	H	H	H	2-H ₂ NOCC ₆ H ₄ CO	—	1139
C ₆ H ₅	H	H	H	3-(3-ClO ₂ SC ₆ H ₄ NH)C ₆ H ₄ CO	188°	67
C ₆ H ₅	H	H	H	3-[(4- <i>i</i> -C ₅ H ₁₁ C ₆ H ₄ O)C ₆ H ₄ NHCO]C ₆ H ₄ SO ₂ NH)C ₆ H ₄ CO CO	—	1602
C ₆ H ₅	H	H	H	3-H ₂ N-4-C ₁₈ H ₃₇ OC ₆ H ₅ CO	138°	1246
C ₆ H ₅	H	H	H	3-NO ₂ -4-C ₁₈ H ₃₇ OC ₆ H ₅ CO	155°	1246
C ₆ H ₅	H	H	H	3-[2-[2,4-(<i>i</i> -C ₅ H ₁₁) ₂ C ₆ H ₃ O]-5-H ₂ NC ₆ H ₅ CO)C ₆ H ₄ CO	—	1087
C ₆ H ₅	H	H	H	3-[2-[2,4-(<i>i</i> -C ₅ H ₁₁) ₂ C ₆ H ₃ O]-5-[2,5-(CH ₃ OOCC ₆ H ₄ NHCOCONH)C ₆ H ₃ CONH)C ₆ H ₄ CO	205°	1087
C ₆ H ₅	H	H	H	3-(3-ClO ₂ SC ₆ H ₄ CONH)-4-C ₁₈ H ₃₇ OC ₆ H ₅ CO	152°	1246
C ₆ H ₅	H	H	H	3-(3-Cl ₂ O ₂ SC ₆ H ₄ CONH)-4-C ₁₂ H ₂₅ OC ₆ H ₅ CO	—	1246

C_6H_5	H	H	H	3-[3,4-(ClO ₂ S) ₂ C ₆ H ₃ CONH]-4-C ₁₂ H ₂₅ OC ₆ H ₃ CO	—	1246
C_6H_5	H	H	H	3-[4-(4- <i>t</i> -C ₃ H ₁₁ -X-ClO ₂ SC ₆ H ₃ O)C ₆ H ₄ CONH]-4-C ₁₂ H ₂₅ -OC ₆ H ₃ CO	—	1246
C_6H_5	H	H	H	3-(2-HO ₃ SC ₆ H ₄ CONH)-4-C ₁₂ H ₂₅ OC ₆ H ₃ CO	—	1246
C_6H_5	H	H	H	3-(2-HOOC-X-ClO ₂ SC ₆ H ₃ CONH)-4-C ₁₈ H ₃₇ OC ₆ H ₃ CO	142°	1246
C_6H_5	H	H	H	3-(2-HO ₃ SC ₆ H ₄ CONH)-4-C ₁₈ H ₃₇ OC ₆ H ₃ CO	210°	1246
C_6H_5	H	H	H	3-[4-(4- <i>t</i> -C ₃ H ₁₁ -X-ClO ₂ SC ₆ H ₃ O)C ₆ H ₄ CONH]-4-C ₁₈ H ₃₇ OC ₆ H ₃ CO	128°	1246
C_6H_5	H	H	H	3-[3,5-(ClO ₂ S) ₂ C ₆ H ₃ CONH]-4-C ₁₈ H ₃₇ OC ₆ H ₃ CO	148°	1246
C_6H_5	H	H	H	2,4-(<i>t</i> -C ₃ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CO	204°	591
C_6H_5	H	H	H	3-{5-NO ₂ -2-[2,4-(C ₃ H ₁₁) ₂ C ₆ H ₃ O]C ₆ H ₃ CONH}C ₆ H ₄ CO	—	1247
C_6H_5	H	H	H	3-{5-H ₂ N-2-[2,4-(C ₃ H ₁₁) ₂ C ₆ H ₃ O]C ₆ H ₃ CONH}C ₆ H ₄ CO	—	1247
C_6H_5	H	H	H	3-{5-[2-HO ₃ SC ₆ H ₄ CONH]-2-[2,4-(C ₃ H ₁₁) ₂ C ₆ H ₃ O]-C ₆ H ₃ CONH}C ₆ H ₄ CO	—	1247
C_6H_5	H	H	H	3-{5-HO ₃ SCH ₂ CH ₂ CONH-2-[2,4-(C ₃ H ₁₁) ₂ C ₆ H ₃ O]-C ₆ H ₃ CONH}C ₆ H ₄ CO	—	1247
C_6H_5	H	H	H	3-(2-HO ₃ SC ₆ H ₄ CONH)C ₆ H ₄ CO	—	1247
C_6H_5	H	H	H	3-(2-HO ₃ SC ₆ H ₄ CONH)-4-C ₁₂ H ₂₅ OC ₆ H ₃ CO	—	1247
C_6H_5	H	H	H	3-(2-HO ₃ SC ₆ H ₄ CONH)-4-C ₁₈ H ₃₇ OC ₆ H ₃ CO	—	1247
C_6H_5	H	H	H	C ₂ H ₅ OOCC	198°	1595
C_6H_5	H	H	H	C ₆ H ₅ NHCO	235°	1595
C_6H_5	H	H	H	C ₆ H ₅ NHCS	227°	705
C_6H_5	H	H	H	H	142°, 160°	1138, 1596, 1599
H	C_6H_5	H	H	C ₆ H ₅	168°	1597
H	C_6H_5	H	H	CH ₃ CO	233°	1599
H	C_6H_5	H	H	C ₆ H ₅ CO	237°	1136, 1138, 1599
H	C_6H_5	H	H	C ₆ H ₅ NHCO	—	1138

(Table continued)

TABLE XLIX, Section A (continued)

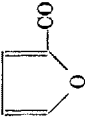
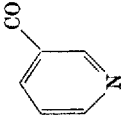
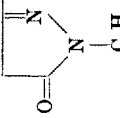
R ¹	R ²	R ³	R ⁴	R ⁵	M.p.	Reference
H	H	C ₆ H ₅	H	H	246°	501
3-CH ₃ C ₆ H ₄	H	H	H	H	182°	1600
4-CH ₃ C ₆ H ₄	H	H	H	H	—	870
4-HOC ₆ H ₄	H	H	H	H	300°	871
4-HOC ₆ H ₄	H	H	H	C ₁₅ H ₃₁ CO	298° (dec.)	871
4-CH ₃ OC ₆ H ₄	H	H	H	H	188°	1600
4-(4- <i>t</i> -C ₄ H ₉ C ₆ H ₄ O)C ₆ H ₄	H	H	H	4-(<i>t</i> -C ₄ H ₉)C ₆ H ₄ OCHCO CH ₃	—	921
4-(4- <i>t</i> -C ₄ H ₉ C ₆ H ₄ O)C ₆ H ₄	H	H	H		260°	595, 596
4-H ₂ NC ₆ H ₄	H	H	H	C ₁₁ H ₂₃ CO	150°	592
4-H ₂ NC ₆ H ₄	H	H	H	C ₁₇ H ₃₅ CO	148°	592
4-H ₂ NC ₆ H ₄	H	H	H	2,4-(C ₆ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CO	198°	592

4-(3-ClO ₂ SC ₆ H ₄ CONH)C ₆ H ₄	H	H	H	H	C ₁₁ H ₂₃ CO	220° (dec.)	592
4-(2-HO ₃ SC ₆ H ₄ CONH)C ₆ H ₄	H	H	H	H	C ₁₇ H ₃₅ CO	130°	592
4-(3-HO ₃ SC ₆ H ₄ CONH)C ₆ H ₄	H	H	H	H	C ₁₇ H ₃₅ CO	—	592
4-(2-HO ₃ SC ₆ H ₄ CONH)C ₆ H ₄	H	H	H	H	4-(4-C ₅ H ₁₁ C ₆ H ₄ O)C ₆ H ₄ CO	—	1247
4-(2-HO ₃ SC ₆ H ₄ CONH)C ₆ H ₄	H	H	H	H	4-[2,4-(C ₅ H ₁₁) ₂ C ₆ H ₃ O]C ₆ H ₄ CO	—	1247
4-(2-HO ₃ SC ₆ H ₄ CONH)C ₆ H ₄	H	H	H	H	4-[2-(C ₆ H ₅)C ₆ H ₄]C ₆ H ₄ CO	—	1247
4-(2-HO ₃ SC ₆ H ₄ CONH)C ₆ H ₄	H	H	H	H	2,4-(C ₅ H ₁₁) ₂ C ₆ H ₃ O(CH ₂) ₈ CO	—	1247
4-(2-HO ₃ SC ₆ H ₄ CONH)C ₆ H ₄	H	H	H	H	3-(4-C ₅ H ₁₁ C ₆ H ₄ O)C ₆ H ₄ CO	—	592
4-(2-HO ₃ SC ₆ H ₄ CONH)C ₆ H ₄	H	H	H	H	2,4-(C ₅ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CH ₂ CH ₂ CO	—	592
4-(2-HO ₃ SC ₆ H ₄ CONH)C ₆ H ₄	H	H	H	H	2,4-(C ₅ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CO	—	592
4-(2-HO ₃ SC ₆ H ₄ CONH)C ₆ H ₄	H	H	H	H	4-[2-(C ₆ H ₅)C ₆ H ₄]C ₆ H ₄ CO	—	592
4-[3-(4-C ₅ H ₁₁ C ₆ H ₄ O)C ₆ H ₄ CONH]C ₆ H ₄	H	H	H	H	3-(4-C ₅ H ₁₁ C ₆ H ₄ O)C ₆ H ₄ CO	117°	592
3-ClC ₆ H ₄	H	H	H	H	H	205°	870, 1600
4-BrC ₆ H ₄	H	H	H	H	H	—	870
4-NO ₂ C ₆ H ₄	H	H	H	H	H	248° (dec.)	1140, 1601
4-NO ₂ C ₆ H ₄	H	H	H	H	C ₁₁ H ₂₃ CO	186°	592
4-NO ₂ C ₆ H ₄	H	H	H	H	C ₁₇ H ₃₅ CO	—	592
4-NO ₂ C ₆ H ₄	H	H	H	H	2,4-(C ₅ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CO	195°	592
3-HOOC ₆ H ₄	H	H	H	H	H	273° (dec.)	871
3-NCC ₆ H ₄	H	H	H	H	C ₆ H ₅ CO	—	1604
4-NCC ₆ H ₄	H	H	H	H	H	224°	1601, 1604
4-NCC ₆ H ₄	H	H	H	H	CH ₃ CO	—	1604
4-NCC ₆ H ₄	H	H	H	H	C ₆ H ₅ CH ₂ CO	—	1604
4-NCC ₆ H ₄	H	H	H	H	3-NO ₂ C ₆ H ₄ CH ₂ CO	—	1604
4-NCC ₆ H ₄	H	H	H	H	2,4-(C ₅ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CO	—	1604
4-NCC ₆ H ₄	H	H	H	H	4-[2,4-(C ₅ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CONH]C ₆ H ₄ CH ₂ CO	—	1604
4-NCC ₆ H ₄	H	H	H	H	3-[2,4-(C ₅ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CONH]C ₆ H ₄ CH ₂ CO	—	1604
4-NCC ₆ H ₄	H	H	H	H	2,4-(C ₅ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CH ₂ CO	—	1604
4-NCC ₆ H ₄	H	H	H	H	4-[2,4-(C ₅ H ₁₁) ₂ C ₆ H ₃ O]C ₆ H ₄ CONHCH ₂ CH ₂ CO	—	1604
4-NCC ₆ H ₄	H	H	H	H	C ₆ H ₅ CO	254°	591, 1604
4-NCC ₆ H ₄	H	H	H	H	2-CH ₃ C ₆ H ₄ CO	—	1604
4-NCC ₆ H ₄	H	H	H	H	4-CH ₃ C ₆ H ₄ CO	—	1604
4-NCC ₆ H ₄	H	H	H	H	4-C ₅ H ₁₁ OC ₆ H ₄ CO	—	1604
4-NCC ₆ H ₄	H	H	H	H	4-s-C ₅ H ₁₁ C ₆ H ₄ CO	—	1604

(Table continued)

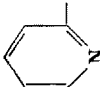
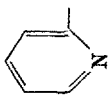
TABLE XLIX, Section A (continued)

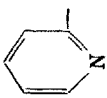
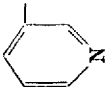
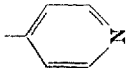
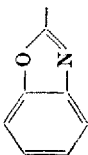
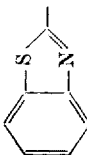
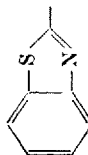
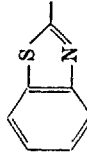
R ¹	R ²	R ³	R ⁴	R ⁵	M.p.	Reference
4-NCC ₆ H ₄	H	H	H	2-CH ₃ OC ₆ H ₄ CO	—	1604
4-NCC ₆ H ₄	H	H	H	3-CH ₃ OC ₆ H ₄ CO	—	1604
4-NCC ₆ H ₄	H	H	H	4-CH ₃ OC ₆ H ₄ CO	—	1604
4-NCC ₆ H ₄	H	H	H	3-H ₂ NC ₆ H ₄ CO	—	1604
4-NCC ₆ H ₄	H	H	H	2-ClC ₆ H ₄ CO	—	1604
4-NCC ₆ H ₄	H	H	H	3-ClC ₆ H ₄ CO	—	1604
4-NCC ₆ H ₄	H	H	H	4-ClC ₆ H ₄ CO	—	1604
4-NCC ₆ H ₄	H	H	H	2-NO ₂ C ₆ H ₄ CO	—	1604
4-NCC ₆ H ₄	H	H	H	3-NO ₂ C ₆ H ₄ CO	254°	1604
4-NCC ₆ H ₄	H	H	H	4-NO ₂ C ₆ H ₄ CO	—	1604
4-NCC ₆ H ₄	H	H	H	4-NCC ₆ H ₄ CO	—	1604
4-NCC ₆ H ₄	H	H	H	2,4-Cl ₂ C ₆ H ₃ CO	—	1604
4-NCC ₆ H ₄	H	H	H	3,4-Cl ₂ C ₆ H ₃ CO	—	1604
4-NCC ₆ H ₄	H	H	H	3-[4-(<i>t</i> -C ₃ H ₁₁) ₂ C ₆ H ₃ O]C ₆ H ₄ CO	—	1604
4-NCC ₆ H ₄	H	H	H	3-[2,4-(<i>t</i> -C ₃ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CONH]C ₆ H ₄ CO	—	1604
4-NCC ₆ H ₄	H	H	H	3-[<i>o</i> -[2,4-(<i>t</i> -C ₃ H ₁₁) ₂ C ₆ H ₃ O]C ₆ H ₄ CONH]C ₆ H ₄ CO	—	1604
4-NCC ₆ H ₄	H	H	H	4-[2,4-(<i>t</i> -C ₃ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CONH]C ₆ H ₄ CO	—	1604
4-NCC ₆ H ₄	H	H	H	2-[2,4-(<i>t</i> -C ₃ H ₁₁) ₂ C ₆ H ₃ O]-5-H ₂ NC ₆ H ₅ CO	—	1604
4-NCC ₆ H ₄	H	H	H	2-[2,4-(<i>t</i> -C ₃ H ₁₁) ₂ C ₆ H ₃ O]-3-NO ₂ C ₆ H ₅ CO	—	1604
4-NCC ₆ H ₄	H	H	H	2-[2,4-(<i>t</i> -C ₃ H ₁₁) ₂ C ₆ H ₃ O]-5-NO ₂ C ₆ H ₃ CO	—	1604
4-NCC ₆ H ₄	H	H	H	4-[2,4-(<i>t</i> -C ₃ H ₁₁) ₂ C ₆ H ₃ O]-3-(4-CH ₃ C ₆ H ₄ CO)C ₆ H ₃ CO	—	1604
4-NCC ₆ H ₄	H	H	H	4-[2,4-(<i>t</i> -C ₃ H ₁₁) ₂ C ₆ H ₃ O]-3-(4-ClC ₆ H ₄ CO)C ₆ H ₃ CO	—	1604
4-NCC ₆ H ₄	H	H	H	2-[2,4-(<i>t</i> -C ₃ H ₁₁) ₂ C ₆ H ₃ O]-5-(4- <i>s</i> -C ₃ H ₁₁ C ₆ H ₄ CO)C ₆ H ₃ CO	—	1604
4-NCC ₆ H ₄	H	H	H	4-[2,4-(<i>t</i> -C ₃ H ₁₁) ₂ C ₆ H ₃ O]-3-(4- <i>s</i> -C ₃ H ₁₁ C ₆ H ₄ CO)C ₆ H ₃ CO	—	1604
4-NCC ₆ H ₄	H	H	H	3-[2-[2,4-(<i>t</i> -C ₃ H ₁₁) ₂ C ₆ H ₃ O]-5-[3,5-(ClO ₂ S) ₂ C ₆ H ₃ CO]]-C ₆ H ₄ CO	—	1604
4-NCC ₆ H ₄	H	H	H	3-[2-[2,4-(<i>t</i> -C ₃ H ₁₁) ₂ C ₆ H ₃ O]-5-[3-HOOC-4-HOC ₆ H ₃ SO ₂ -NH]C ₆ H ₃ CO)C ₆ H ₄ CO	—	1604

4-NCC ₆ H ₄	H	H	H	4-[2-(C ₆ H ₅)C ₈ H ₄]C ₆ H ₄ CO	—	13, 1604
4-NCC ₆ H ₄	H	H	H		—	1604
4-NCC ₆ H ₄	H	H	H		—	1604
4-HO ₃ SC ₆ H ₄	H	H	H	H	258° (dec.)	870, 871
4-H ₂ NO ₂ SC ₆ H ₄	H	H	H	C ₁₃ H ₂₁ CO	199° (dec.)	695
4-HO ₃ SC ₆ H ₄	H	H	H	C ₆ H ₅ CO	220°	871
4-HO ₃ SC ₆ H ₄	H	H	H	C ₈ H ₅ CO	194°	695
4-HO ₃ SC ₆ H ₄	H	H	H		—	705
4-H ₂ NO ₂ SC ₆ H ₄	H	H	H	H	258°	1600
2,4-Cl ₂ C ₆ H ₃	H	H	H	3-[2,4-(s-C ₄ H ₉) ₂ C ₆ H ₃ OCH ₂ CONH]C ₆ H ₄ CO	133°	922
2,5-Cl ₂ C ₆ H ₃	H	H	H	3-[2,4-(s-C ₄ H ₉) ₂ C ₆ H ₃ OCH ₂ CONH]C ₆ H ₄ CO	—	922
2,5-Cl ₂ C ₆ H ₃	H	H	H	3-[4-(t-C ₅ H ₁₁)C ₆ H ₄ O]C ₆ H ₄ CO	110°	922
4-C ₆ H ₅ O-3-HO ₃ SC ₆ H ₃	H	H	H	H	> 300°	871
4-C ₆ H ₅ O-3-HO ₃ SC ₆ H ₃	H	H	H	C ₁₅ H ₃₁ CO	249° (dec.)	871
4-C ₆ H ₅ O-3-HO ₃ SC ₆ H ₃	H	H	H	C ₈ H ₅ CO	> 300°	871
4-C ₆ H ₅ O-X-HO ₃ SC ₆ H ₃	H	H	H	H	> 300°	871
4-C ₆ H ₅ O-X-HO ₃ SC ₆ H ₃	H	H	H	C ₁₇ H ₃₅ CO	> 300°	871
4-[3-(4-C ₅ H ₁₁ C ₆ H ₄ O)-X-ClO ₂ -SC ₆ H ₃ O]C ₆ H ₃	H	H	H	2,4-(C ₅ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CO	135°	592

(Table continued)

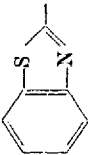
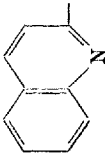
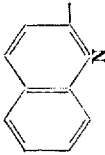
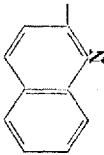
TABLE XLIX, Section A (continued)

R ¹	R ²	R ³	R ⁴	R ⁵	M.p.	Reference
2,4,6-Cl ₃ C ₆ H ₂	H	H	H	H	—	1254
2,4,6-Cl ₃ C ₆ H ₂	H	H	H	C ₆ H ₅ CH ₂ CO	—	922
2,4,6-Cl ₃ C ₆ H ₂	H	H	H	C ₆ H ₅ CO	—	922
2,4,6-Cl ₃ C ₆ H ₂	H	H	H	3-H ₂ NC ₆ H ₄ CO	—	1254
2,4,6-Cl ₃ C ₆ H ₂	H	H	H	3-NO ₂ C ₆ H ₄ CO	—	1254
2,4,6-Cl ₃ C ₆ H ₂	H	H	H	3-(2,4-(6-C ₄ H ₉) ₂ C ₆ H ₃ OCH ₂ CONH)C ₆ H ₄ CO	—	922
2,4,6-Cl ₃ C ₆ H ₂	H	H	H	3-[2,4-(t-C ₆ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CONH]C ₆ H ₄ CO	138°, 220°	922, 1603
2,4,6-Br ₃ C ₆ H ₂	H	H	H	H	—	922
2,4,6-Br ₃ C ₆ H ₂	H	H	H	C ₆ H ₅ CH ₂ CO	—	922
2,4,6-Br ₃ C ₆ H ₂	H	H	H	C ₆ H ₅ CO	274°	922
2,4,6-Br ₃ C ₆ H ₂	H	H	H	3-(4-t-C ₃ H ₁₁ C ₆ H ₄ O)C ₆ H ₄ CO	270°	922
2,4,6-Br ₃ C ₆ H ₂	H	H	H	3-[2,4-(6-C ₄ H ₉) ₂ C ₆ H ₃ OCH ₂ CONH]C ₆ H ₄ CO	—	922
2,4,6-Br ₃ C ₆ H ₂	H	H	H	3-[2,4-(t-C ₆ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CONH]C ₆ H ₄ CO	225°	922
2,6-Cl ₂ -4-NCC ₆ H ₂	H	H	H	2,4-(t-C ₆ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CH ₂ CO	—	1604
2,6-Cl ₂ -4-NCC ₆ H ₂	H	H	H	C ₆ H ₅ CO	—	1604
2,6-Cl ₂ -4-NCC ₆ H ₂	H	H	H	3-[2,4-(t-C ₆ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CO]C ₆ H ₄ CO	—	1604
4-[2-(C ₆ H ₅)C ₆ H ₄]C ₆ H ₄	H	H	H	H	223°	13, 14
4-[2-(C ₆ H ₅)C ₆ H ₄]C ₆ H ₄	H	H	H	C ₆ H ₅ CO	234°	13, 14
	H	H	H	H	277°	1142, 1601
H		H	H	H	188°	1600

	H	H	H	C_6H_6	201°	1601
	H	H	H	H	216° (dec.)	1142, 1600, 1601
	H	H	H	H	239° (dec.)	1142, 1600, 1601
	H	H	H	H	220° (dec.)	1142, 1601
	H	H	H	H	254°	1601
	H	H	H	C_6H_5CO	225°	1601
	H	H	H	H	234° (dec.)	1600

(Table continued)

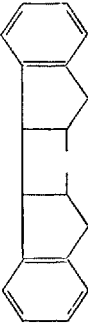
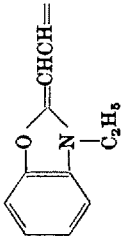
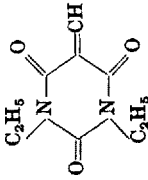
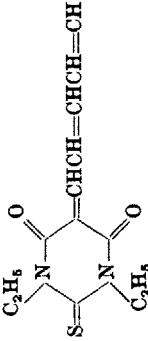
TABLE XLIX, Section A (continued)

R ¹	R ²	R ³	R ⁴	R ⁵	M. p.	Reference
H		H	H	CH ₃ CO	252°	1600
		H	H	H	196°	1601
		H	H	C ₆ H ₅ CO	187°	1142, 1601
H		H	H	H	218° (dec.)	1600
CH ₃	H	CH ₃	H	H	140°	499
CH ₃	H	CH ₃	H	C ₂ H ₅ COO	250°	499
H	CH ₃	CH ₃	H	H	223°	499
H	H	CH ₃	CH ₃	H	249°	507
CH ₃	CH ₃	H	H	CH ₃ COO	200°	167
H	H	CH ₃	C ₄ H ₉	H	196°	391
H	CH ₃	C ₅ H ₁₁	H	H	85°	499
H	CH ₃	C ₆ H ₁₃	H	H	101°	499
H	CH ₃	C ₇ H ₁₅	H	H	79°	499
H	CH ₃	C ₈ H ₁₇	H	H	86°	499

H	H	C ₂ H ₅	C ₂ H ₅	H	208°	391
H	H	C ₂ H ₅	C ₄ H ₉	H	192°	391
H	H	C ₃ H ₇	C ₃ H ₇	H	175°, 236°	391, 507
H	H	C ₄ H ₉	C ₄ H ₉	H	223°	507
H	H	C ₄ H ₁₁	C ₄ H ₁₁	H	200°	507
H	H	C ₆ H ₅ CH ₂	C ₆ H ₅ CH ₂	H	242°	501
C ₆ H ₅	CH ₃	H	H	H	230°	167, 697, 1339, 1387
C ₆ H ₅	CH ₃	H	C ₆ H ₅ CH ₂	C ₆ H ₅ CH ₂	69°	1052
C ₆ H ₅	CH ₃	H	CH ₃ CO	CH ₃ CO	257°	1339
C ₆ H ₅	CH ₃	H	C ₆ H ₅ CO	C ₆ H ₅ CO	233°	1339
C ₆ H ₅	CH ₃	H	C ₂ H ₅ COO	C ₂ H ₅ COO	222°	167, 1387
C ₆ H ₅	CH ₃	H	C ₄ H ₉ COO	C ₄ H ₉ COO	194°	167
C ₆ H ₅	CH ₃	H	HOCH ₂ CH ₂ COO	HOCH ₂ CH ₂ COO	212°	167
C ₆ H ₅	H	CH ₃	H	H	137°	499
C ₆ H ₅	C ₆ H ₅	CH ₃	C ₂ H ₅ COO	C ₂ H ₅ COO	242°	499
H	C ₆ H ₅	CH ₃	H	H	227°	501
C ₆ H ₅	C ₂ H ₅	H	H	H	145°, 226°	167, 499, 1395
C ₆ H ₅	C ₂ H ₅	H	H	C ₂ H ₅ COO	213°	167, 499, 1395
C ₆ H ₅	C ₂ H ₅	H	H	iso-C ₃ H ₇ COO	211°	167
H	C ₂ H ₅	C ₂ H ₅	H	H	213°	501
H	H	C ₆ H ₅	C ₆ H ₅	H	215°	391
H	C ₆ H ₅	C ₆ H ₁₉	H	H	167°	498
H	C ₆ H ₅		H	H	154°	498
C ₆ H ₅	H	C ₆ H ₅ CH ₂	C ₆ H ₅ CH ₂	H	206°	498
C ₆ H ₅	H	C ₆ H ₅ CH ₂	C ₆ H ₅ CH ₂	C ₂ H ₅ COO	178°	498
C ₆ H ₅	H	C ₆ H ₅ CH ₂	C ₆ H ₅ CH ₂	C ₆ H ₅ CO	225°	498

(Table continued)

TABLE XLIX, Section A (continued)

R ¹	R ²	R ³	R ⁴	R ⁵	M.p.	Reference
H	C ₆ H ₅	C ₆ H ₅ CH ₂	H	H	160°	498, 501
H	C ₆ H ₅	C ₆ H ₅ CH ₂	H	C ₆ H ₅ CO	197°	498
C ₆ H ₅	H	4-CH ₃ OC ₆ H ₄ CH=		CH ₃ CH ₂ CHCO C ₆ H ₅	162°	1255
H	C ₆ H ₅	C ₆ H ₅ OCH ₂ CH ₂	H	H	136°	501
H	C ₆ H ₅	C ₆ H ₅ OCH ₂ CH ₂ CH ₂	H	H	108°	501
H	H			H	238°	501
C ₆ H ₅	H			H	206° (dec.)	1330
C ₆ H ₅	H		H	H	165°	776
C ₆ H ₅	H		H	CH ₃ COSCH ₂ CO	219°	776

	H	C_2H_5CHCO $ $ C_6H_5	220°	1253
	H	H	153°	506
	H	C_6H_5OOC	193°	506
	C_6H_5	H	234°	506
	H	H	—	1083
	H	H	152°	1254
	H	$3-[2,4-(t-C_3H_7)_2-$ $C_6H_5OCH_2-$ $CONH]C_6H_4CO$	120°	1253

(Table continued)

TABLE XLIX, Section A (continued)

R ¹	R ²	R ³	R ⁴	R ⁵	M.p.	Reference
CH ₃	H	CH ₃	C ₄ H ₉	H	140°	391
CH ₃	H	C ₂ H ₅	C ₂ H ₅	H	190°	391
CH ₃	H	C ₂ H ₅	C ₂ H ₅	CH ₃ CO	206°	391
CH ₃	H	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅ CO	178°	391
H	CH ₃	C ₄ H ₉	C ₄ H ₉	H	141°	499
H	CH ₃	C ₆ H ₁₃	C ₆ H ₁₃	H	188°	499
H	CH ₃	C ₇ H ₁₅	C ₇ H ₁₅	H	135°	499
C ₆ H ₅	CH ₃	CH ₃	H	H	196°	167
C ₆ H ₅	CH ₃	CH ₃	H	CH ₃ COO	188°	167
C ₆ H ₅	CH ₃	CH ₃	H	iso-C ₃ H ₇ COO	157°	167
C ₆ H ₅	CH ₃	C ₂ H ₅	H	H	157°	167
C ₆ H ₅	CH ₃	C ₂ H ₅	H	CH ₃ COO	144°	167
CH ₃	H	C ₂ H ₅	C ₆ H ₅	H	141°	391
C ₆ H ₅	CH ₃	iso-C ₃ H ₇	H	H	204°	167, 1395, 1400
C ₆ H ₅	CH ₃	iso-C ₃ H ₇	H	CH ₃ COO	126°	167
C ₆ H ₅	CH ₃	iso-C ₃ H ₇	H	C ₂ H ₅ COO	141°	167
C ₆ H ₅	CH ₃	iso-C ₃ H ₇	H	iso-C ₃ H ₇ COO	139°	167
C ₆ H ₅	CH ₃	iso-C ₃ H ₇	H	C ₃ H ₅ COO	102°	167
C ₆ H ₅	CH ₃	iso-C ₃ H ₇	H	ClCH ₂ CH ₂ COO	135°	167
C ₆ H ₅	CH ₃	iso-C ₃ H ₇	H	HOCH ₂ CH ₂ COO	136°	167
C ₆ H ₅	CH ₃	iso-C ₃ H ₇	H	H ₂ NOC	165°	167
C ₆ H ₅	CH ₃	s-C ₄ H ₉	H	H	204°	167
C ₆ H ₅	CH ₃	C ₆ H ₅ CH ₂	H	CH ₃ COO	109°	167
C ₆ H ₅	CH ₃	C ₆ H ₅ CH ₂	H	H	137°	167
C ₆ H ₅	CH ₃	C ₂ H ₅	H	CH ₃ COO	158°	167
H	C ₂ H ₅	C ₂ H ₅	C ₆ H ₅	H	138°	391
H	C ₂ H ₅	iso-C ₃ H ₇	H	H	105°	391
C ₆ H ₅	C ₂ H ₅	iso-C ₃ H ₇	H	H	204°, 230°	1395, 1400
C ₆ H ₅	C ₂ H ₅	iso-C ₃ H ₇	H	CH ₃ COO	126°	1395
C ₆ H ₅	C ₂ H ₅	iso-C ₃ H ₇	H	C ₂ H ₅ COO	141°	1395

C_6H_5	C_6H_5	$\text{s-C}_4\text{H}_9$	H	H	204°	1395
C_6H_5	C_2H_5	$\text{s-C}_4\text{H}_9$	H	CH_3OOC	126°	1395
H	C_6H_5	C_6H_7	C_6H_7	H	211°	317
H	C_6H_5	$\text{C}_6\text{H}_5\text{CH}_2$	$\text{C}_6\text{H}_5\text{CH}_2$	H	259°	501
C_6H_5	CH_3	C_6H_5	H	H	241°	167
C_6H_5	CH_3	C_6H_5	H	CH_3OOC	124°	167
$4\text{-CH}_3\text{C}_6\text{H}_4$	CH_3	$\text{iso-C}_3\text{H}_7$	H	H	205°	167
$4\text{-CH}_3\text{C}_6\text{H}_5$	CH_3	$\text{iso-C}_3\text{H}_7$	H	CH_3OOC	191°	167
CH_3	CH_3	C_2H_5	C_2H_5	H	76°	391
CH_3	CH_3	C_2H_5	C_2H_5	$\text{C}_2\text{H}_5\text{OOC}$	b_{13} 173°	391
CH_3	CH_3	C_2H_5	C_6H_5	H	$b_{0.1}$ 155°	391

TABLE XLIX (continued)

Section B. Acyl, Carboxyl, and Carboxyl Derivatives

R ¹	R ²	R ³	R ⁴	R ⁵	M.p.	Reference
H	C_6H_5	CH_3CO	H	H	233°	498, 1399
H	H	HOOC	H	H	> 300°	557
H	H	$\text{C}_2\text{H}_5\text{OOC}$	H	H	—	1083
H	H	$\text{C}_2\text{H}_5\text{OOC}$	H	C_6H_5	194°	1650
H	H	$\text{C}_2\text{H}_5\text{OOC}$	H	$2\text{-CH}_3\text{C}_6\text{H}_4$	215°	1650
H	H	$\text{C}_2\text{H}_5\text{OOC}$	H	$4\text{-CH}_3\text{C}_6\text{H}_4$	200°	1650
H	H	$\text{C}_2\text{H}_5\text{OOC}$	H	HOOC	187°	557
C_6H_5	H	CH_3C	H	H	185° (dec.)	557
		NNHC_6H_5				
C_6H_5	H	$2,4\text{-(t-C}_3\text{H}_{11})_2\text{C}_6\text{H}_3\text{OCH}_2\text{CO}$	H	$2,4\text{-(t-C}_3\text{H}_{11})_2\text{C}_6\text{H}_3\text{OCH}_2\text{CO}$	140°	591

(Table continued)

TABLE XLIX, Section B (continued)

R ¹	R ²	R ³	R ⁴	R ⁵	M.p.	Reference
CH ₃ CO	H	H	H	C ₆ H ₅	207° (dec.)	1598
H	CH ₃ CO	H	H	C ₆ H ₅	203°	1598
CH ₃ CO	H	H	H	CH ₃ CO	195°	594
C ₆ H ₅ CO	H	H	H	C ₆ H ₅	198°	1598
C ₆ H ₅ CO	H	H	H	C ₆ H ₅ CO	171°	594
C ₆ H ₅ CO	H	C ₆ H ₅ CH ₂	H	C ₆ H ₅ COO	160°	497
H	C ₆ H ₅ CO	C ₃ H ₇	H	H	234°	497
H	C ₆ H ₅ CO	C ₄ H ₉	H	H	232°	497
H	C ₆ H ₅ CO	C ₆ H ₁₁	H	H	233°	497
H	C ₆ H ₅ CO	C ₆ H ₁₃	H	H	236°	497
H	C ₆ H ₅ CO	C ₇ H ₁₅	H	H	234°	497
H	C ₆ H ₅ CO	C ₉ H ₁₇	H	H	236°	497
H	C ₆ H ₅ CO	C ₆ H ₅ CH ₂	H	H	236°	497
H	C ₆ H ₅ CO	C ₃ H ₇	C ₃ H ₇	H	236°	497
H	C ₆ H ₅ CO	C ₄ H ₉	C ₄ H ₉	H	235°	497
H	C ₆ H ₅ CO	C ₆ H ₁₁	C ₆ H ₁₁	H	236°	497
H	C ₆ H ₅ CO	C ₆ H ₁₃	C ₆ H ₁₃	H	236°	497
H	C ₆ H ₅ CO	C ₇ H ₁₅	C ₇ H ₁₅	H	237°	497
H	C ₆ H ₅ CO	C ₆ H ₅ CH ₂	C ₆ H ₅ CH ₂	H	238°	497
H	H ₂ NOC	C ₃ H ₇	C ₃ H ₇	H	304°	498
H	H ₂ NOC	C ₄ H ₉	C ₄ H ₉	H	278°	498
H	H ₂ NOC	C ₃ H ₇ CH	C ₃ H ₇ CH	H	300°	498
		CH ₃	CH ₃			
H	H ₂ NOC	C ₆ H ₁₁	C ₆ H ₁₁	H	273°	498
H	H ₂ NOC	C ₆ H ₁₃	C ₆ H ₁₃	H	261°	498
H	H ₂ NOC	C ₇ H ₁₅	C ₇ H ₁₅	H	270°	498
H	H ₂ NOC	C ₆ H ₁₇	C ₆ H ₁₇	H	266°	498
H	H ₂ NOC	C ₆ H ₁₉	C ₆ H ₁₉	H	259°	498
H	C ₆ H ₅ NHOC	C ₄ H ₉	H	H	117°	506

H	C ₆ H ₅ NHOC	C ₆ H ₁₁	H	H	115°	506
H	C ₆ H ₅ NHOC	C ₆ H ₁₃	H	H	113°	506
H	C ₆ H ₅ NHOC	C ₇ H ₁₅	H	H	110°	506
H	C ₆ H ₅ NHOC	C ₆ H ₁₇	H	H	264°	506
H	C ₆ H ₅ NHOC	C ₆ H ₅ CH ₃	H	H	240°	506
H	C ₆ H ₅ NHOC	C ₄ H ₉	C ₄ H ₉	H	234°	506
H	C ₆ H ₅ NHOC	C ₆ H ₁₁	C ₃ H ₁₁	H	95°	506
H	C ₆ H ₅ NHOC	C ₆ H ₁₃	C ₆ H ₁₃	H	100°	506
H	C ₆ H ₅ NHOC	C ₈ H ₁₇	C ₈ H ₁₇	H	167°	506

TABLE XLIX (continued)

Section C. Halogen, Nitroso, Amino, Imino, Azo, and Amido Substituents

R ¹	R ²	R ³	R ⁴	R ⁵	M.p.	Reference
H	C ₆ H ₅			H	223°	317
C ₆ H ₅	CH ₃	Br	H	CH ₃ COO	102°	167
C ₆ H ₅	CH ₃	Br	H	C ₆ H ₅ CH ₂ COO	212° (dec.)	697
H	H	H ₂ N	H	H	—	644
H	H	HOCH ₂ NH	H	H	—	644
C ₆ H ₅	CH ₃	H ₂ N	H	H	180°	1339
C ₆ H ₅	H	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=		H	78°	519
C ₆ H ₅	H	4-(C ₂ H ₅) ₂ NC ₆ H ₄ N=		CH ₃ CO	125°	519
C ₆ H ₅	H	4-(HOCH ₂ CH ₂ N)C ₆ H ₄ N=		H	180°	519
		$\downarrow$ C ₂ H ₅				
C ₆ H ₅	H	2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=		H	148°, 169°	244, 519
C ₆ H ₅	H	2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=		C ₆ H ₅	173°	244

(Table continued)

TABLE XLIX, Section C (continued)

R ¹	R ²	R ³	R ⁴	R ⁵	M. p.	Reference
C ₆ H ₅	H	2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=		CH ₃ CH ₂ CHCO C ₆ H ₅	168°	1255, 1539
C ₆ H ₅	H	2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=		C ₆ H ₅ CO	207°	1538
C ₆ H ₅	H	2-CH ₃ -4-(C ₂ H ₅) ₂ NC ₆ H ₃ N=		4-ClC ₆ H ₄ CO	215°	1538
H	H	NO	H	H	> 300°	644
H	H	NO	H	CH ₃ COO	218° (dec.)	337
H	H	NO	H	C ₂ H ₅ COO	174° (dec.)	337
H	H	NO	H	C ₆ H ₅	—	1649
C ₆ H ₅	CH ₃	NO	H	H	193° (dec.)	1339
H	H	C ₆ H ₅ N=N	H	C ₆ H ₅	211° (dec.)	1649
H	H	4-H ₂ NO ₂ SC ₆ H ₄ N=N	H	H	274°	356
H	H	2-HO-4-HO ₃ S-1-C ₁₀ H ₆ N=N	H	H	—	920
H	H	2-HO-4-HO ₃ S-1-C ₁₀ H ₆ N=N	H	C ₆ H ₅	—	920
H	H	2-HO-4-HO ₃ S-1-C ₁₀ H ₆ N=N	H	CH ₃ CO	—	920
CH ₃	H	4-CH ₃ OC ₆ H ₄ N=N	H	H	172°	594
CH ₃	H	4-CH ₃ OC ₆ H ₄ N=N	H	C ₂ H ₅ COO	181°	594
H	CH ₃	4-CH ₃ OC ₆ H ₄ N=N	H	H	240°	594
C ₆ H ₅	H	C ₆ H ₅ N=N	H	2,4-(5-C ₃ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CO	175°	591
C ₆ H ₅	H	4-CH ₃ OC ₆ H ₄ N=N	H	CH ₃ CH ₂ CHCO C ₆ H ₅	192°	1255, 1539
C ₆ H ₅	H	2-HOOC-5-HO ₃ SC ₆ H ₃ N=N	H	H	—	920
C ₆ H ₅	H	2-HOOC-4-HO ₃ SC ₆ H ₃ N=N	H	H	—	920
C ₆ H ₅	H	2-HOOC-4-HO ₃ SC ₆ H ₃ N=N	H	CH ₃ CO	—	920
C ₆ H ₅	H	2-HO-3-NO ₂ -5-HO ₃ SC ₆ H ₂ N=N	H	H	—	920
C ₆ H ₅	H	2,5-(CH ₃ COO) ₂ C ₆ H ₃ N=N	H	3-(2-[2,4-(4-C ₆ H ₁₁) ₂ C ₆ H ₃ O]-5-(2-HO ₃ -SC ₆ H ₄ CONH)C ₆ H ₃ CONH)C ₆ H ₄ CO	—	1247
C ₆ H ₅	H	4-HOOCCH ₂ OC ₆ H ₄ N=N	H	3-(2-[2,4-(4-C ₆ H ₁₁) ₂ C ₆ H ₃ O]-5-[3,5-(CH ₃ COO) ₂ -C ₆ H ₃ NHCOCONH]C ₆ H ₃ CONH)C ₆ H ₄ CO	205°	1087

4-NO ₂ C ₆ H ₄	H	4-CH ₃ OC ₆ H ₄ N=N	H	CH ₃ CH ₂ CHCO C ₆ H ₅	250°	1539
4-NCC ₆ H ₄	H	C ₆ H ₅ N=N	H	C ₆ H ₅ CO	258°	591
C ₆ H ₅	CH ₃	C ₆ H ₅ N=N	H	H	224°	1339
H	H	H ₂ NCONH	H	H	—	644
H	H	C ₆ H ₅ NHSCNH	H	C ₆ H ₅ NHSC	—	644

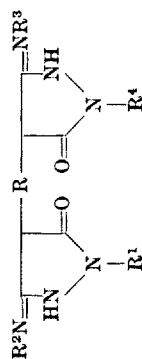


TABLE L. 4,4'-Bis(5-imino-3-pyrazolidinones)

R = Single Bond R¹ = R²		R² = R³	M.p.	Reference
H	C ₆ H ₅	C ₆ H ₅	—	72
C ₆ H ₅	C ₆ H ₅	4-CH ₃ OC ₆ H ₄	—	72
C ₆ H ₅	C ₆ H ₅	1-C ₁₀ H ₇ CH ₂ CO	—	72
		C ₆ H ₅	—	72

(Table continued)

TABLE L (continued)

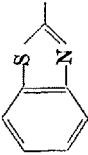
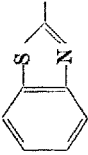
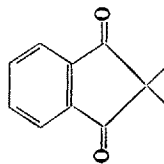
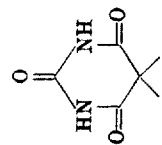
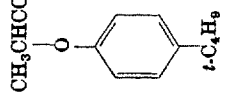
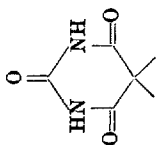
R	R ¹	R ²	R ³	R ⁴	M.p.	Reference
4-CH ₃ OC ₆ H ₄ CH	C ₆ H ₅	CH ₃ CH ₂ CHCO C ₆ H ₅	CH ₃ CH ₂ CHCO C ₆ H ₅	C ₆ H ₅	142°	1255
4-CH ₃ OC ₆ H ₄ CH		3-[3-(4-C ₆ H ₁₁)C ₆ H ₄]C ₆ H ₄ CO	H	C ₆ H ₅	145°	1254
4-CH ₃ OC ₆ H ₄	C ₆ H ₅	CH ₃ CH ₂ CHCO C ₆ H ₅	4-[4-(4-C ₆ H ₉)C ₆ H ₄ O]C ₆ H ₄	4-[4-(C ₄ H ₉)- C ₆ H ₄ O]C ₆ H ₄ CO	120°	1254
4-CH ₃ O ₂ HC ₄		4-{4-[3-(4-C ₆ H ₁₁)C ₆ H ₄ O]C ₆ - H ₄ CONH}C ₆ H ₄ (CH ₂) ₄ CO	CH ₃ CH ₂ CHCO C ₆ H ₅	C ₆ H ₅	150°	1254

TABLE L (continued)

R	R ¹ = R ⁴	R ² = R ³	M.p.	Reference
C ₆ H ₅ CH	2,4,6-Cl ₃ C ₆ H ₂	3-[2,4-(4-C ₆ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CONH]C ₆ H ₄ CO	170°	1603
4-HOC ₆ H ₃ CH	2,4,6-Cl ₃ C ₆ H ₂	3-[2,4-(4-C ₆ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CONH]C ₆ H ₄ CO	173°	1603
4-CH ₃ OC ₆ H ₄ CH	2,4,6-Cl ₃ C ₆ H ₂	3-[2,4-(4-C ₆ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CONH]C ₆ H ₄ CO	215°	1603
2-ClC ₆ H ₄ CH	2,4,6-Cl ₃ C ₆ H ₂	3-[2,4-(4-C ₆ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CONH]C ₆ H ₄ CO	218°	1603
4-ClC ₆ H ₄ CH	2,4,6-Cl ₃ C ₆ H ₂	3-[2,4-(4-C ₆ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CONH]C ₆ H ₄ CO	203°	1603
4-NO ₂ C ₆ H ₄ CH	2,4,6-Cl ₃ C ₆ H ₂	3-[2,4-(4-C ₆ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CONH]C ₆ H ₄ CO	192°	1603
3-CH ₃ O-4-HOC ₆ H ₃ CH	2,4,6-Cl ₃ C ₆ H ₂	3-[2,4-(4-C ₆ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CONH]C ₆ H ₄ CO	195°	1603
3,5-(CH ₃ O) ₂ -4-HOC ₆ H ₃ CH	2,4,6-Cl ₃ C ₆ H ₂	3-[2,4-(4-C ₆ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CONH]C ₆ H ₄ CO	170°	1603

	2,4,6-Cl ₃ C ₆ H ₂	3-[2,4-(<i>t</i> -C ₅ H ₁₁) ₂ C ₆ H ₃ OCH ₂ CONH]C ₆ H ₄ CO	190°	1253
	4-(4- <i>t</i> -C ₄ H ₉ C ₆ H ₄ O)C ₆ H ₄	CH ₃ CHCO 	164°	1253
	4-(4- <i>t</i> -C ₄ H ₉ C ₆ H ₄ O)C ₆ H ₄	3-(3- <i>t</i> -C ₅ H ₁₁ C ₆ H ₄ O)C ₆ H ₄ CO	225°	1253
S	4-[4-(<i>t</i> -C ₄ H ₉)C ₆ H ₄ O]C ₆ H ₄	4-(<i>t</i> -C ₄ H ₉)C ₆ H ₄ OCHCO 	134°	921
S	C ₆ H ₅	H	> 300° (2 HCl)	693
S	C ₆ H ₅	CH ₃ CO	> 300°	693
S-S	C ₆ H ₅	H	> 300° (2 HCl)	693
S-S	C ₆ H ₅	C ₆ H ₅ CO	> 300°	693

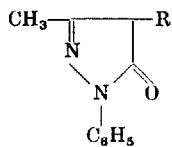
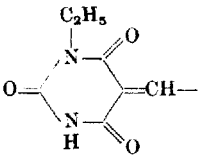
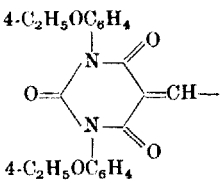
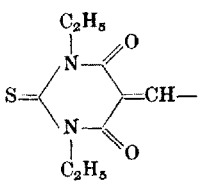
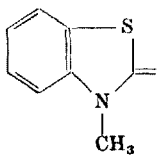
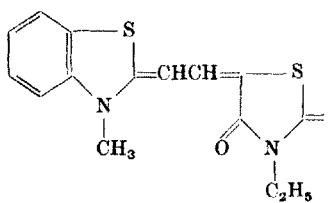
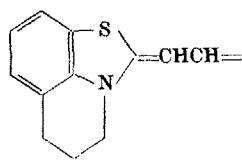


TABLE I. 3-Methyl-1-phenyl-2-pyrazolin-5-ones. Dyes

R	M.p.	Reference
	257° (dec.)	754
	—	703
	—	33
	290°	761
	—	237
	285°	411

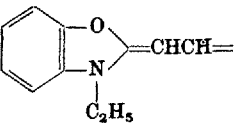
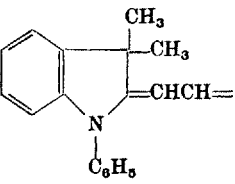
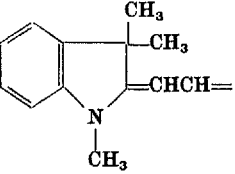
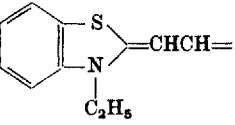
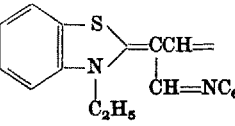
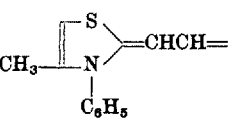
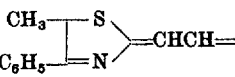
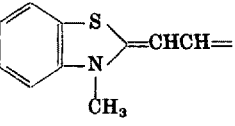
(Table continued)

TABLE LI (*continued*)

R	M.p.	Reference
	234°	776
	255°	776
	188°	776
	—	1516
	287°	488
	238°	235

(Table continued)

TABLE LI (continued)

R	M.p.	Reference
	210°	236, 1667
	218	237
	184°, 212°	237, 747, 772, 773
	216° (dec.)	620, 772, 1668
	205°	620
	—	706
	—	707
	257°	747

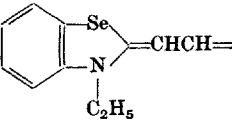
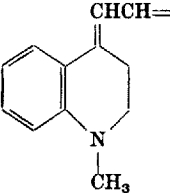
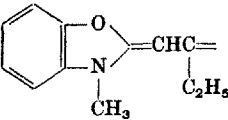
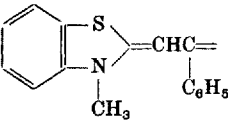
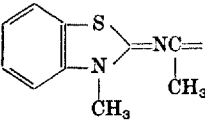
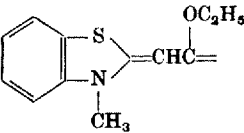
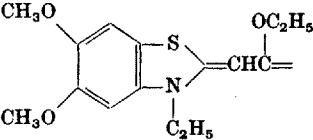
(Table continued)

TABLE LI (continued)

R	M.p.	Reference
	248°, 261°	747, 764, 772
	254°	747, 764, 765
	130° (dec.)	747
	183°	747, 772
	100°	747
	197°	747
	209°	747
	180°	747, 764

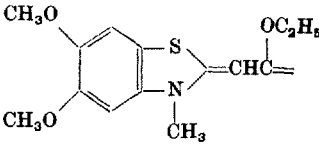
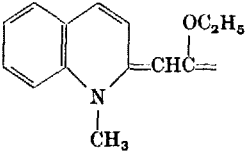
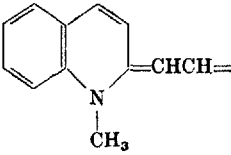
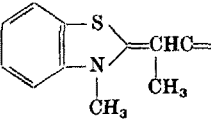
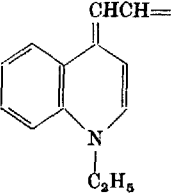
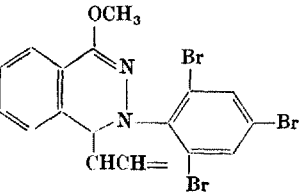
(Table continued)

TABLE LI (continued)

R	M.p.	Reference
	222°	747
	251°	747
	100°	764
	238°	764
	260°	764
	208°	771
	226°	771

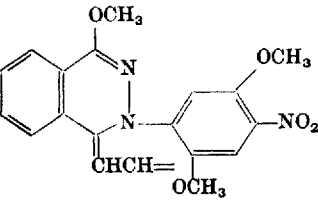
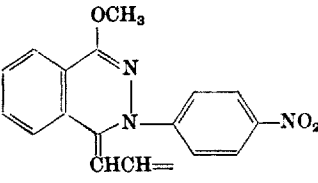
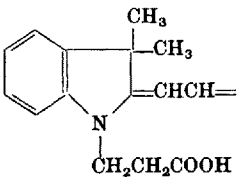
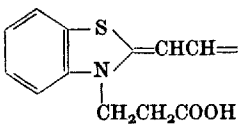
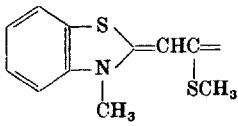
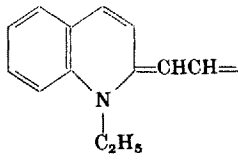
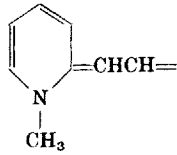
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TABLE LI (continued)

R	M.p.	Reference
	233°	771
	145° (dec.)	771
	90°, 171° (dec.)	772, 1668
	171°	772
	162°	1069
	224°	1110

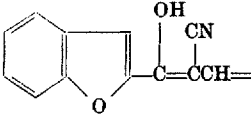
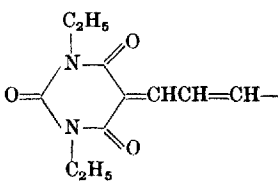
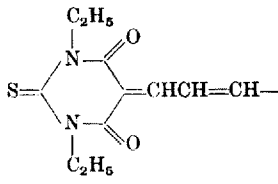
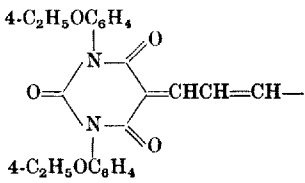
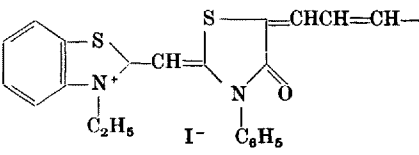
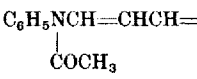
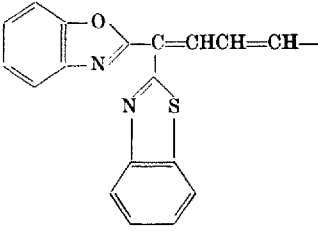
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TABLE LI (continued)

R	M.p.	Reference
	258°	1213
	258°	1214
	156°	1328
	239°	1328
	—	1516
	178° (dec.)	1668
	287° (dec.)	1670

(Table continued)

TABLE LI (continued)

R	M.p.	Reference
	141°	775
	248°	776
	165°	78
	194°	776
	—	1488
	—	30
	—	29, 30, 31

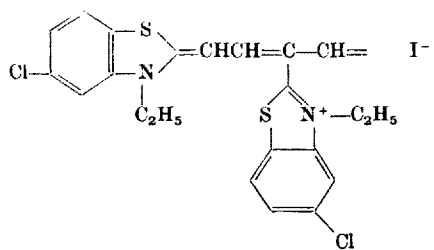
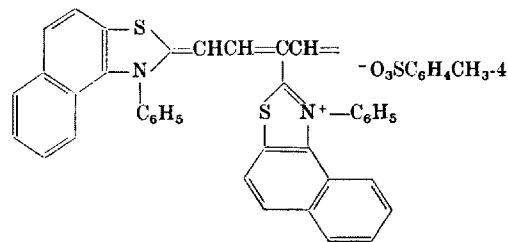
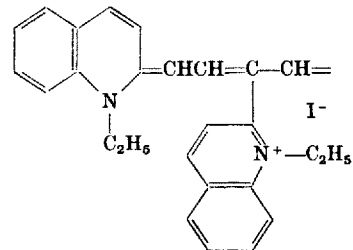
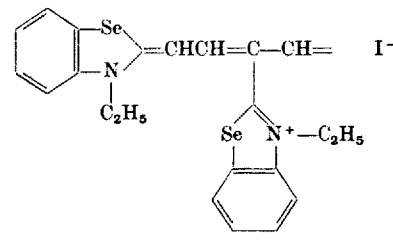
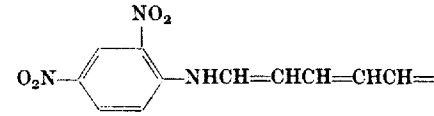
(Table continued)

TABLE LI (continued)

R	M.p.	Reference
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	219°	749
	293° (dec.)	241
	194°	755
	258°	755

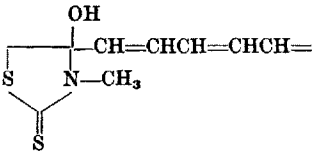
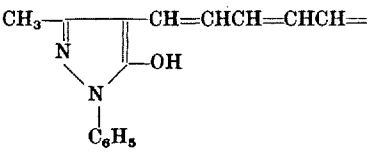
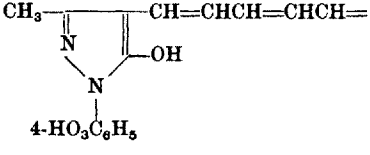
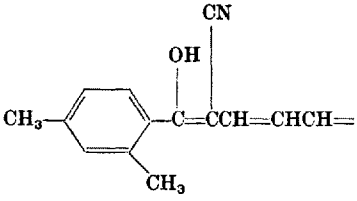
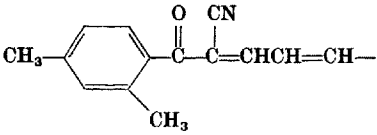
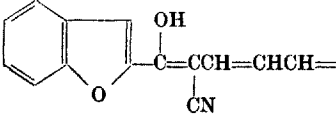
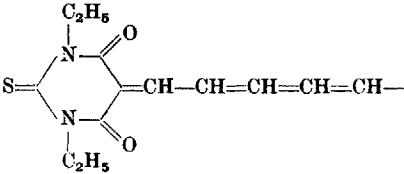
(Table continued)

TABLE LI (continued)

R	M.p.	Reference
	236°	755
	212°	755
	260°	755
	193°	755
	257°	382

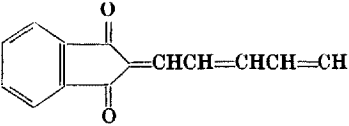
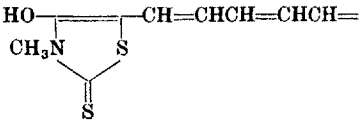
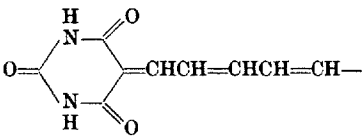
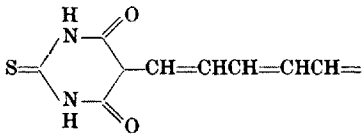
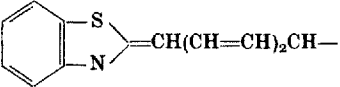
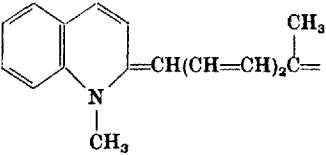
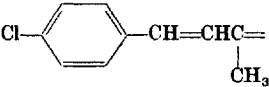
(Table continued)

TABLE LI (continued)

R	M.p.	Reference
	—	382
	—	382
	—	382
	139° (dec.)	775
	139°	775
	242°	775
	225°	776

(Table continued)

TABLE LI (*continued*)

R	M.p.	Reference
	169°	776
$\text{C}_6\text{H}_5\text{NCH}=\text{CHCH}=\text{CHCH}=\text{CH}-$ $\quad \quad \quad $ $\quad \quad \quad \text{COCH}_3$	—	776
$\text{C}_6\text{H}_5\text{NHCH}=\text{CHCH}=\text{CHCH}=\text{CH}-$	185°	1519
	230° (dec.)	1519
	242°	1472
	240° (dec.)	1519
	—	382
	215°	763
	154°	1129

(*Table continued*)

TABLE LI (continued)

R	M.p.	Reference
$(\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_4-\text{CH}=\text{CHC}(\text{CH}_3)=$	178°	1129
$\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}=\text{CHC}(\text{CH}_3)=$	171°	1129
$\text{C}_6\text{H}_4(\text{NO}_2)-\text{CH}=\text{CHC}(\text{CH}_3)=$	—	1129
$\text{C}_6\text{H}_4(\text{NO}_2)-\text{CH}=\text{CHC}(\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2)=$	150°	1129
$3\text{-HOC}_6\text{H}_4\text{CH}=\text{CHC}(\text{C}_6\text{H}_5)=$	77°	1129
$4\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{CH}=\text{CHC}(\text{C}_6\text{H}_5)=$	210°	1129
$4\text{-(C}_2\text{H}_5)_2\text{NC}_6\text{H}_4\text{CH}=\text{CHC}(\text{C}_6\text{H}_5)=$	167°	1129
$4\text{-ClC}_6\text{H}_4\text{CH}=\text{CHC}(\text{C}_6\text{H}_5)=$	146°	1129
$2\text{-NO}_2\text{C}_6\text{H}_4\text{CH}=\text{CHC}(\text{C}_6\text{H}_5)=$	194°	1129
$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}=\text{CHC}(\text{C}_6\text{H}_5)=$	218°	1129
$2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{CH}=\text{CHC}(\text{C}_6\text{H}_5)=$	155°	1129
$4\text{-HO-3-CH}_3\text{OC}_6\text{H}_3\text{CH}=\text{CHC}(\text{C}_6\text{H}_5)=$	220°	1129

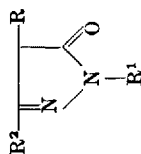
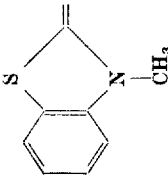
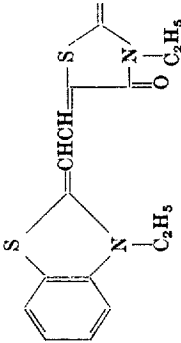
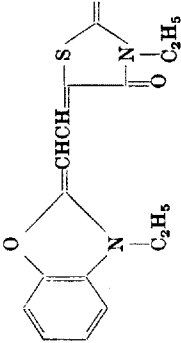


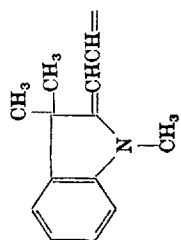
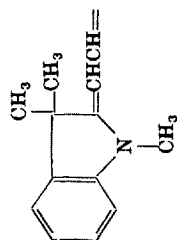
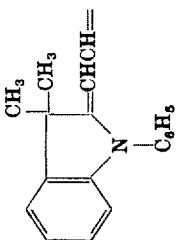
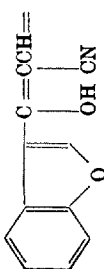
TABLE LII. 2-Pyrazolin-5-ones. Dyes

R	R ¹	R ²	M.p.	Reference
	4-NaO ₃ SC ₆ H ₄	CH ₃	—	703
	4-HO ₃ SC ₆ H ₄	CH ₃	311°	238, 242
	4-HO ₃ SC ₆ H ₄	CH ₃	325°	242

(Table continued)

TABLE LII (continued)

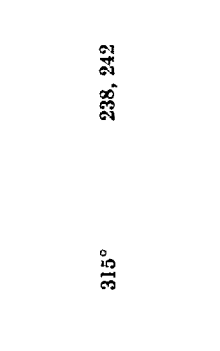
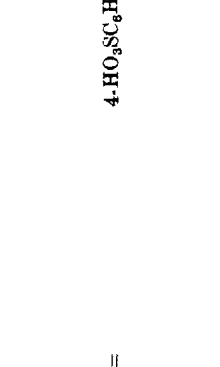
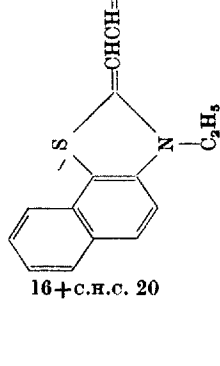
R	R ¹	R ²	M.P.	Reference
	4-HO ₃ SC ₆ H ₄	CH ₃	—	381
	4-HO ₃ SC ₆ H ₄	CH ₃	287°	238, 242
	4-HO ₃ CC ₆ H ₄	CH ₃	—	238
4-(CH ₃) ₂ NC ₆ H ₄ CH=	C ₆ H ₅	H	216°	237

	H	CH ₃	240°	772
	C ₆ H ₅	H	244°	237
	C ₆ H ₅	H	234°	237
	4-CH ₃ C ₆ H ₄	CH ₃	243°	775

(Table continued)

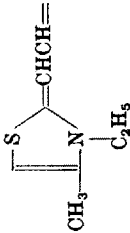
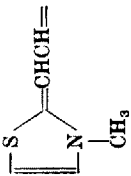
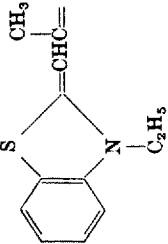
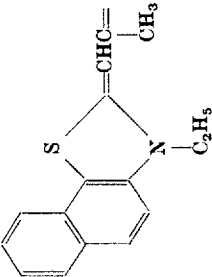
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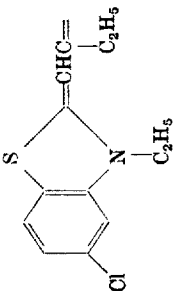
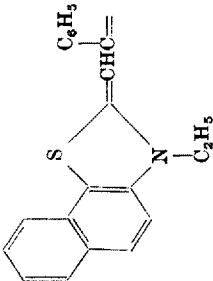
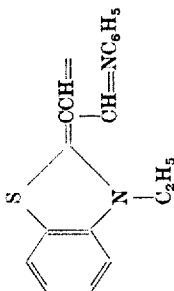
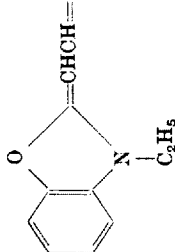
R	R ¹	R ²	M.p.	Reference
	4-HO ₃ SC ₆ H ₄	CH ₃	> 325°	236, 220
	4-HO ₃ SC ₆ H ₄	CH ₃	315°	238, 242
	4-HO ₃ SC ₆ H ₄	CH ₃	> 325°	238, 242
	4-HO ₃ SC ₆ H ₄	CH ₃	> 315°	238, 242

 16 + c.h.c. 20	4-HO₃SC₆H₄	CH₃	315°	238, 242
	4-HO₃SC₆H₄	CH₃	> 325°	238, 242
	4-HO₃SC₆H₄	CH₃	> 310°	238, 242
	4-HO₃SC₆H₄	CH₃	> 315°	238, 242

(Table continued)

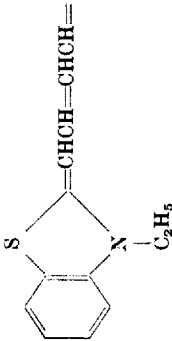
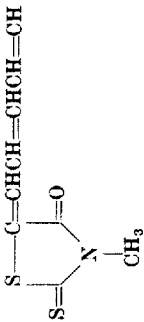
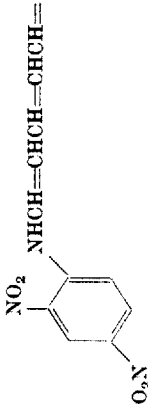
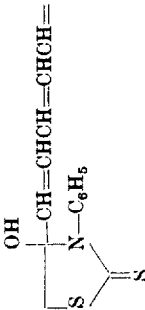
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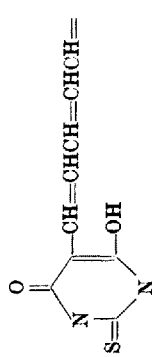
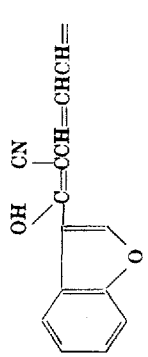
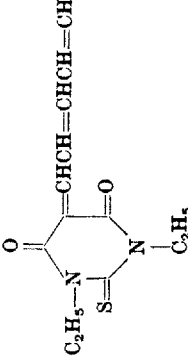
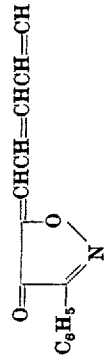
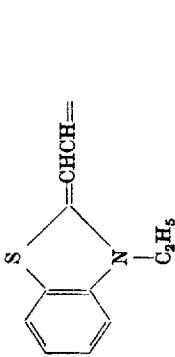
R	R ¹	R ²	M.p.	Reference
	4-HO ₃ SC ₆ H ₄	CH ₃	> 315°	238, 242
	4-HO ₃ SC ₆ H ₄	CH ₃	> 315°	238, 242
	4-HO ₃ SC ₆ H ₄	CH ₃	> 315°	238, 242
	4-HO ₃ SC ₆ H ₄	CH ₃	> 300°	238, 242

	4-HO ₃ SC ₆ H ₄	CH ₃	294°	238, 242
	4-HO ₃ SC ₆ H ₄	CH ₃	285°	238, 242
	4-HO ₃ SC ₆ H ₄	CH ₃	240°	620
	4-HO ₃ SC ₆ H ₄	CH ₃	—	1301

(Table continued)

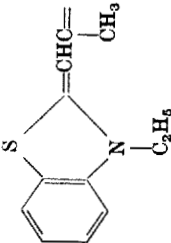
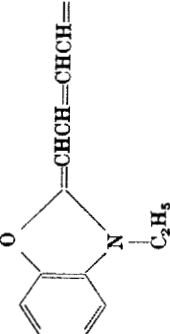
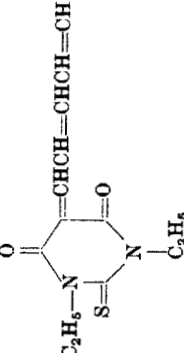
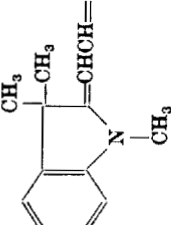
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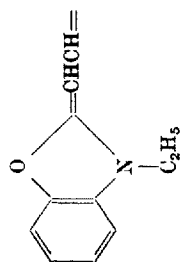
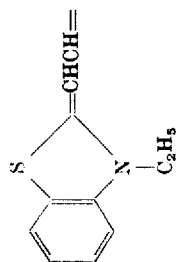
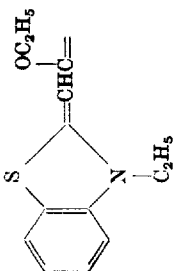
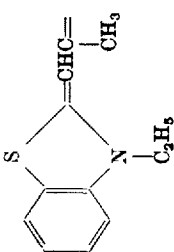
R	R ¹	R ²	M.p.	Reference
	4-HO ₃ SC ₆ H ₄	CH ₃	279°	238, 242
	4-HO ₃ SC ₆ H ₄	CH ₃	—	1519
	4-HO ₃ SC ₆ H ₄	CH ₃	200°	382
	4-KO ₃ SC ₆ H ₄	CH ₃	—	382

	4-KO ₃ SC ₆ H ₄	CH ₃	—	382
	4-HO ₃ SC ₆ H ₄	CH ₃	240°	775
	4-HO ₃ SC ₆ H ₄	CH ₃	196°	776
	4-HO ₃ SC ₆ H ₄	CH ₃	188°	776
	4-HOOC ₆ H ₄	CH ₃	> 315°	238, 242

(Table continued)

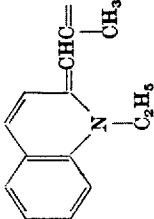
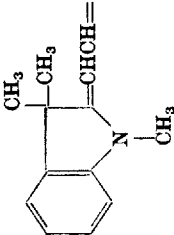
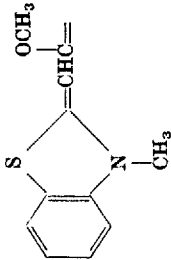
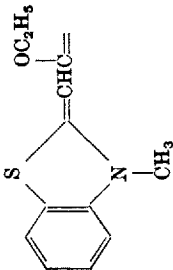
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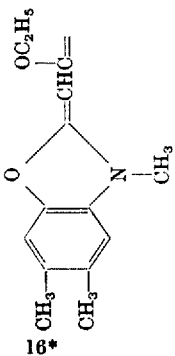
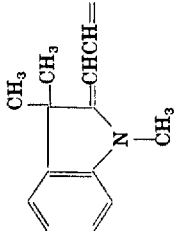
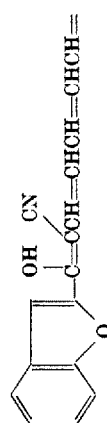
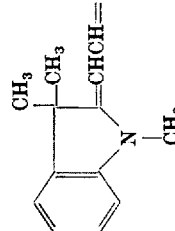
R	R ¹	R ²	M.p.	Reference
	4-HOOC ₆ H ₄	CH ₃	289°	238, 242
	4-HOOC ₆ H ₄	CH ₃	232°	238
	4-HOOC ₆ H ₄	C ₁₅ H ₃₁	184°	776
	2-C ₁₀ H ₇	CH ₃	245°	747

	$4\text{-HO}_3\text{S-1-C}_{10}\text{H}_6$	CH_3	—	1301
	$4\text{-KO}_3\text{S-1-C}_{10}\text{H}_6$	CH_3	$> 310^\circ$	238, 242
	C_6H_5	C_6H_5	135°	771
	C_6H_5		250°	764

(Table continued)

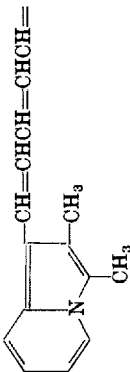
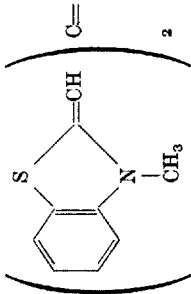
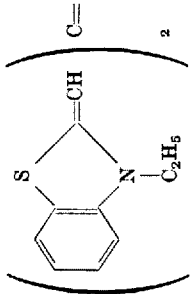
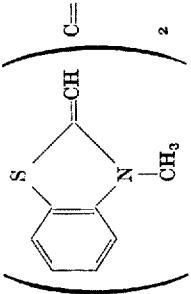
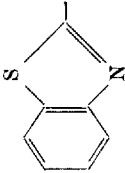
TABLE LII (continued)

R	R ¹	R ²	M.P.	Reference
	C ₆ H ₅		> 185°	764
	C ₆ H ₅		180°	747
	C ₆ H ₅		183°	771
	C ₆ H ₅		190°	771

	C_6H_5		175°	771
	$2 \cdot C_{10}H_7$		212°	747
	C_6H_5	$HOOCCH_2$	153°	775
	C_6H_5	C_2H_5OOC	190°	772
	$4 \cdot HOOC C_6H_4$	$C_{13}H_{31}$	—	1329

(Table continued)

TABLE LII (continued)

R	R ¹	R ²	M.P.	Reference
	4-HOCC ₆ H ₄	C ₁₃ H ₃₁	—	1329
	C ₆ H ₅	H	175°	241
	C ₆ H ₅	H	249°	241
		CH ₃	333°	241

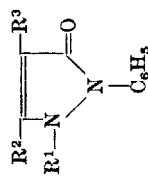
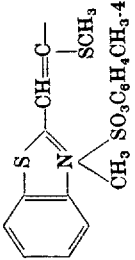
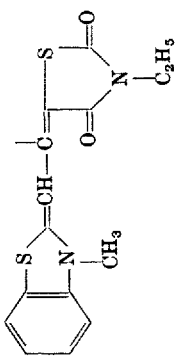
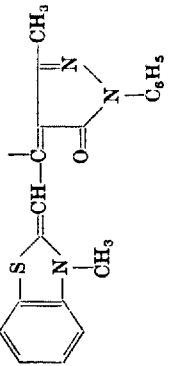
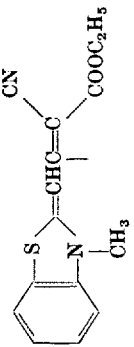


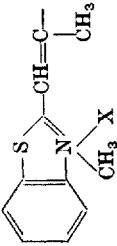
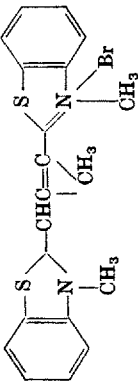
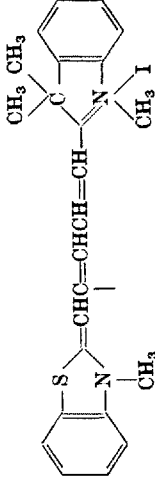
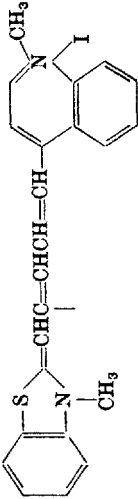
TABLE LIII. 3-Pyrazolin-5-ones. Dyes

R ¹	R ²	R ³	M.p.	Reference
CH ₃	H		247° (dec.)	765
CH ₃	H		—	765
CH ₃			224° (dec.)	765
CH ₃			208°	1516

(Table continued)

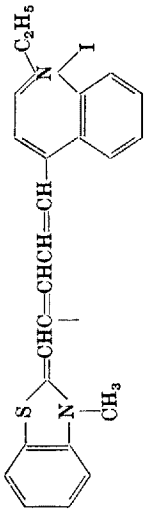
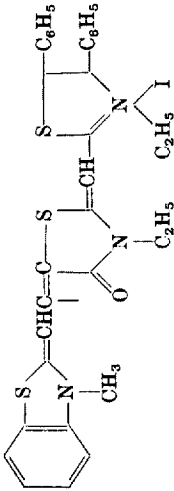
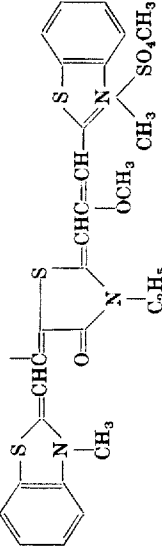
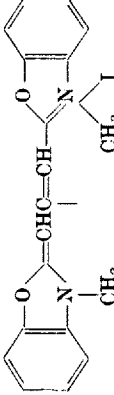
TABLE LIII (continued)

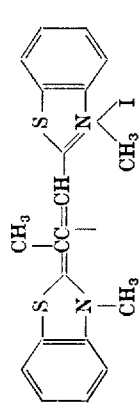
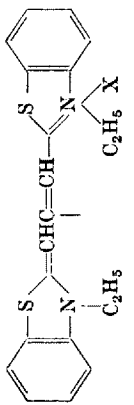
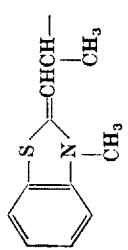
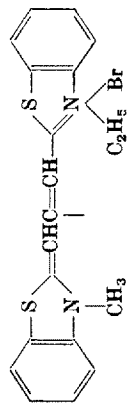
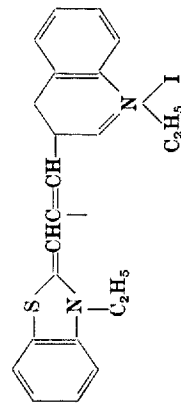
R ¹	R ²	R ³	M.p.	Reference
CH ₃	CH ₃		—	1517
CH ₃	CH ₃		259°	1517
CH ₃	CH ₃		208°	1517
CH ₃	CH ₃		140°	1517

CH ₃	CH ₃		—	1516
CH ₃	CH ₃		230° (dec.)	765
CH ₃	CH ₃		194° (dec.)	765
CH ₃	CH ₃		248° (dec.)	765
CH ₃	CH ₃		205°	765

(Table continued)

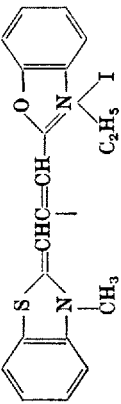
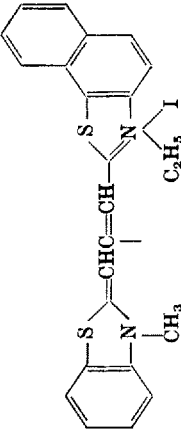
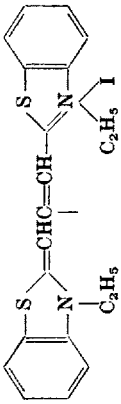
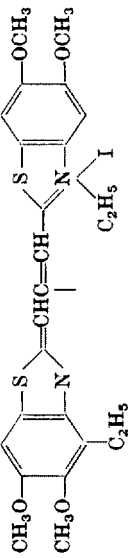
TABLE LIII (continued)

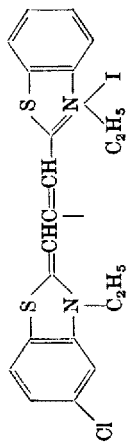
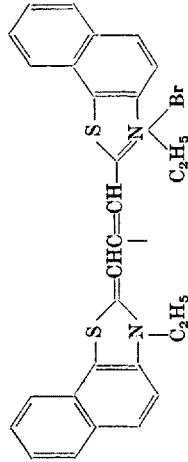
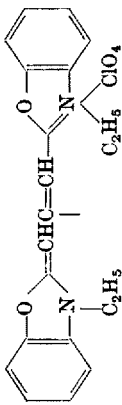
R ¹	R ²	R ³	M.p.	Reference
CH ₃	CH ₃		196° (dec.)	765
CH ₃	CH ₃		286°	1517
CH ₃	CH ₃		260°	1517
CH ₃	CH ₃		270° (dec.)	765

CH_3	CH_3		—	765
C_2H_5	CH_3		250°	1516
C_2H_5	CH_3		—	1516
C_2H_5	CH_3		280° (dec.)	765
C_2H_5	CH_3		197° (dec.)	765

(Table continued)

TABLE LIII (continued)

R ¹	R ²	R ³	M. p.	Reference
C ₂ H ₅	CH ₃		198°	765
C ₂ H ₅	CH ₃		281° (dec.)	765
C ₂ H ₅	CH ₃		248° (dec.)	765
C ₂ H ₅	CH ₃		285° (dec.)	765

C_2H_5	CH_3		233°	765
C_2H_5	CH_3		> 300°	765
C_2H_5	CH_3		285° (dec.)	765

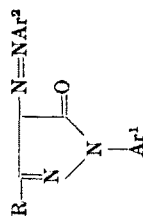


TABLE LIV. 4-Arylaazo-3-pyrazolin-5-ones. Dyes

Name	R	Ar ¹	Ar ²
Tartrazine	NaOOC	4-NaO ₃ SC ₆ H ₄	4-NaO ₃ SC ₆ H ₄
Kiton Yellow S	HOOC	4-HO ₃ SC ₆ H ₄	C ₆ H ₅
Wool Silk Yellow G	H ₅ C ₂ OOC	4-NaO ₃ SC ₆ H ₄	2-ClC ₆ H ₄
Fast Light Yellow G	CH ₃	4-NaO ₃ SC ₆ H ₄	C ₆ H ₅
Saturn Yellow GG	H ₅ C ₂ OOC	2-Cl-4-NaO ₃ S-6-CH ₃ C ₆ H ₂	2-CH ₃ -3-ClC ₆ H ₃
Wool Fast Yellow 3GL	CH ₃	2-Cl-5-NaO ₃ SC ₆ H ₃	C ₆ H ₅
Xylene Light Yellow	CH ₃	2,5-Cl ₂ -4-NaO ₃ SC ₆ H ₂	4-NaO ₃ SC ₆ H ₄
Normal Yellow 3GL	HOOC	4-HO ₃ SC ₆ H ₄	2,4-(CH ₃) ₂ -5-HO ₃ SC ₆ H ₂
Pyrazole Orange	NaOOC	4-NaO ₃ SC ₆ H ₄	4-[4-(2-NaOOC-4-HOC ₆ H ₃ N=N)C ₆ H ₄]C ₆ H ₄
Acid Alizarin Bordeaux B	H ₂ NOC	C ₆ H ₅	2-HO-3-NaO ₃ S-5-ClC ₆ H ₂
Anthralan Yellow G	CH ₃	2-CH ₃ -4-NaO ₃ S-6-ClC ₆ H ₂	4-NaO ₃ SC ₆ H ₄
Eriochrome Red B	CH ₃	CH ₃	2-HO-4-NaO ₃ S-1-C ₁₀ H ₅ C ₂ H ₅
Supramine Yellow 3G	CH ₃	2-Cl-4-NaO ₃ SC ₆ H ₃	2-CH ₃ -5-(CH ₃ CON)C ₆ H ₃
Polar Yellow 5G	CH ₃	3-NaO ₃ S-4-ClC ₆ H ₃	4-(4-CH ₃ C ₆ H ₄ SO ₂ O)C ₆ H ₄
Diamond Red G	CH ₃	4,8-(NaO ₃ S) ₂ -2-C ₁₀ H ₅	2-HO-4-NO ₂ C ₆ H ₄
Acid Alizarin Flavin GF	CH ₃	2-HO-3-NaOOC-5-NaO ₃ SC ₆ H ₂	2-NaOOC ₆ H ₄
Metachrome Red 5G	CH ₃	C ₆ H ₅	2-HO-3-HO ₃ S-5-ClC ₆ H ₂
Pigment Fast Yellow G	CH ₃	C ₆ H ₅	2-HOOC-5-HO ₃ SC ₆ H ₃

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