

# THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS



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**FIVE-MEMBERED HETEROCYCLIC COMPOUNDS  
WITH NITROGEN AND SULFUR  
OR NITROGEN, SULFUR, AND OXYGEN  
(EXCEPT THIAZOLE)**

**L. L. BAMBAS**

*Parke, Davis and Company, Detroit, Michigan*

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## INTRODUCTION TO THE SERIES

### **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.

*Research Laboratories  
Eastman Kodak Company  
Rochester, New York*

ARNOLD WEISSBERGER

## Preface

The purpose of this book is the presentation of a complete and critical review of the literature on five-membered heterocyclic compounds containing nitrogen and sulfur, or nitrogen, sulfur and oxygen, as members of the ring. Spot checks and cross references to related substances have revealed that occasionally compounds have been omitted; the latter, however, comprise a very small percentage of the whole work.

While a reviewer should be an authority on the subject which he treats, this criterion can hardly be satisfied in a field as broad as that of this book. Therefore, the author has described the historical development of the chemistry of these compounds and usually followed this presentation by a discussion giving his own point of view, a résumé, or his evaluation of the subject. Thus, it behooves the reader to be critical rather than passive in accepting the interpretation of the facts.

In such a treatise, the question of nomenclature arises to plague both author and reader. In general, the systems employed by *Chemical Abstracts* and *Ring Index* are used, with occasional modifications for the sake of consistency. Unfortunately, such modifications add confusion to chaos. To assist the reader, structural formulas are given whenever feasible. In general, the index follows *Chemical Abstracts* as regards nomenclature, irrespective of the manner in which the chemical name appears in the text; an attempt has also been made to cross index the minor variations from the *Chemical Abstracts* nomenclature.

The contents of this book are divided into three unrelated sections: (1) the thiadiazoles; (2) the five-membered rings containing nitrogen, sulfur and oxygen; and (3) the isothiazoles. Each section is then subdivided into small closely related classes of compounds. For instance, the 2-amino-1,3,4-thiadiazoles constitute such a small class of compounds while the 2,5-diamino-1,3,4-thiadiazoles are included in another class. This type of grouping assists in the understanding of these compounds and also in the location of a particular compound.

The author wishes to acknowledge with sincere thanks the cooperation and assistance of the following members of the staff at Parke, Davis and Company: Dr. L. A. Sweet, Director of Research and Development;

Dr. G. Rieveschl, Jr., Director of Chemical Research; Dr. George W. Moersch, Dr. J. Controulis, Dr. Eldon M. Jones, Mr. Leonard Doub, Dr. J. M. Vandebelt, Miss Lenore Schroeder, Mrs. Roberta Waddell, Mrs. Mary Martina, Mrs. Margaret Petoklep, and Miss Stella Albert and her library staff.

*Detroit, Michigan*  
*April, 1952*

L. L. BAMBAS

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## **PART I**

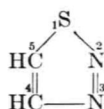
### **Thiadiazoles, Their Derivatives and Selenium Analogs**



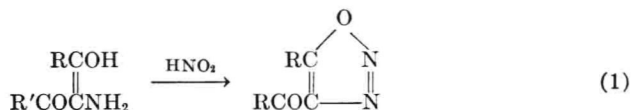
# Derivatives of the 1,2,3-Thiadiazoles and Their Selenium Analogs

## 1,2,3-Thiadiazoles

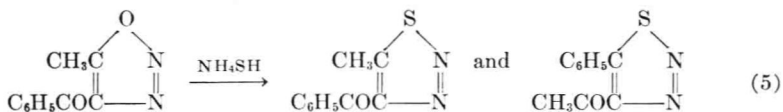
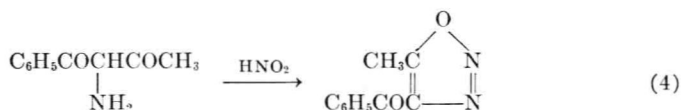
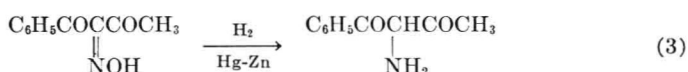
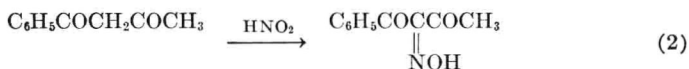
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Wolff and his co-workers<sup>1</sup> studied the reactions of aliphatic diazoanhydrides, or 1,2,3-oxadiazoles. The diazoanhydrides, prepared by diazotizing  $\alpha$ -aminoketones (1), when reacted with ammonium hydrosulfide



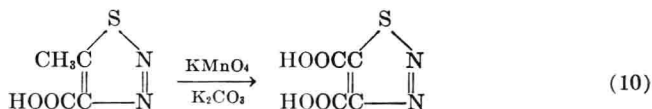
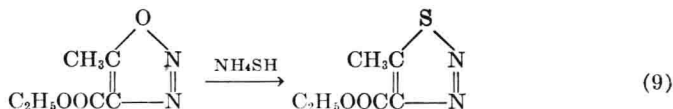
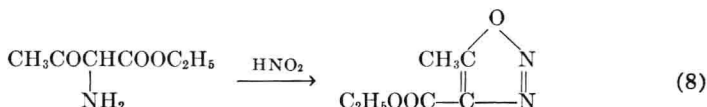
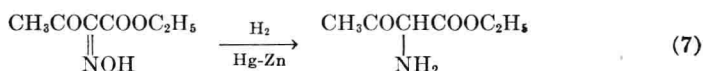
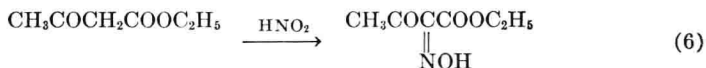
gave disubstituted 1,2,3-thiadiazoles. Wolff's synthesis proceeded as shown by equations (2-5). The two isomeric 1,2,3-thiadiazoles were readily separated, since 4-benzoyl-5-methyl-1,2,3-thiadiazole formed a mercuric chloride double salt while the other isomer did not form this complex.



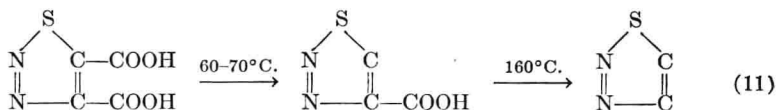
<sup>1</sup> Wolff, *Ann.*, **325**, 129 (1902).

Dimroth<sup>2</sup> and Staudinger<sup>3</sup> felt that the formation of the two isomers cast some doubt as to the structure of the diazoanhydride. They believed that the diazoanhydrides were true aliphatic diazo compounds which were more stable than the usual aliphatic diazo compounds.

Wolff<sup>4</sup> continued his studies with the preparation of a number of derivatives of 1,2,3-thiadiazole. Ethyl acetoacetate was the starting material in a number of these syntheses (6-9). Oxidation of 4-carboxy-5-methyl-1,2,3-thiadiazole gave 4,5-dicarboxy-1,2,3-thiadiazole (10). This compound was



also prepared by starting with ethyl oxalacetate. The carboxyl group in the 5-position readily ruptured from the 1,2,3-thiadiazole nucleus at 60 to 70°C. The carboxyl group in the 4-position split off when the temperature was raised to 160°C. or higher (11). The 5-methyl and 5-phenyl-1,2,3-thiadiazoles also were prepared by this synthesis.



<sup>2</sup> Dimroth, *Ann.*, **373**, 339 (1910).

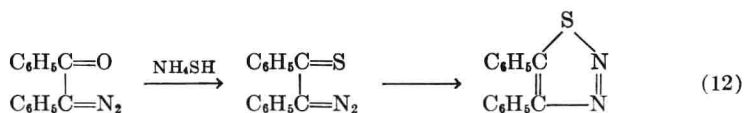
<sup>3</sup> Staudinger, *Helv. Chim. Acta*, **4**, 239 (1921).

<sup>4</sup> Wolff, *Ann.*, **333**, 1 (1904).

The 1,2,3-thiadiazoles were much more stable than the 1,2,3-oxadiazoles. Strong mineral acids caused very little decomposition and hot sodium hydroxide and alcoholic potassium hydroxide decomposed these compounds very slowly with the formation of hydrogen sulfide. 1,2,3-Thiadiazole decomposed in sodium hydroxide at 90–95°C. with the brisk evolution of a gas, while the homologs and the carboxy acids decomposed to a very slight extent.

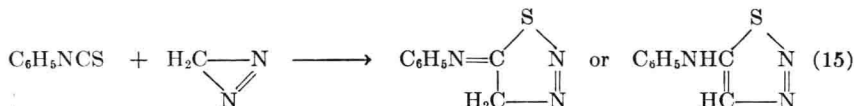
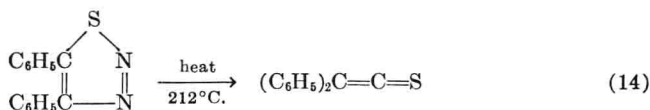
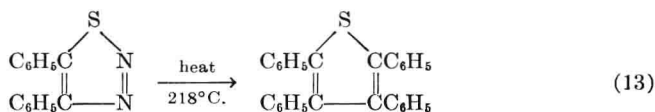
1,2,3-Thiadiazole and its homologs are very weak bases. They form hydrochlorides with concentrated hydrochloric acid which are hydrolyzed in water. They react with methyl iodide at elevated temperatures to give quaternary salts.

Staudinger and Seigwart<sup>5</sup> found that phenylbenzoyldiazomethane and ammonium hydrosulfide give 4,5-diphenyl-1,2,3-thiadiazole (12), which



when heated in naphthalene at 218°C. produces tetraphenylthiophene. At a slightly lower temperature (212°C.) an intermediate, believed to be diphenyl methylene thioketone, was obtained (13,14).

Pechmann and Nold<sup>6</sup> allowed diazomethane to react with phenyl isothiocyanate and obtained 5-anilino-1,2,3-thiadiazole (15). This compound reacted with nitrous acid, acetic anhydride, and benzoyl chloride to give the monosubstituted products.



<sup>5</sup> Staudinger and Siegwart, *Ber.*, **49**, 1918 (1916).

<sup>6</sup> Pechmann and Nold, *Ber.*, **29**, 2588 (1896).

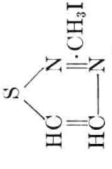
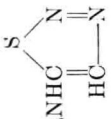
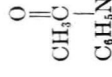
TABLE I. Preparation of the 1,2,3-Thiadiazoles

| No. | Name                                 | Ref. | Preparation                                                                                                                                                                                                                                                                                  | Structure                                                                                                                                                                                                                                                                                    | Solubility                                 | M.p., °C.                       |
|-----|--------------------------------------|------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------|---------------------------------|
| 1   | 1,2,3-Thiadiazole                    | 1    | $  \begin{array}{c}  \text{S} \\  \diagup \quad \diagdown \\  \text{HC} \quad \text{N} \\  \parallel \quad \parallel \\  \text{HOOC} \text{---} \text{C} \text{---} \text{N}  \end{array}  $                                                                                                 | $  \begin{array}{c}  \text{S} \\  \diagup \quad \diagdown \\  \text{HC} \quad \text{N} \\  \parallel \quad \parallel \\  \text{HC} \quad \text{C} \text{---} \text{N}  \end{array}  $                                                                                                        | very sol. in alc. and ether, sol. in water | liquid, boils 83-5 at 60 mm. Hg |
| 2   | 5-Methyl-1,2,3-thiadiazole           | 1    | $  \begin{array}{c}  \text{S} \\  \diagup \quad \diagdown \\  \text{CH}_3\text{C} \quad \text{N} \\  \parallel \quad \parallel \\  \text{HOOC} \text{---} \text{C} \text{---} \text{N}  \end{array}  $                                                                                       | $  \begin{array}{c}  \text{S} \\  \diagup \quad \diagdown \\  \text{CH}_3\text{C} \quad \text{N} \\  \parallel \quad \parallel \\  \text{H} \text{---} \text{C} \text{---} \text{N}  \end{array}  $                                                                                          | very sol. in alc. and ether, sol. in water | liquid 91 at 38 mm. Hg          |
| 3   | 5-Phenyl-1,2,3-thiadiazole           | 1    | $  \begin{array}{c}  \text{S} \\  \diagup \quad \diagdown \\  \text{C}_6\text{H}_5\text{C} \quad \text{N} \\  \parallel \quad \parallel \\  \text{HOOC} \text{---} \text{C} \text{---} \text{N}  \end{array}  $                                                                              | $  \begin{array}{c}  \text{S} \\  \diagup \quad \diagdown \\  \text{C}_6\text{H}_5\text{C} \quad \text{N} \\  \parallel \quad \parallel \\  \text{H} \text{---} \text{C} \text{---} \text{N}  \end{array}  $                                                                                 | sol. in ether, alc., and chloroform        | 53-3.5                          |
| 4   | 4,5-Diphenyl-1,2,3-thiadiazole       | 2    | $  \begin{array}{c}  \text{S} \\  \diagup \quad \diagdown \\  \text{C}_6\text{H}_5\text{C} \quad \text{N} \\  \parallel \quad \parallel \\  \text{C}_6\text{H}_5\text{C} \text{---} \text{C} \text{---} \text{N} \\  \parallel \quad \parallel \\  \text{O} \quad \text{N}_2  \end{array}  $ | $  \begin{array}{c}  \text{S} \\  \diagup \quad \diagdown \\  \text{C}_6\text{H}_5\text{C} \quad \text{N} \\  \parallel \quad \parallel \\  \text{C}_6\text{H}_5\text{C} \text{---} \text{C} \text{---} \text{N} \\  \parallel \quad \parallel \\  \text{O} \quad \text{N}_2  \end{array}  $ | sol. in ether                              | 93-4                            |
| 5   | 4-Carboxy-1,2,3-thiadiazole          | 1    | $  \begin{array}{c}  \text{S} \\  \diagup \quad \diagdown \\  \text{HOOC} \quad \text{N} \\  \parallel \quad \parallel \\  \text{HOOC} \text{---} \text{C} \text{---} \text{N}  \end{array}  $                                                                                               | $  \begin{array}{c}  \text{S} \\  \diagup \quad \diagdown \\  \text{HC} \quad \text{N} \\  \parallel \quad \parallel \\  \text{HOOC} \text{---} \text{C} \text{---} \text{N}  \end{array}  $                                                                                                 | sol. in alc. and hot water                 | 228 dec.                        |
| 6   | 4-Carboxy-5-methyl-1,2,3-thiadiazole | 1    | $  \begin{array}{c}  \text{S} \\  \diagup \quad \diagdown \\  \text{CH}_3\text{C} \quad \text{N} \\  \parallel \quad \parallel \\  \text{HOOC} \text{---} \text{C} \text{---} \text{N}  \end{array}  $                                                                                       | $  \begin{array}{c}  \text{S} \\  \diagup \quad \diagdown \\  \text{CH}_3\text{C} \quad \text{N} \\  \parallel \quad \parallel \\  \text{HOOC} \text{---} \text{C} \text{---} \text{N}  \end{array}  $                                                                                       | sol. in alc.                               | 35                              |
| 7   | 4-Carboxy-5-methyl-1,2,3-thiadiazole | 1    | saponification of 6 with 20% NaOH                                                                                                                                                                                                                                                            | $  \begin{array}{c}  \text{S} \\  \diagup \quad \diagdown \\  \text{CH}_3\text{C} \quad \text{N} \\  \parallel \quad \parallel \\  \text{C}_2\text{H}_5\text{OOC} \text{---} \text{C} \text{---} \text{N}  \end{array}  $                                                                    | sol. in water                              | 113                             |

| No. | Name                                 | Ref. | Preparation                                                     | Structure | Solubility                                                | M.p., °C. |
|-----|--------------------------------------|------|-----------------------------------------------------------------|-----------|-----------------------------------------------------------|-----------|
| 8   | 4-Carboxy-5-phenyl-1,2,3-thiadiazole | 1    | diazohydrate of ethyl benzoylacetate<br><br>→                   |           | sol. in alc. and ether                                    | 42        |
| 9   | 4-Carboxy-5-phenyl-1,2,3-thiadiazole | 1    | saponification of 8 with alkali                                 |           | sol. in water                                             | 157 dec.  |
| 10  | 4,5-Dicarboxy-1,2,3-thiadiazole      | 1    | <br>diazohydrate of ethyl oxalacetate + NH <sub>4</sub> SH<br>→ |           | sol. in alc.                                              | 98 dec.   |
| 11  | 4-Benzoyl-5-methyl-1,2,3-thiadiazole | 3    | diazohydrate of benzoylacetone<br>+ NH <sub>4</sub> SH<br>→     |           | sol. in hot alc., forms HgCl <sub>2</sub> complex         | 43        |
| 12  | 4-Methyl-5-benzoyl-1,2,3-thiadiazole | 3    | same as 11                                                      |           | sol. in hot alc., does not form HgCl <sub>2</sub> complex | 70        |
| 13  | 5-Methyl-4-acetyl-1,2,3-thiadiazole  | 3    | diazohydrate of acetylacetone<br>NH <sub>4</sub> SH<br>→        |           | sol. in alc. and ether                                    |           |

(Table continued)

TABLE I. Preparation of the 1,2,3-Thiadiazoles (Continued)

| No. | Name                                       | Ref. | Preparation                                                                         |                                           | Structure                                                                         | Solubility                                        | M.p., °C.  |
|-----|--------------------------------------------|------|-------------------------------------------------------------------------------------|-------------------------------------------|-----------------------------------------------------------------------------------|---------------------------------------------------|------------|
| 14  | 1,2,3-Thiadiazolium methyl iodide          | 1    | compound 1 + CH <sub>3</sub> I                                                      | $\xrightarrow{110-120^{\circ}\text{C.}}$  |  | sol. in 6-7 parts water, difficultly sol. in alc. | 220-2 dec. |
| 15  | 5-Methyl-1,2,3-thiadiazolium methyl iodide | 1    | compound 2 + CH <sub>3</sub> I                                                      | $\xrightarrow{\text{reflux in methanol}}$ | exact structure unknown                                                           |                                                   |            |
| 16  | 5-Phenyl-1,2,3-thiadiazolium methyl iodide | 1    | compound 3 + CH <sub>3</sub> I                                                      | $\xrightarrow{110-120^{\circ}\text{C.}}$  | see 14                                                                            | very sol. in water                                | 76-7       |
| 17  | 5-Anilino-1,2,3-thiadiazole                | 4    | $\text{C}_6\text{H}_5\text{NCS} + \text{H}_2\text{C}=\text{N}-\text{N}=\text{CH}_2$ | $\longrightarrow$                         |  | sol. in water                                     | 158        |
| 18  | Trinitro derivative of 17                  | 4    | compound 17 + HNO <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub>                     | $\longrightarrow$                         | structure unknown                                                                 | sol. in warm alc., insol. in water                | 173        |
| 19  | 5-Acetanilido-1,2,3-thiadiazole            | 4    | compound 17 + acetic anhydride                                                      | $\longrightarrow$                         |  | —                                                 | 221        |
| 20  | 5-Benzanilido-1,2,3-thiadiazole            | 4    | compound 17 + benzoyl chloride                                                      | $\longrightarrow$                         | see 19                                                                            | sol. in dil. alc.                                 | 157        |
| 21  | 5-N-Nitrosoanilino-1,2,3-thiadiazole       | 4    | compound 17 + HNO <sub>2</sub>                                                      | $\longrightarrow$                         | see 19                                                                            | sol. in dil. alc.                                 | 98         |

<sup>1</sup> Wolff, *Ann.*, **333**, 1 (1904).<sup>2</sup> Staudinger and Siegart, *Ber.*, **49**, 1918 (1916).<sup>3</sup> Wolff, *Ann.*, **325**, 129 (1902).<sup>4</sup> Pechmann and Nold, *Ber.*, **29**, 2588 (1896).