posite is true. In these compounds the preferred form is the exo double bond structures.

It is therefore clear that no simple generalization can hope to predict the relative stabilities of exo *versus* endo double bonds *within any single ring system.*[6] The original generalization was not intended to handle such problems.

The generalization does predict that both the rate and the equilibrium for the reaction of a nucleophilic reagent, such as cyanide ion, should be favored for cyclohexanone as compared to cyclopentanone. It likewise predicts that the amount of enol present in the ketone at equilibrium should be greater for cyclohexanone as compared to cyclopentanone. Both predictions are supported by the available experimental data.

The following revised generalization is offered in the hope that it may avoid some of the misunderstandings which have resulted from the version in its original form.

Double bonds which are exo to a 5-ring are less reactive and more stable (relative to the saturated derivatives) than related double bonds which are exo to a 6-ring. Reactions which involve the formation or retention of an exo double bond in a 5-ring derivative will be favored over corresponding reactions which involve the formation or retention of an exo double bond in a 6-ring derivative. Reactions which involve the loss of an exo double bond will be favored in the 6-ring as compared to the corresponding 5-ring derivative.

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[6] On this basis Brother Fleck's suggestion that "reactions will proceed in such a manner as to avoid the formation or retention of an exo double bond in a 6-ring system" cannot be applied generally since it would predict the preferred existence of cyclohexanone in the enol form.

Infrared Spectrum of the So-called 5-Amino-1,2,3,4-thiatriazole

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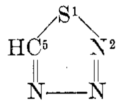
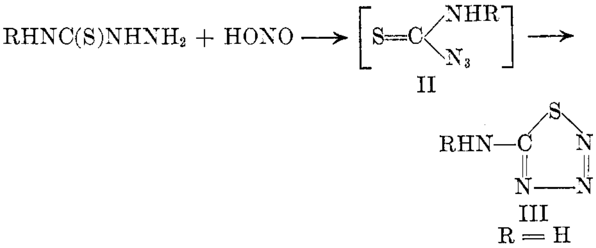
The so-called 1,2,3,4-thiatriazole ring,[1] I, has



I

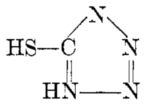
received practically no attention in the literature since Freund and Schander,[2] in 1896, reported on the basis of degradative evidence, that the product of the reaction of one mole of nitrous acid with thiosemicarbazide had the structure now designated as 5-amino-1,2,3,4-thiatriazole, III:



II

III
R = H

While the data presented[2] clearly exclude the isomeric tetrazole structure, IV, it is not as unequivocal in differentiating the acyclic thiocarbamyl azide, II, and the isomeric thiatriazole ring, III.



IV

On evidence also not unequivocal, Olivari-Mandala[3] suggested that the product of Freund and Schander,[2] III, was identical to the reaction products of isothiocyanates with hydrazoic acid to which he gave the structure II:

$$RNCS + HN_3 \longrightarrow II$$

The only additional work which contributes to the structure of the thiosemicarbazide–nitrous acid reaction product is by Sahasrabudhey and Krall[4] in 1941. A gasometric study revealed that thiosemicarbazide absorbs one molar proportion of nitrous acid in the presence of N-hydrochloric acid, without gas evolution. They accepted structure III without further evidence.

The two key features upon which Freund and Schander[2] based their selection of III were: (1) its decomposition in aqueous solution with precipitation of sulfur and evolution of nitrogen (or at least of a gas identified merely as inert) and (2) the lack of hydrazoic acid among the degradation products. This latter point, however, can be refuted from the experimental data of Freund and Schander,[2] since in one of their experiments on treatment of III (or II[?]) with aqueous sodium hydroxide and subsequent acidification, they reported "an odor of hydrazoic acid," unfortunately

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[1] Nomenclature and ring number system from A. M. Patterson and L. T. Capell, *The Ring Index,* Reinhold Publishing Corp., New York, 1940.

[2] M. Freund and A. Schander, *Ber.,* **29,** 2500 (1896).

[3] E. Olivari-Mandala, *Gazz. chim. ital.,* **44** (1), 670 (1914).

[4] Sahasrabudhey and Krall, *J. Indian Chem. Soc.,* **13,** 226 (1941).

not identified any further. While it is true that the hydrazoic acid could arise by alkaline ring opening of III to II, the data nevertheless, indicate that structure II cannot be precluded from consideration.

Accordingly, the simplest and most decisive method of making a choice between II and III would be to examine the infrared spectrum of the thiosemicarbazide–nitrous acid product for the presence of the azido group, since this latter group, if present in a molecule, is easily detected by such means.[5] The infrared spectrum of a specimen, having a nitrogen and sulfur content corresponding to the theoretical of II or III, showed no absorbance in the 4.5- to 5-micron range, the range characteristic of the azido group.[5] Thus, structure II can be eliminated from consideration.[6] This datum, however, is not offered as complete proof of structure III, although the compound can now provisionally be assigned this structure.

During the course of this study on the preparation of III it was found advantageous to control the thiosemicarbazide–nitrous acid ratio by adding a standard solution of sodium nitrite from a buret to a cooled aqueous solution of thiosemicarbazide containing one equivalent of hydrochloric acid and removing the product as it precipitates. The crude product, so obtained, is substantially pure, and is not improved by further recrystallization.

EXPERIMENTAL[7,8]

5-Amino-1,2,3,4-thiatriazole. To an ice cold solution of 20 g. (0.21 mole) of thiosemicarbazide in 95 cc. of 2.2*N* hydrochloric acid (0.21 mole), was added from a buret, with stirring, three 50-ml. portions of sodium nitrite solution containing a total of 14.7 g. (0.21 mole) of sodium nitrite. After each 50-ml. portion was added the product was collected and washed with 10 ml. of ice water, the filtrate being returned to the reaction vessel. For analysis, the crude product was vacuum dried. Yield 18.4 g. (82%).

Anal. Calcd. for CH_2N_4S: N, 54.87; S, 31.39. Found: N, 55.58; S, 31.08.

Recrystallization from methanol yielded fine, colorless needles which decomposed with a slight explosion at 136° in a capillary tube. On a hot plate the decomposition point was 128–130° (reported,[2] 128–130° dec.).

Anal. Calcd. for CH_2N_4S: N, 54.87; S, 31.39. Found: N, 55.39; S, 31.00.

The decomposition of III depends on the rate of heating. This was studied by placing a small quantity of recrystallized III on a Parr-Block preheated to a specific temperature. The following represents temperature and time required for decomposition, in minutes: 120°, 10; 110°, 20; 100°, 60; 95°, 150.

Infrared spectrum of III. The infrared absorption spectrum was obtained on a Perkin-Elmer spectrometer, Model 12-C. The sample consisted of 15 mg. of III mulled in 10 drops of white mineral oil for 5 to 10 min. The spectrum was taken over the range of 2 to 15 microns, using an automatic slit-drive and a scanning rate of 30 min. The following absorption peaks were observed, after subtraction of the white mineral oil background (in microns): 2.99, 3.12, 3.28, 6.14, 6.64, 7.48, 7.69, 7.84, 8.11, 8.61, 9.00, 10.60.

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(5) E. Lieber, D. R. Levering, and L. Patterson, *Anal. Chem.*, **23**, 1594 (1951).

(6) A more complete investigation and analysis of the ultraviolet and infrared absorption spectra of the products of the reaction of one mole of nitrous acid with a series of 4-substituted thiosemicarbazides is in progress. We are indebted to one of the referees for the comment that the band at 6.14 microns, which is the result of C=N group vibration, provides further evidence for structure III in preference to II, since C=S does not absorb in this region.

(7) Melting points are uncorrected.

(8) Microanalyses by Dr. C. Weiler and Dr. F. B. Strauss, Oxford, England.

Improved Procedure for Preparing 3-, 5-, or 3,5-Substituted Hydantoins[1]

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Hydantoin and its substituted derivatives are frequently prepared by the cyclization of the corresponding ureidoacetic esters, amides, or acids. Various methods have been employed to prepare the latter derivatives, often involving the preparation of difficultly accessible reagents. A convenient method of preparation of these hydantoic acid esters and amides which is capable of wide application, is described.

As a general preparative method, an α-isocyanato ester was allowed to react with ammonia or a primary amine to give the hydantoic ester in good yield. In some instances, the corresponding amide was obtained. Cyclization of these esters or amides by mineral acids in the conventional manner gave the corresponding 3-, 5-, or 3,5-substituted hydantoins.

Hydantoin, or a 3-substituted hydantoin, was obtained by cyclizing the hydantoic ester (or amide) obtained by the reaction of ammonia or a primary amine with ethyl isocyanatoacetate. This ester, readily prepared in high yield by the reaction of carbonyl chloride with glycine ester hydrochloride, was first described by Morel,[2] and later by Siefken,[3] whose preparative procedure was used in this work. α-Amino-acid ester hydrochlorides other than glycine produced substituted α-isocyanatoacetic esters which, when allowed to react with

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(1) Communication No. 1803 from the Kodak Research Laboratories.

(2) A. Morel, *Compt. rend.*, **143**, 119 (1906).

(3) W. Siefken, *Ann.*, **562**, 105 (1949).