TABLE IV

BOILING TEMPERATURES AND OPERATING RANGES FOR A SOLUTION OF METAPHOSPHORIC ACID

T. b., °C.	105	110	115	120
Op. r., °C.	−75 to −65	−60 to −50	−40 to −30	−15 to 0

Sodium metaphosphate solutions have more limited usefulness as low temperature lubricants. Those boiling at 104–106° have an operating range of −25 to 0°. More dilute solutions freeze when cooled to a temperature of a few degrees below zero.

Lubricating cream mixtures of salt solutions and finely divided solids may be prepared in the usual way and can then be used at temperatures down to approximately the freezing points of the respective solutions. Thus, a 35% solution of calcium chloride mixed with kaolin may be used as a lubricating paste to temperatures as low as −20°.

CONTRIBUTION FROM THE
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[CONTRIBUTION FROM THE ORGANIC CHEMISTRY DEPARTMENT, INDIAN INSTITUTE OF SCIENCE]

CONSTITUTION OF THE SO-CALLED DITHIOURAZOLE OF MARTIN FREUND. IV. ISOMERISM OF HYDRAZODITHIODICARBONAMIDES, IMINO-THIOL-THIOBIAZOLES AND IMINO-THIOBIAZOLONES

BY SHAHA L. JANNIAH AND P. C. GUHA

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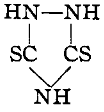
The ring-closing action of various reagents upon hydrazodithiodicarbonamides and their alkyl and aryl substituted derivatives has been studied by a number of workers, *viz.*, by Freund, Busch, Arndt, Fromm, Guha and their collaborators beginning from the year 1893, and all the possible four types of triazoles and thio-biazole compounds, I, II, III and IV, obtainable from the hydrazides, have been isolated.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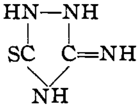
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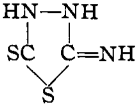
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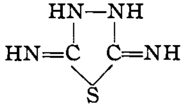
IV

A careful survey of the literature reveals the fact that various authors attribute different melting points to one and the same substance. As an example, to imino-thio-tetrahydro-4,1,2-thiodiazole, Freund[1] gives the

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[1] Freund, *Ber.*, **28**, 946 (1895).

melting point 243°; Guha[2] attributes three different melting points, *viz.*, 244, 233 and 224°, and Fromm[3] gives 228–235°. So it appears that the various investigators did not take sufficient care to define exactly the conditions under which they worked, so that the attempted repetitions were hindered by a lack of exact knowledge of the experimental conditions employed by earlier investigators. The present work was, therefore, undertaken with a view to defining more clearly the various factors which are concerned in the formation of each of the types of compounds.

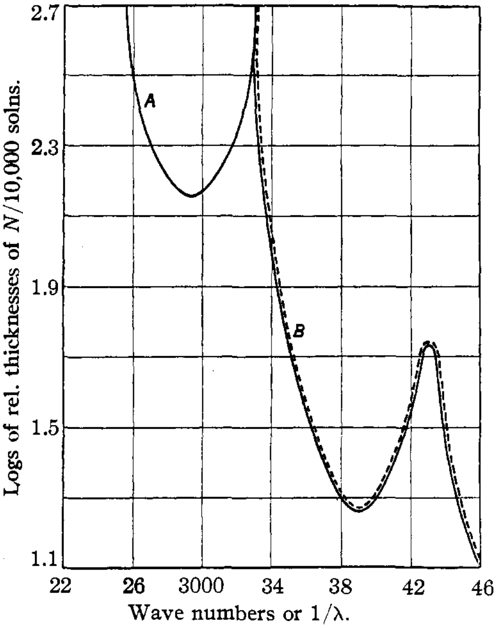

Fig. 1.—A, $NH{=}C(SH)NHNHC(SH){=}NH$, m. p. 203°; B, $NH_2CSNHNHC(SH){=}NH$, m. p. 223°.

In this paper, which forms the beginning of a series of investigations, it is proposed to deal with hydrazodithiodicarbonamides and the imino-thiolthiobiazoles.

Hydrochloric acid being rather an important ring-closing agent, its behavior on the hydrazides has now been very systematically studied and the utmost care has been taken to learn the influence of two important factors, *viz.*, the concentration of the acid and duration of treatment. After several trials 2 *N* acid, 5 *N* acid, strong (*d* 1.16) acid and concentrated (*d* 1.19) hydrochloric acid have been found to be suitable.

Hydrazo-dithio-dicarbonamide (m. p. 223°) on being boiled with dilute hydrochloric acid for a short time gave instead of a ring compound another hydrazide having the same chemical composition, $C_2H_6N_4S_2$, yielding derivatives (acetyl, methyl ether) identical with those of the parent hydrazide but differing in the melting point (m. p. 203°), suggesting thereby that the new compound is an isomer. While the hydrazide (m. p. 223°) has given only one absorption band (B) in Fig. 1, the isomer has given two bands (Curve A); and when the lower-melting variety was reconverted to the higher one, only one band, identical with that of the parent hydrazide, was obtained.

In these substances, we are dealing with a simple case of tautomerism,

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[2] Guha, This Journal, **44,** 1502–1517 (1922).

[3] Fromm, *Ann.*, **426,** 313 (1922).

for they do not contain anything benzenoid in structure, which is always accompanied by absorption bands. From a consideration of the investigation on the ultraviolet absorption spectra of some enol–keto tautomerides by Baly and Desch,[4] the conclusion to be drawn from these results can only be that the 223° variety exists in the monothiol form, whilst the new variety exists in the dithiol form, thus

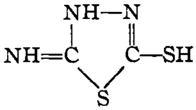
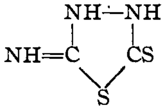
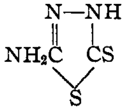
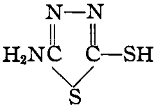
$$\mathrm{NH_2CSNHNHC(SH){=}NH} \quad \text{(m. p. 223°)}$$
$$\mathrm{NH{=}(HS)CNHNHC(SH){=}NH} \quad \text{(m. p. 203°)}$$

In the former, the hydrogen atom of only one of the ($\mathrm{—CSNH_2}$) groups can oscillate to give rise to the tautomeric thiolimino form $\mathrm{—C(SH){=}NH}$, accounting for one absorption band; and in the latter, the hydrogen atoms of both such groups can oscillate, as the result of which it gives two bands.

Both the hydrazides on being boiled with dilute hydrochloric acid for a long time, or with concentrated acid for a short time, yielded a ring compound of composition $C_2H_3N_3S_2$ melting at 234°.[3] In all chemical behavior it was identical with Freund's compound melting at 244–245°.

The acetyl derivative (m. p. 303°) of the above compound (m. p. 234°) when hydrolyzed with hydrochloric acid, gave back a substance possessing the same chemical composition, *viz.*, $C_2H_3N_3S_2$, but melting at 245°. This compound was obtained also by boiling the hydrazodithiodicarbonamide with concentrated hydrochloric acid (sp. gr. 1.19) for about half an hour. It does not respond to the tests of the amino group and behaves chemically identical with the parent substance (m. p. 234°).

It has also been observed that the higher-melting variety, obtained by either of the methods as stated above, on standing for several weeks is converted into the lower-melting variety 234°. The question naturally arises whether it is possible to explain this difference by any other tautomeric formula.

Of these the third and the fourth can easily be discarded owing to the fact that the substances do not respond to any test for the amino group. As regards the first and the second, it is very doubtful whether any such tautomeric compounds can exist at all as separate individuals.

Chemical methods proving of no avail in finding out the real cause of the difference, it was thought advisable to examine and compare the absorption spectra of these two compounds. It will be noticed that the difference existing among all the four suggested formulas is only due to a labile hydrogen atom. If this is really the case, then there ought to have been only

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[4] Baly and Desch, *J. Chem. Soc.*, **85**, 1033–1036 (1904).

a slight difference either in the persistence of the band or in the number of bands obtained from the two varieties. It has been actually found that the lower-melting variety gives a band between the wave numbers 3400 and 4200 in Fig. 2, while the higher-melting variety gives the band in the region between 2500 and 3600. This means that there has been a shift in the curve while passing from one variety to the other isomeric form. This eliminates the possibility of the difference being due only to a labile hydrogen atom.

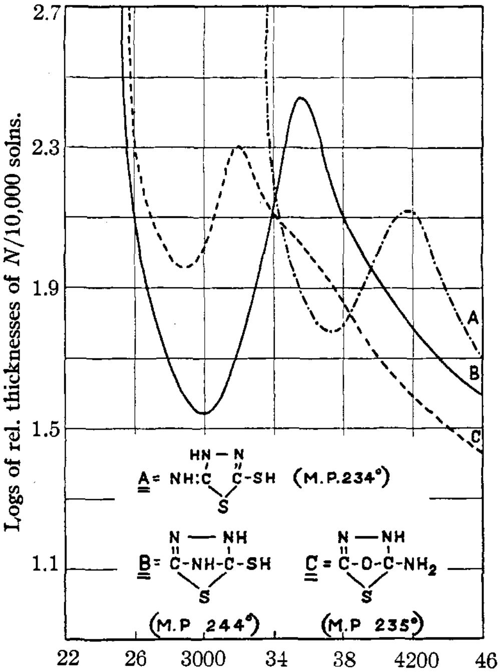
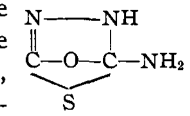


Fig. 2.

It is necessary here to describe another case of isomerism observed by us. Martin Freund, by treating hydrazomonothio-dicarbonamide with strong hydrochloric acid, obtained a compound (m. p. 177°) which he called monothiourazole.[5] The same hydrazide on being treated with acetic anhydride[6] was found to give a basic compound possessing the same chemical composition as that of Freund, but melting at 235°. The latter compound differs from the former in that it forms derivatives with aldehydes, isocyanates, and mustard oils, proving conclusively the presence of an amino group.

In view of these observations the new isomeric compound can only be represented by an endo formula, *viz.*, 3-amino-3,5-endoxy-2,3-dihydro-4, 1,2-thiodiazole (X). Freund's compound possesses none of these properties, and is feebly acidic in character, due evidently to the presence of an (—NH—CO—) group. So, to account for the pronounced basic nature of the new compound and to explain the mechanism of conversion of Freund's monothiourazole to that obtained by Guha, it is proposed to attribute an endo structure to the latter, and the changes involved in the transformation can be represented thus



X

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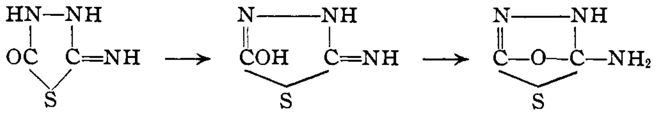
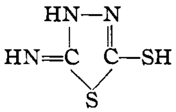
[5] Proved by Arndt to be imino-thiobiazolone, *Ber.*, **55**, 341 (1922).

[6] Guha, THIS JOURNAL, **45**, 1038 (1923).

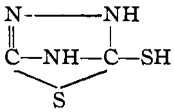


For purposes of analogy the curve of the endoxy-aminothiodiazole is also given, and it will be noticed that the curve of the 245° variety occupies almost the same region.

From all that has been said so far, and also to explain the difference between the two forms, melting at 234 and 245°, on a structural basis, as distinct from a basis of tautomerism, as established by absorption spectra curves, it is proposed that an imino-thio-tetrahydro-thio-diazole (A) structure be attributed to the lower-melting variety and an endo structure (*viz.*, 3-thiol-3,5-endo-imino-2,3-dihydro-4,1,2-thiodiazole) to the higher-melting variety.



(A, m. p. 234°)



(B, m. p. 245°)

Similar experiments have also been made with the substituted hydrazides. The results have corroborated the observations made in this paper and will be communicated shortly.

Experimental

Isomeric Hydrazodithiodicarbonamide.—Five grams of hydrazo-dithio-dicarbonamide, m. p. 223° (prepared according to the method of Freund[1]), was heated with 100 cc. of 2 *N* hydrochloric acid over a small flame until dissolved and the solution kept boiling for just ten minutes. The solution was then allowed to cool slowly, when colorless tiny needles separated. These were filtered, washed with a little water and recrystallized from hot water. The colorless crystalline needles thus obtained melted sharply at 203°. The melting point remained unchanged on repeated crystallizations; yield almost quantitative. This substance was found to be soluble in alkali more readily than the parent hydrazide; but both the hydrazides gave identical compounds when treated with dimethyl sulfate (m. p. 174°), and even the analytical values were the same. (The absorption spectra of the two have been studied in aqueous solutions.)

Anal. Calcd. for $C_2H_6N_4S_2$: N, 37.33; S, 42.66. Found: N, 37.2; S, 43.0.

Interconversion of the Two Hydrazides.—Two grams of hydrazodithiodicarbonamide (m. p. 223°), was dissolved in a little excess of 2 *N* sodium hydroxide and the clear solution kept aside in a closed flask for about twenty-four hours. The solution was then acidified with dilute hydrochloric acid, when a thick colorless solid was thrown down. This solid was filtered, washed and crystallized from hot water, when colorless tiny needles were obtained, melting sharply at 203°. This was proved by mixed melting point to be identical with the isomeric hydrazide obtained previously. The yield was almost quantitative except for a little loss during crystallization.

Two grams of the hydrazide (m. p. 203°) was placed in a glass dish, covered with a watch glass, in an air-oven at 120° for about four hours, when the hydrazide was found to melt at 223°. The higher-melting variety thus obtained showed no change in the melting point on repeated crystallization and was proved to be identical with the parent hydrazide (m. p. 223°) by taking the mixed melting point. The absorption spectra of the 223° variety as obtained by conversion were found to be identical with that of the parent hydrazide.

Imino-thiol-dihydro-thiobiazole.—Two grams of hydrazodithiodicarbonamide (m. p. 223°) or its isomer (m. p. 203°) was boiled with 25 cc. of concd. hydrochloric acid (*d* 1.19) for about ten minutes. The crystalline solid obtained from the clear solution on cooling was carefully washed and recrystallized from hot water (m. p. 234°).

When the experiment was repeated with 2 *N* hydrochloric acid, about 60 cc. of the dilute acid was required to dissolve 3 g. of the hydrazide on heating, and the solution had to be kept boiling for half an hour. The imino-thiol-dihydrothiobiazole thus obtained crystallized as very pale yellow needles, melting sharply at 234°, the yield being about 1.4 g. from 3 g. of hydrazide. It dissolves in cold dilute sodium hydroxide solution, and with iodine it gives the disulfide (m. p. 240°); with methyl sulfate it gives the thiomethyl ether (m. p. 178°); with acetic anhydride, the acetyl derivative (m. p. 303°).

Anal. Calcd. for $C_2H_3N_3S_2$: N, 31.6; S, 48.1. Found: N, 31.8; S, 47.8.

Endo-imino-thiol-thiobiazole.—Three grams of imino-thiol-dihydro-thiobiazole (m. p. 234°) was heated with 20 cc. of concentrated hydrochloric acid (*d* 1.19) to boiling for about ten minutes and the solution was allowed to cool. Dull yellow prismatic crystals were found to separate out from the solution gradually, and were filtered, washed and recrystallized from hot water; m. p. 244°; yield, 1.2 g.

Two normal acids failed to give the endo compound (m. p. 244°) even when the solution was boiled for more than an hour, but 5 *N* hydrochloric acid was found to be better than concentrated acid, as it gave greater yield. The actual yield of the endo compound from 3 g. of the parent thiobiazole was 1.8 g. as compared with 1.2 g. with concentrated acid.

Starting with hydrazodithiodicarbonamide (m. p. 233°) or its isomer (m. p. 203°), 5 g. of the hydrazide was heated with 40 cc. of 5 *N* hydrochloric acid until dissolved. The solution was kept boiling over a small flame for a quarter of an hour and then cooled. The solid obtained was filtered, washed and crystallized from hot water, m. p. 244°; it was found to be identical with that obtained from imino-thiobiazole (and behaving chemically identically with the "so-called 'dithio-urazole' " of Martin Freund).[1] 5 *N* hydrochloric acid was employed in preference to concentrated acid for good yields; yield, 3.2 g.

The substance gave with methyl sulfate the methyl ether, m. p. 178°, and the acetyl derivative, m. p. 303°, both identical with those of imino-thiol-dihydro-thiobiazole.

Acetyl Derivative of Imino-thiol-dihydro-thiobiazole.—Two and one-half grams of the thiobiazole was heated gently with 15 cc. of acetic anhydride until dissolved. The brownish-yellow solution obtained was heated to boiling and kept at that temperature for about twenty minutes. The clear solution was poured into about 100 cc. of water and when thoroughly stirred by a glass rod, a yellow solid separated, which was filtered, washed with water and crystallized from very dilute acetic acid. The pale yellow needles thus obtained melted at 303° to a dark brown liquid; yield, 1.4 g.

Hydrolysis.—The acetyl compound was boiled gently with 2 *N* hydrochloric acid until very little acetic acid was present in the vapors. The insoluble solid which separated on slight cooling was filtered off from the mother liquor, washed and crystallized from boiling water. The crystalline needles so obtained melted sharply at 243–244°, identical with the endo-imino-thiol-thiobiazole.[7]

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[7] The endo-imino-thiol-thiobiazole when treated similarly with acetic anhydride gave the same acetyl derivative, m. p. 303°, which on hydrolysis gave back the endo compound.

Summary

1. Hydrazodithiodicarbonamide has been found to tautomerize into the thiol-imino form under experimental conditions which have been determined, and the interconvertibility of the two forms established.

2. Imino-thiol-thiobiazole has been isolated as an intermediate compound during the formation of Freund's "Dithio-urazole"—now shown to be endo-imino-thiol-thiobiazole; the latter has been found to be formed either by the prolonged action of hydrochloric acid on the hydrazide or the imino-thiol-thiobiazole, or by acetic anhydride treatment on the thiobiazole with subsequent deacetylation.

3. Similar cases of isomerism have been observed with the alkyl and aryl substituted mono- and dithio-hydrazides.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE COLLEGE OF WASHINGTON]

SOME HALOGEN DERIVATIVES OF ACYL AND ALKYL RESORCINOLS

BY C. M. BREWSTER AND J. C. HARRIS[1]

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Since the acyl and alkyl resorcinols have been given much attention by investigators recently, due to their germicidal and other interesting properties, we have undertaken to prepare and study certain halogen derivatives of these compounds, and also to improve the methods of preparation of the intermediate compounds already reported by others.

The acyl groups were introduced into the resorcinol nucleus by condensing the latter with the desired fatty acid in the presence of fused zinc chloride, a method proved to be very satisfactory for this purpose by Nencki[2] and others. The ketones were prepared without difficulty, and increased yields obtained by varying the conditions of temperature, concentration and time, as shown in the tables in the dissertation.[3] These acyl compounds were then reduced according to Clemmensen's method,[4] which employs amalgamated zinc with hydrochloric acid as reducing agent. The alkyl compounds obtained by reduction were halogenated in various solvents and in the presence of carriers.

The same halogenated alkyl resorcinol was obtained whether the halogenated ketone was reduced or the ketone reduced before halogenation. For example, dibromo-ethylresorcinol was prepared as follows.

[1] This paper is an abstract of part of a thesis presented by J. C. Harris in partial fulfilment of the requirements for the degree of Master of Science.

[2] Nencki and Schmid, *J. prakt. Chem.*, **23**, 546 (1881).

[3] Dissertation, by J. C. Harris, 1930.

[4] Clemmensen, *Ber.*, **46**, 1837 (1913).