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PART V. ISOMERISM OF HYDRAZODITHIODICARBONAMIDES, IMINOTHIOLTHIOBIAZOLES AND DI-R-IMINOTHIOTIAZOLES.

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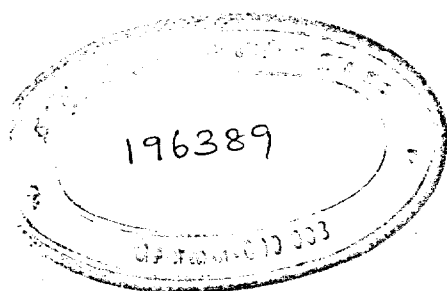
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CONSTITUTION OF THE SO-CALLED DITHIOURAZOLE OF MARTIN FREUND.

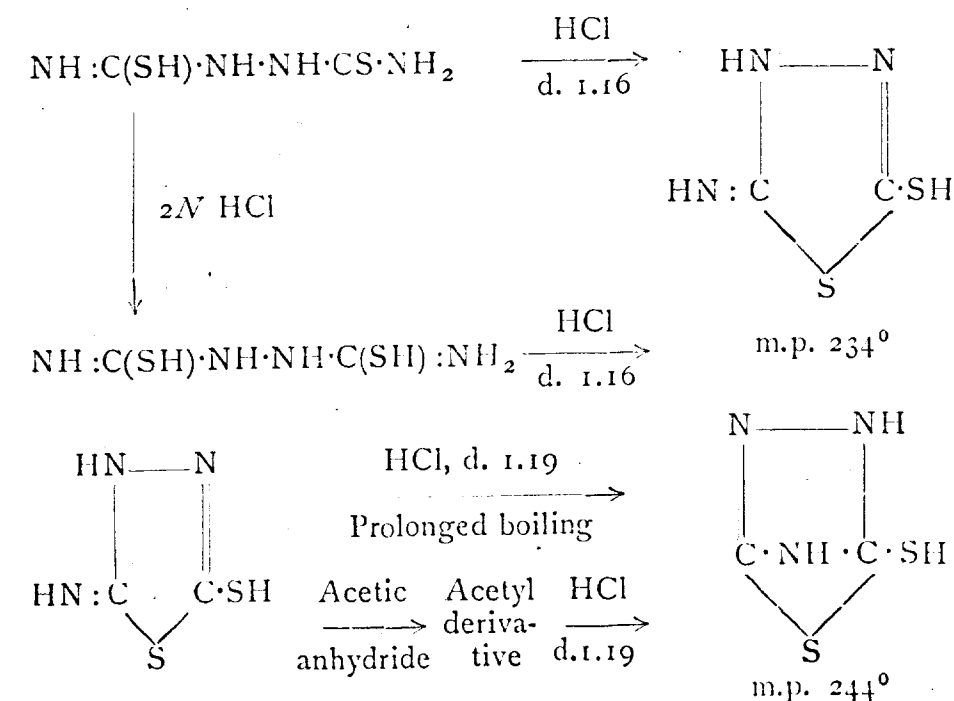
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By Shaha L. Janniah and P. C. Guha.

In part IV (*J. Amer. Chem. Soc.*, 1930, **52**, 4860) hydrazo-dithiodicarbonamide has been found to exist in two tautomeric forms,



and their interconvertibility established. Iminothioltthiobiazole has been isolated as an intermediate compound during the formation of Freund's so-called dithiourazole (*Ber.*, 1895, **28**, 946) which has been shown to be *endo*iminothioltthiobiazole; the latter has been found to be formed either by the prolonged action of hydrochloric acid (d. 1.19) on either the hydrazide or the iminothioltthiobiazole, or by acetic anhydride treatment of the thiobiazole with subsequent deacetylation.

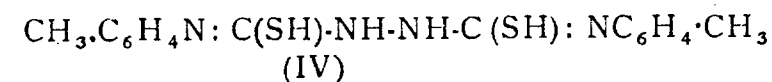
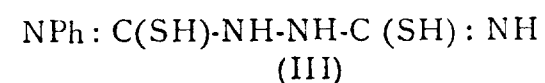
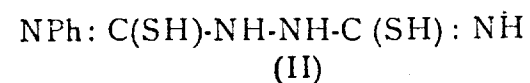
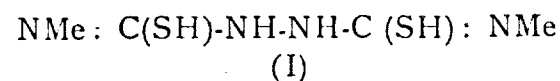


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In the present paper, the action of hydrochloric acid of different strengths and of acetic anhydride has been studied upon the mono- and di-substituted hydrazodithiocarbonamide of the types,

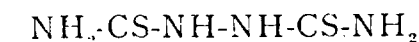
$\text{NHR-CS-NH-NH-CS-NH}_2$ and $\text{NHR-CS-NH-NH-CS-NHR}$ and the isomeric thiobiazoles obtained from them by the action of hydrochloric acid of different strengths, and of acetic anhydride have been studied.

The action of 2*N* hydrochloric acid upon the mono- and di-substituted hydrazides is the same as with the unsubstituted hydrazide (described in part IV) and thus *sym*-dimethyl, mono-phenyl, *sym*-diphenyl and *sym*-di-*o*-tolylhydrazodithiocarbonamides have yielded isomeric compounds I-IV.

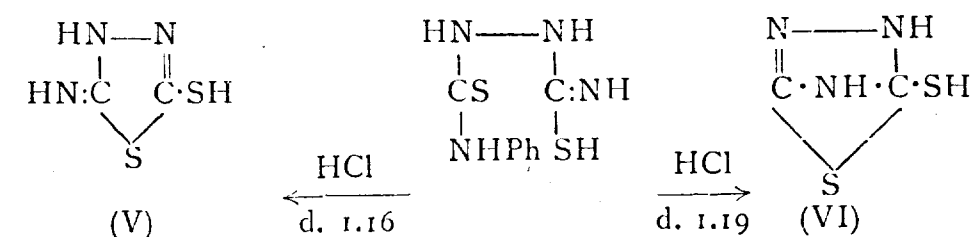


The isomeric dimethylhydrazides give quite different absorption bands thus fulfilling the expectation that substituted hydrazides resemble the unsubstituted in undergoing isomeric change. The absorption spectra of the isomeric aryl-substituted hydrazides have not been studied as their aryl groups were likely to produce complicated absorption bands in addition to those due to the labile hydrogen atoms in the CS.NH_2 group of the hydrazides.

Attempts to obtain heterocyclic compounds of the types III and IV mentioned in part I from the mono-substituted hydrazides were unsuccessful; both hydrochloric acid and acetic anhydride eliminate the corresponding amines forming unsubstituted thiobiazoles. Mono-phenylhydrazodithiocarbonamide (m.p. 180°) and its isomer (m.p. 162°) give iminothiolthiobiazole, m.p. 234° (V) and the *endo*iminothiolthiobiazole, m.p. 245° (VI) with hydrochloric acid of d. 1.16 and 1.19 respectively, conditions of experiments scarcely differing from those of their formation from the unsubstituted hydrazide,

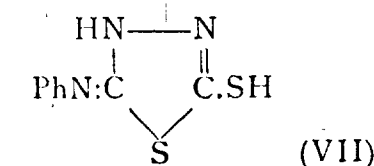


The reaction evidently proceeds in the following manner:

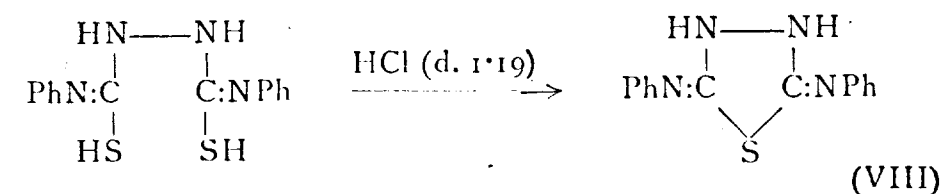


The literature does not appear to describe the action of acids upon the mono-substituted hydrazodithiocarbonamides.

The symmetrical disubstituted hydrazides have given interesting results. Freund and Imgart (*Ber.*, 1895, **28**, 946) obtained by the action of hydrochloric acid upon diphenylhydrazodithiocarbonamide an alkali-soluble compound, $\text{C}_8\text{H}_7\text{N}_2\text{S}_2$, melting at 210° which they called phenyldithiourazole, proved subsequently by Guha to be 3-thiol-5-phenylimino-4:1:2-thiobiazole (VII).



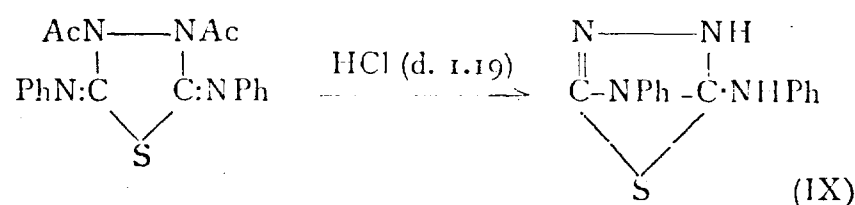
It has now been found, however, that this thiobiazole is formed in good yield only when the hydrazide is treated with hydrochloric acid (d. 1.16) and not with concentrated acid (d. 1.19), in which case an alkali-insoluble compound, $\text{C}_{11}\text{H}_{12}\text{N}_4\text{S}$, m.p. 249° is obtained as the main product. This contains two phenyl groups, and the sulphur atom is a member of the ring. It is therefore formed by the elimination of a molecule of hydrogen sulphide from the diphenylhydrazide thus:



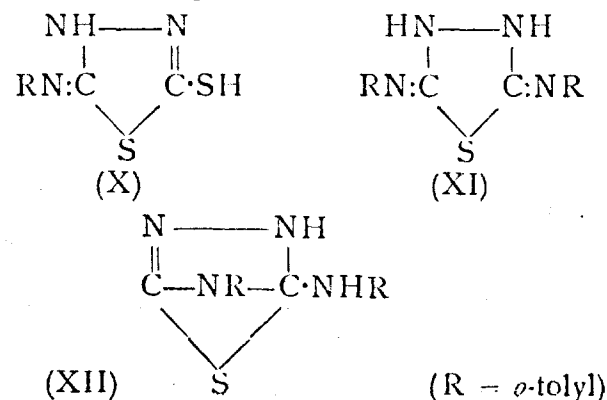
Identity of this (VIII) with that obtained by Guha from diphenylhydrazodithiocarbonamide and acetic anhydride (*J. Amer. Chem. Soc.*, 1923, **45**, 1036) has been established.

It is, however, interesting to note that the acetyl derivative (m.p. 224°) of 3:5-diphenyliminothiobiazole, whether obtained from the diphenylhydrazide or the thiobiazole by the action of acetic anhydride, regenerates the same thiobiazole melting at 249° when treated with dilute hydrochloric acid (1:1). If concentrated hydrochloric acid (d. 1.19) is used as hydrolysing agent, an alkali-insoluble thiobiazole (IX) melting at 208° and isomeric with (VIII) and with the thiobiazole, m.p. 249° , is obtained. This product has escaped previous workers because they used less concentrated hydrochloric acid. Since Guha employed hydrochloric acid of which the strength is not mentioned, it is probable that his sample was mixed with a trace of the 208° variety, thus accounting for the slightly lower melting point (viz., 247°) recorded for the 249° variety.

Compounds (VIII) and (IX) contain two phenyl groups and one sulphur atom; they are insoluble in alkali, do not form disulphides and are not desulphurised by mercuric oxide. Guha (*J. Amer. Chem. Soc.*, 1923, **45**, 1040) has already proved the constitution of the thiobiazole (VIII) and shown it to be 3:5-diphenylimino-4:1:2-thiobiazole. By analogy with the compounds discussed in part IV, the new thiobiazole melting at 208° is in all probability, 2:3-dihydro-3-anilino-3:5-*endo*phenylimino-4:1:2-thiobiazole, formed from the acetyl derivative of compound (VIII) by molecular rearrangement during hydrolysis with acid (d. 1.19):—



Di-*o*-tolylhydrazodithiodicarbonamide resembles its phenyl analogue and yields three thiobiazole compounds X, XI and XII:—



EXPERIMENTAL.

Isomer of dimethylhydrazodithiodicarbonamide (I).—Dimethylhydrazodithiodicarbonamide (5 g.), prepared according to the method of Freund (*Ber.*, 1895, **28**, 946), was dissolved in 2*N* hydrochloric acid (100 c.c.) over a small flame and the solution boiled for exactly ten minutes. On slow cooling minute needles separated and were recrystallised from hot water in colourless needles, m.p. 198° , the yield being almost quantitative. This substance was found to be more readily soluble in alkali than the parent hydrazide (m.p. 224°) and the analytical values were the same (Found: N, 31.6; S, 36.0; $\text{C}_4\text{H}_{10}\text{N}_4\text{S}_2$ requires N, 31.4; S, 35.9 per cent.). The absorption spectra of both have been studied in aqueous solutions.

Isomer of monophenylhydrazodithiodicarbonamide (II).—Experimental procedure was that adopted in the case of the unsubstituted hydrazide (*J. Amer. Chem. Soc.*, 1930, **52**, 4864). The crystalline solid obtained on cooling the solution from 3 g. of the hydrazomono-phenyldithiodicarbonamide (m.p. 180°) in 2*N* acid (80 c.c.) was filtered, washed with water and recrystallised from dilute alcohol, m.p. 162° ; yield, 1.6 g. (Found: N, 24.9; S, 28.5. $\text{C}_8\text{H}_{10}\text{N}_4\text{S}_2$ requires N, 24.7; S, 28.31 per cent.).

Action of strong hydrochloric acid on monophenylhydrazodithiodicarbonamide: Formation of compounds V and VI.—No phenylthiobiazole could be obtained from the hydrazide by treating it with hydrochloric acid of various higher concentrations in the manner described in part IV; aniline was liberated in all cases together with a small quantity of phenyl mustard oil. Only iminothiolthiobiazole (m.p. 234°) was obtained as the final product with hydrochloric acid (d. 1.16) and *endo*iminothiolthiobiazole (m.p. 244°) with acetic anhydride followed by deacetylation with hydrochloric acid (d. 1.19) or direct treatment with the latter (Found: N, 31.5; S, 47.9. $\text{C}_2\text{H}_3\text{N}_3\text{S}_2$ requires N, 31.6; S, 48.1 per cent.).

Isomer of diphenylhydrazodithiodicarbonamide (III).—Diphenylhydrazodithiodicarbonamide (m.p. 187°) on treatment with 2*N* hydrochloric acid gave an isomeric hydrazide, which on recrystallisation from hot dilute alcohol melted sharply at 173° . The mixed melting point of the two hydrazides was quite indefinite, gradually rising from 155° to about 180° (Found: N, 18.6; S, 21.23. $\text{C}_{11}\text{H}_{14}\text{N}_4\text{S}_2$ requires N, 18.54; S, 21.19 per cent.).

Diphenylhydrazodithiodicarbonamide and hydrochloric acid (d. 1.16); Formation of 3-thiol-1:5-dihydro-5-phenylimino-4:1:2-thiobiazole (VII).—The hydrazide (3 g.) soon dissolved in the boiling acid

(20 c.c.), but after 3-4 minutes some reddish-brown, oily drops separated with odour of phenyl mustard oil; after about ten minutes the solution became turbid and a white solid separated rapidly on cooling. This was filtered, well pressed, washed with a little water and ether to remove mustard oil, and finally recrystallised from 95 per cent. alcohol, m.p. 219°. Yield, 1.8 g. It dissolved easily in cold dilute alkali (Found: N, 20.4; S, 30.2. $C_8H_7N_3S_2$ requires N, 20.1; S, 30.6 per cent.).

3:5-Diphenylimino-2:3:5:1-tetrahydro-4:1:2-thiobiazole (VIII). Diphenylhydrazodithiodicarbonamide (3 g.) dissolved when gently heated with concentrated acid (d. 1.19, 20 c.c.); after boiling over a small flame for nearly fifteen minutes a very small quantity of phenyl isothiocyanate was liberated. The clear, filtered solution when cold gave a curdy white solid which after being washed with water and ether was crystallised from 95 per cent. alcohol, m.p. 249° (decomp.). Yield, 1.2 g. The substance was insoluble in cold dilute alkali but was decomposed when boiled with sodium hydroxide solution liberating phenyl isocyanide. It did not give any disulphide with iodine, which was not even decolorised, and could not be desulphurised by mercuric oxide (Found: N, 21.2; S, 11.6. $C_{14}H_{12}N_4S$ requires N, 20.9; S, 11.9 per cent.). The strongly acid filtrate on being neutralised with dilute ammonia gave a small quantity of the alkali-soluble phenyliminothiolthiobiazole melting at 219°.

The *diacetyl* derivative, prepared by heating the diphenyliminothiodiazole, m.p. 249°, with acetic anhydride, crystallised from hot water acidified with acetic acid, m.p. 224°. It is identical with that obtained by treating the diphenylhydrazodithiodicarbonamide (m.p. 187°) with acetic anhydride (Found: N, 16.2; S, 8.9. $C_{18}H_{16}O_2N_4S$ requires N, 15.9; S, 9.09 per cent.).

Hydrolysis of the diacetyl derivative with 5N hydrochloric acid: Formation of compound (VIII).—The diacetyl derivative dissolved after about five minutes in the boiling acid the solution becoming turbid during the next ten minutes. After crystallisation from alcohol the product was found to be the diphenyliminothiobiazole, m.p. 249°.

The endophenyliminothiobiazole (IX).—When the diacetyl derivative was hydrolysed by concentrated hydrochloric acid (d. 1.19) the solution did not become turbid as with 5N acid, although the boiling was prolonged for about twenty minutes. Drops of phenyl mustard oil separated, and the solution on cooling deposited white crystals which separated from absolute alcohol in cubes, m.p. 208°. It was insoluble in sodium hydroxide solution, but decomposed on boiling with the alkali and could not be desulphurised by mercuric oxide (Found: N, 21.15; S, 11.7. $C_{14}H_{12}N_4S$ requires N, 20.9; S, 11.9 per cent.).

Isomer of di-o-tolylhydrazodithiodicarbonamide (IV).—On treatment with 2N hydrochloric acid, the ordinary hydrazide (m.p. 171°) yielded the isomeric compound, obtained from dilute alcohol as minute, colourless crystals m.p. 178°. The melting point of a mixture with the original hydrazide ranged from about 162° to 176° (Found: N, 16.8; S, 19.2. $C_{16}H_{18}N_4S_2$ requires N, 16.99; S, 19.4 per cent.).

o-Ditolylhydrazodithiodicarbonamide and strong hydrochloric acid (d. 1.16): Formation of 3-thiol-5:1-dihydro-5-tolylimino-4:1:2-thiobiazole (X).—The hydrazide soon dissolved in the hot acid and further boiling of the solution gave a white solid with a few drops of tolyl mustard oil. At this stage the mixture was allowed to cool and the solid washed with water and then with a little ether; it crystallised from 95 per cent. alcohol in minute, colourless prisms m.p. 195°. This thiobiazole was readily soluble in cold dilute alkali and decolourised iodine with the formation of a disulphide (Found: N, 19.1; S, 28.4. $C_9H_9N_3S_2$ requires N, 18.8; S, 28.7 per cent.).

3:5-Di-o-tolylimino-2:3:5:1-tetrahydro-4:1:2-thiobiazole (XI).—On heating, di-o-tolyl-hydrazodithiodicarbonamide soon dissolved in boiling concentrated hydrochloric acid (d. 1.19) and a very small quantity of the isothiocyanate was liberated. The clear solution gave on cooling a white solid, which after being washed with water and ether was crystallised from 95 per cent. alcohol, m.p. 217° (decomp.) (Found: N, 19.2; S, 11.1. $C_{16}H_{16}N_4S$ requires N, 18.9; S, 10.8 per cent.). The substance was insoluble in cold dilute alkali, but decomposed on boiling and did not give a disulphide. As in the case of the diphenylhydrazide the acid filtrate from the foregoing substance on neutralisation gave a white solid which crystallised from alcohol, m.p. 195° and was identical with the alkali-soluble thiobiazole (X).

The *diacetyl* derivative from the above thiobiazole (m.p. 217°) after crystallisation from dilute acetic acid melted with decomposition at 262° (Found: N, 14.4; S, 8.2. $C_{20}H_{20}O_2N_4S$ requires N, 14.7; S, 8.4 per cent.).

Hydrolysis of the diacetyl derivative with 5N hydrochloric acid: Formation of 3:5-ditolyliminothiobiazole (XI).—The boiling acid dissolved the diacetyl derivative in about five minutes, and after another ten minutes the clear solution became turbid; when cold, the solid product was filtered, washed, and recrystallised from alcohol, m.p. 217°, being identical with the di-o-tolyliminothiobiazole.

Hydrolysis with concentrated acid (d. 1.19): Formation of 2:3-dihydro-3-tolylimino-3:5-endo-o-tolylimino-4:1:2-thiobiazole (XII).—The clear solution obtained on boiling the diacetyl derivative with the

acid deposited white cubic crystals on cooling. These after recrystallisation from absolute alcohol melted at 133° . It was insoluble in cold dilute alkali but decomposed on boiling and did not decolourise iodine (Found: N, 18.8; S, 11.0. $C_{16}H_{16}N_4S$ requires N, 18.9; S, 10.8 per cent.).

It is to be mentioned that both of the isomeric monophenyl, diphenyl- and di-*o*-tolylhydrazodithiodicarbonamides have been found to yield identical compounds on treatment with hydrochloric acid of density 1.16 and 1.19, and acetic anhydride respectively.

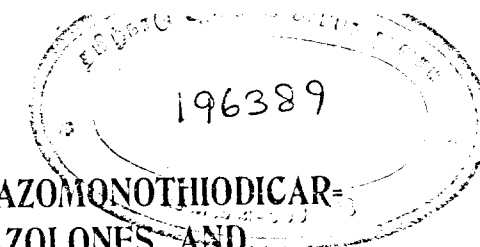
SUMMARY

The action of 2*N* hydrochloric acid on mono- and di-substituted hydrazodithiodicarbonamides is the same as on the unsubstituted hydrazide in giving the corresponding isomers. Stronger acids eliminate the amine from the mono-substituted hydrazide yielding the isomeric iminothiol- and *endo*iminothiolthiobiazoles (V) and (VI).

In the case of disubstituted hydrazides, hydrochloric acid (d. 1.16) gives the alkali-soluble *R*-iminothiolthiobiazole (VII) as the main product; concentrated acid (d. 1.19) on the other hand yields isomeric 3:5-di-*R*-iminothiobiazole (VIII) and 3:5-*endo*-*R*-imino-3-*R*-iminothiobiazole (IX).

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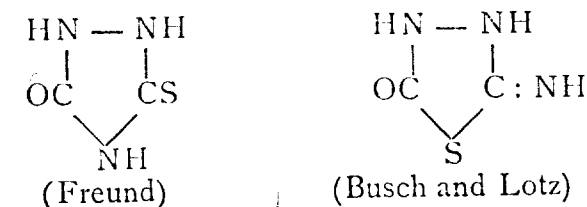
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PART VI. ISOMERISM OF HYDRAZOMONOTHIODICARBONAMIDES, IMINOTHIOTIAZOLONES AND MONOTHIOURAZOLES.

By S. L. Janniah and P. C. Guha.

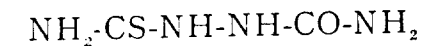
Freund and Schander (*Ber.*, 1896, **29**, 2506), by heating the hydrazide $NH_2-CS-NH-NH-CO-NH_2$ with concentrated hydrochloric acid obtained a compound, $C_2H_3ON_3S$, to which they ascribed the monothiourazole formula. Busch and Lotz (*J. pr. Chem.*, 1914, **90**, ii, 257) have shown Freund's monothiourazole to be 3-imino-4:1:2-thiobiazole-5-one



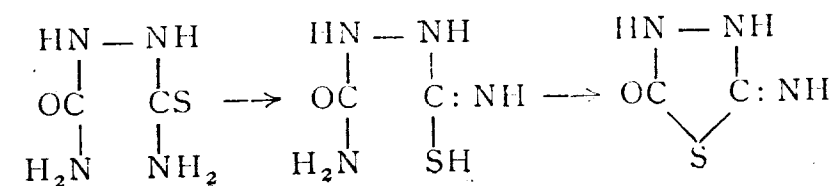
Arndt, Milde, and Tschenschner (*Ber.*, 1922, **55**, 341) found that of the two isomeric hydrazides,

$NHPh-CO-NH-NH-CS-NH_2$ and $NHPh-CS-NH-NH-CO-NH_2$ the former gave thiourazole (m.p. 206°) and 4-phenylthiourazole, and the latter phenylthiourazole, on being boiled with a solution of sodium hydroxide.

While attempting the ring-closure of hydrazomonothio- (and dithio-) dicarbonamides with acetic anhydride, Guha (*J. Amer. Chem. Soc.*, 1923, **45**, 1036) found that the hydrazide



instead of giving 3:5-diiminotetrahydro-4:1:2-thiobiazole according to the general rule holding good in the case of the hydrazodithiodicarbonamides, gave ketoiminothiobiazole m.p. 235° , thus:



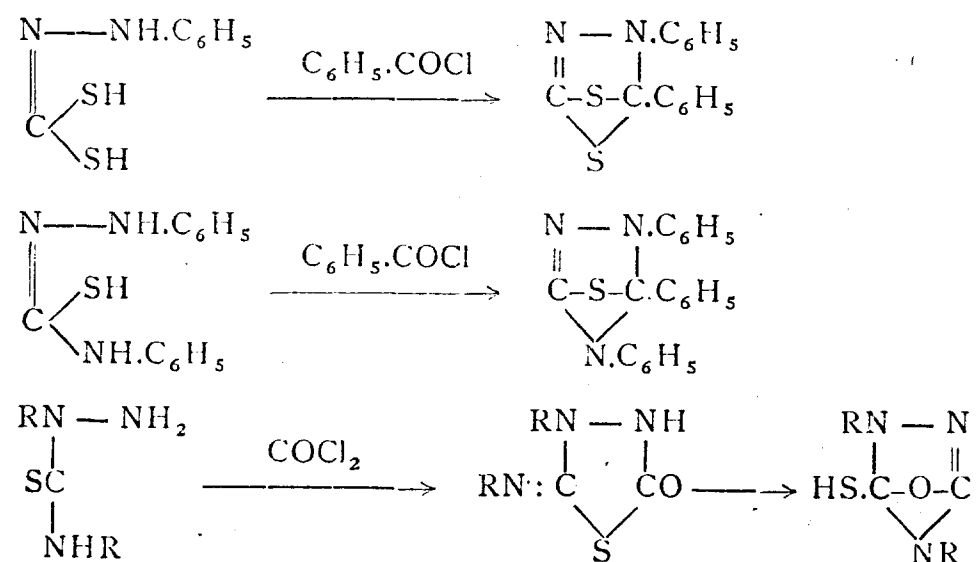
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P. C. Guha, 1933

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and that his compound was quite different from Freund's compound (m.p. 177°).

Guha and Sen (*J. Ind. Chem. Soc.*, 1927, **4**, 43) obtained by the action of urea upon substituted thiosemicarbazides four types of compounds namely, 3-R-5-keto-3-thioldihydro-4:1:2-triazole, 5-keto-3-R-aminodihydro-4:1:2-thiobiazole, 4-R-3-thiol-5-R-amino-4:1:2-triazole and 3:5-*endoxy*-4:1:2-triazole. Of the above four types, ketothioltriazoles have been prepared also by Freund and Schneider, Arndt and his collaborators (*loc. cit.*) and by Fromm and Nehring (*Ber.*, 1923, **56**, 1370) ketoaminothiobiazoles by Busch (*Ber.*, 1901, **34**, 320, 2328; 1902, **35**, 973; 1904, **37**, 2333; 1909, **42**, 4763; 1911, **44**, 561, 1580) and by Nirdlinger and Acree (*J. Amer. Chem. Soc.*, 1922, **44**, 224). Lastly, though Schneider (*J. pr. Chem.*, 1890, **67**, 263), Marckwald (*Ber.*, 1892, **25**, 3113; 1896, **29**, 2923), Busch (*loc. cit.*) and Nirdlinger and Acree have prepared the derivatives of *endoxy*-, *endothio*-, and *endoiminotriazoles* and thiobiazoles by methods fundamentally different from that of Guha, e.g.:-

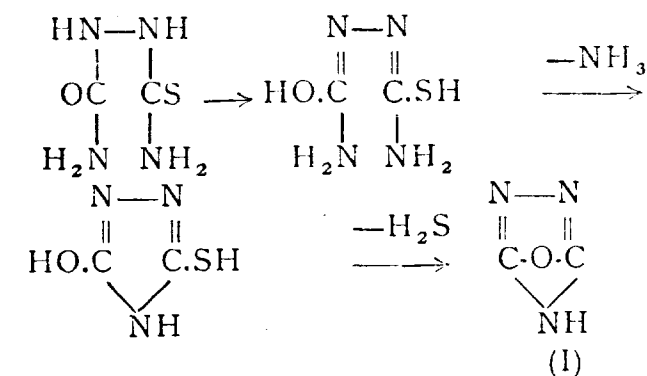


the parent *endoxy*triazole was prepared for the first time by Guha and Sen. Guha and Chakraborti (*J. Ind. Chem. Soc.*, **6**, 99-110) while studying the ring-closure of hydrazomonothiodicarbonamide and its mono- and sym-di-substitution products with acetic anhydride, obtained iminothiobiazolones and iminothioltriazoles.

The present investigation is a continuation of the work described in parts IV and V, undertaken with the expectation that interesting cases of isomerism amongst the hydrazomonothiodicarbonamides, as also

amongst the thiobiazoles and triazoles obtained from them by ring-closure might yet arise, and these have been found.

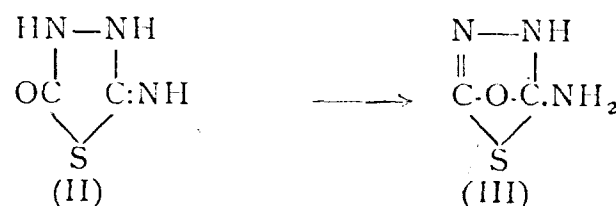
Our first attempt was to study the effect of 2*N* hydrochloric acid upon hydrazomonothiodicarbonamide, but this failed to give an isomer; under the various conditions tried only thiosemicarbazide hydrochloride (m.p. 190°) could be obtained. With boiling 5*N* hydrochloric acid, however, the hydrazide gave a substance, C₂HON₃, m.p. 255°, identical with 3:5-*endoxy*-4:1:2-triazole prepared by Guha and Sen (*J. Ind. Chem. Soc.*, 1927, **4**, 43). The reaction evidently takes the following course:-



By repeating Freund's experiment with hydrochloric acid (d. 1.16) under varied experimental conditions it has now been found that iminothiobiazolone, m.p. 177°, is formed in poor yield; and with concentrated hydrochloric acid (d. 1.19) both compounds (m.p. 177° and 235°) are produced, the latter due to its pronounced basic property remaining in the acidic mother liquor after the separation of the former.

This thiobiazolone (m.p. 177°) gives with acetic anhydride an acetyl derivative (m.p. 295°) which on being hydrolysed with concentrated hydrochloric acid gives a hydrochloride (m.p. 107-108°), and a free base (m.p. 235°) identical with the corresponding compounds obtained from hydrazomonothiodicarbonamide with acetic anhydride (Guha, *J. Amer. Chem. Soc.*, 1923, **45**, 1036). The substance has the composition, C₂H₃ON₃S, and is therefore isomeric with the substance melting at 177°. It is insoluble in alkali, remains unchanged on mercuric oxide treatment, and forms compounds with phenyl isocyanate, phenyl mustard oil, and benzaldehyde. It is thus clear that (1) the sulphur atom is a member of the ring, and (2) an amino-group is present. All these facts give further support to the *endoaminothiobiazole* structure (III) ascribed to compound, m.p. 235° (compare part IV, 4863). It appears very probable that by the action of concen-

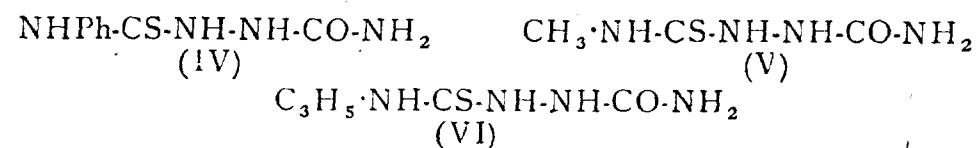
trated hydrochloric acid the hydrazide is first converted into iminothio-
biazolone, m.p. 177° (II) which then rearranges itself into the *endo*-
oxyaminothiobiazole, m.p. 235° (III):—



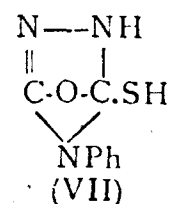
Mono-substituted hydrazides of the type,



give the corresponding isomeric hydrazides (IV, V, VI) with 2*N* hydro-
chloric acid similar to those described in parts IV and V.



Although hydrochloric acid of different strength (d. 1.16 and 1.19) produces different thiobiazoles in the case of the mono- and di-substituted hydrazodithiodicarbonamides, their effect as ring-closing agents on the hydrazides of the monothio-series is similar. Strong hydrochloric acid brings about a ring-closure in the hydrazide (IV) producing a compound (m.p. 184°) of the empirical formula, $\text{C}_8\text{H}_7\text{ON}_3\text{S}$. This is soluble in dilute alkali, gives a thiomethyl ether, m.p. $90\text{--}91^{\circ}$, and a disulphide, m.p. 196° . These properties eliminate the possibility of the compound being 3-phenylimino-5-keto-4:1:2-thiobiazole (m.p. 246°) synthesised by Guha and Sen (*J. Ind. Chem. Soc.*, 1927, 4, 44) by the action of urea on phenylthiosemicarbazide. It therefore follows that the substance under consideration must be a triazole containing a thiol group. 4-phenylthiourazole (m.p. 196°) of Arndt (*Ber.*, 1922, 55, 341), obtained by the action of alkali on the same hydrazide has a mercaptanic group (thiomethyl ether m.p. 208° , disulphide, m.p. 285°), and is evidently a different substance. There thus remains the only alternative *endo*-formula (VII) for the substance melting at 184° , viz., 3-thiol-3:5-*endoxy*-2:3-dihydro-4-phenyl-4:1:2-triazole,

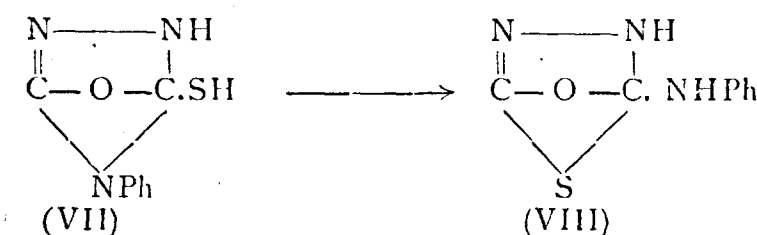


Compound (VII) gives with acetic anhydride a diacetyl derivative (m.p. $213\text{--}214^{\circ}$) which on deacetylation gives a substance (m.p. 206°) having the same composition ($\text{C}_8\text{H}_7\text{ON}_3\text{S}$) as the parent *endoxy*triazolethiol but without mercaptanic properties. Thus compound (VII) after acetylation and deacetylation is no longer a triazole, and must have been changed into a substance with the sulphur atom in the ring. The diacetyl derivative (m.p. 214°) and the deacetylated compound (m.p. 206°) have been proved identical with the corresponding compounds obtained by Guha and Chakraborti from the hydrazide by the action of acetic anhydride (*loc. cit.*). To distinguish their compound, m.p. 206° , from that having m.p. 246° (Guha and Sen, *loc. cit.*) Guha and Chakraborti ascribed a ketophenyliminotetrahydrothiobiazole structure to the former as distinct from the ketophenylaminodihydrothiobiazole structure of the latter

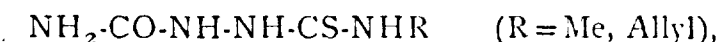


(m.p. 206° , Guha and Chakraborti) (m.p. 246° , Guha and Sen)

Seeing that both compounds (m.p. 206° and 246°) are quite stable and show no sign of interconvertibility under ordinary conditions, unexpectedly from the tautomeric nature of the above formulae, and from analogy with the *endo*-isomers of the thiobiazoles and triazoles obtained from the hydrazomono- and dithiodicarbonamides, it is now proposed to attribute an *endo*-formula, namely, 3-phenylamino-3:5-*endoxy*-4:1:2-thiobiazole, to the compound melting at 206° ; and its formation from compound (VII) is explained on the assumption that an interchange of position between NPh and S takes place:—

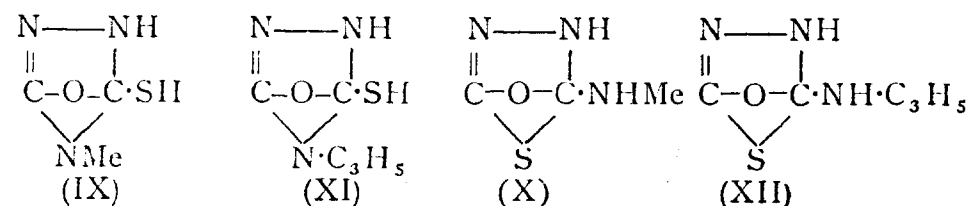


Methyl- and allyl-substituted hydrazomonothiodicarbonamides,



by the action of concentrated hydrochloric acid and acetic anhydride, have yielded the corresponding methyl and allyl substituted *endoxy*-

thioltriazoles (IX and XI) and endoxy-R-iminothiobiazoles (X and XII) respectively :



EXPERIMENTAL.

Hydrazomonothiodicarbonamide and 5N hydrochloric acid: Formation of 3:5-endoxy-4:1:2-triazole (I).—The hydrazide (m.p. 220°; 5 g.) was heated with the acid (50 c.c.) and the clear solution thus obtained was boiled during half an hour, when hydrogen sulphide and a small quantity of sulphur separated. The clear solution on cooling gave a small quantity of white crystalline solid, increased on concentrating the mother liquor. This crystallised from hot water, m.p. 255°; yield, about 2 g. The substance was insoluble in alkali and was identical with the endoxytriazole (m.p. 255°) of Guha and Sen (*loc. cit.*) (Found: N, 50.85; C_2HON_3 requires N, 50.6 per cent.).

Hydrazomonothiodicarbonamide and concentrated hydrochloric acid (d. 1.19): Formation of 3-imino-5-keto-4:1:2-thiobiazole.—The hydrazide (5 g.) was boiled vigorously with the acid (25 c.c.) during half an hour when sulphuretted hydrogen was evolved profusely. On cooling, a very small quantity of a crystalline solid separated which crystallised from hot water, m.p. 255°, and was identical with the endoxytriazole obtained above. The mother liquor on concentration gave a little more of the endoxytriazole and the filtrate from the latter on being evaporated to dryness left a white residue which crystallised from a small quantity of water, m.p. 177°. The yield was only about 0.5 g., but the hydrazide, when gently boiled with hydrochloric acid (d. 1.19) for only 15 minutes, gives a better yield of 177° compound (Found: N, 36.3; S, 27.5. $\text{C}_2\text{H}_3\text{ON}_3\text{S}$ requires N, 35.9; S, 27.35 per cent.).

Iminothiobiazolone and acetic anhydride.—The pale yellow solution obtained on heating the substance with acetic anhydride, on being boiled for a quarter of an hour, gave a brownish yellow solid which crystallised from water, m.p. 295°.

The free base: 3-Amino-3:5-endoxy-2:3-dihydro-4:1:2-thiobiazole (III).—The acetyl derivative dissolved in gently boiling concentrated hydrochloric acid and deposited the hydrochloride on cooling; this crystallised from dilute hydrochloric acid, m.p. 107°, and gave the free base with sodium carbonate, m.p. 235° (Found: N, 36.15; S, 27.4. $\text{C}_2\text{H}_3\text{ON}_3\text{S}$ requires N, 35.9; S, 27.35 per cent.).

The identity of the acetyl derivative, the hydrochloride and the free base with the corresponding compounds of Guha (*loc. cit.*) was established. The free base gave compounds with phenyl isocyanate m.p. 228°; with phenyl mustard oil, m.p. 256°; and with benzaldehyde m.p. 216°.

Isomer of phenylhydrazomonothiodicarbonamide (IV; m.p. 200°).—Procedure adopted in the case of hydrazodithiodicarbonamide (part IV, 8) was followed. The crystalline solid obtained on cooling the solution of the hydrazide in 2N hydrochloric acid, was filtered, washed, and recrystallised from dilute alcohol, m.p. 175° (Found: N, 26.5; S, 15.1. $\text{C}_8\text{H}_{10}\text{ON}_4\text{S}$ requires N, 26.6; S, 15.25 per cent.).

Phenylhydrazomonothiodicarbonamide and concentrated hydrochloric acid (d. 1.19): Formation of 3-thiol-3:5-endoxy-4-phenyl-2:3-dihydro-4:1:2-triazole (VII).—The hydrazide was boiled with the acid for fifteen minutes when from the clear solution a white solid began to separate; it crystallised from dilute alcohol, m.p. 184°, is soluble in alkali, gives a disulphide with iodine, m.p. 196°, and a thiomethyl ether, m.p. 90-91° (Found: N, 21.9; S, 16.3. $\text{C}_8\text{H}_7\text{ON}_3\text{S}$ requires N, 21.75; S, 16.5 per cent.).

The diacetyl derivative crystallised from dilute alcohol, m.p. 213-214° (Found: N, 15.0; S, 11.3. $\text{C}_{12}\text{H}_{11}\text{O}_3\text{N}_3\text{S}$ requires N, 15.2; S, 11.5 per cent.).

3-Phenylamino-3:5-endoxy-2:3-dihydro-4:1:2-thiobiazole (VIII).—The above diacetyl derivative was boiled with concentrated hydrochloric acid and the cooled solution diluted with water when a crystalline white solid separated out slowly and was recrystallised from dilute alcohol, m.p. 206°. It is insoluble in cold dilute alkali, but on boiling the solution becomes pale green and liberates phenyl mustard oil. It is not desulphurised with mercuric oxide (Found: N, 21.95; S, 11.95. $\text{C}_8\text{H}_7\text{ON}_3\text{S}$ requires N, 21.7; S, 11.4 per cent.). It is identical with Guha and Chakraborti's compound obtained by the action of acetic anhydride directly on the hydrazide (*loc. cit.*).

Isomer of methylmonothiohydrazodicarbonamide (V; m.p. 212°).—The isomeric hydrazide obtained by the action of 2N hydrochloric

acid melted at 168° (Found: N, 37.7; S, 21.45. $C_3H_5ON_4S$ requires N, 37.8; S, 21.6 per cent.).

3-Thiol-3:5-endoxy-4-methyl-4:1:2-triazole (IX).—The clear solution obtained by boiling the hydrazide with concentrated hydrochloric acid (d. 1.19) gave a solid on cooling which crystallised from dilute alcohol, m.p. 182° . It was soluble in cold dilute alkali, and with iodine gave a disulphide, m.p. 265° (Found: N, 31.6; S, 24.3. $C_3H_5ON_3S$ requires N, 32.06; S, 24.4 per cent.).

The *acetyl* derivative obtained from compound (IX) crystallised from dilute alcohol, m.p. $196-197^{\circ}$ (Found: N, 24.05; S, 18.4. $C_5H_7O_2N_3S$ requires N, 24.3; S, 18.5 per cent.).

3-Methylamino-3:5-endoxy-2:3-dihydro-4:1:2-thiobiazole (X).—The above acetyl derivative with boiling concentrated hydrochloric acid (d. 1.19) gave on cooling a small quantity of a crystalline solid increased on concentration; it crystallised from aqueous alcohol, m.p. 232° , and was insoluble in cold dilute alkali (Found: N, 31.85; S, 24.45. $C_3H_5ON_3S$ requires N, 32.06; S, 24.4 per cent.).

Isomer of allylhydrazomonothiodicarbonamide (m.p. 190° ; VI).—The isomeric hydrazide after crystallisation from alcohol melted at 192° . The difference between the melting points of the two isomeric hydrazides was only 2° , but a melting point of the mixture was $8-9^{\circ}$ lower (Found: N, 32.42. $C_5H_{10}ON_4S$ requires N, 32.18 per cent.).

3-Thiol-3:5-endoxy-4-allyl-2:3-dihydro-4:1:2-triazole (XI).—The above hydrazide treated with concentrated hydrochloric acid as with the other hydrazides gave a product crystallising from dilute alkali; the disulphide melted at 174° (Found: N, 26.6; S, 20.3. $C_5H_7ON_3S$ requires N, 26.75; S, 20.4 per cent.).

The *acetyl* derivative from the triazole (X) and acetic anhydride had m.p. 171° (Found: N, 21.3; S, 15.74. $C_7H_9ON_3S$ requires N, 21.11; S, 16.08 per cent.).

3-Allylamino-3:5-endoxy-2:3-dihydro-4:1:2-thiobiazole (XII).—The acetyl derivative was deacetylated by boiling concentrated hydrochloric acid, and the solution on concentration deposited the free *endoxytriazole* as a white solid which crystallised from dilute alcohol, m.p. $210-211^{\circ}$. The substance is insoluble in cold dilute alkali (Found: N, 26.7; S, 20.32. $C_5H_7ON_3S$ requires N, 26.75; S, 20.4 per cent.).

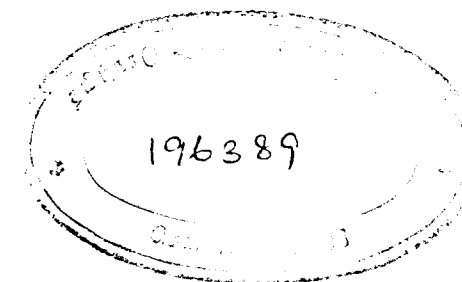
SUMMARY.

The isomeric form of hydrazomonothiodicarbonamide could not be obtained, owing to ready decomposition; but isomers of the substituted hydrazides have been isolated. Besides Freund's iminothiobiazolone, m.p. 177° , the unsubstituted hydrazide has yielded *3:5-endoxytriazole*, m.p. 255° (I) and *3:5-endoxy-3-aminothiobiazole*, m.p. 235° (III) on treatment with hydrochloric acid of different concentration.

Hydrochloric acid (d. 1.16 and 1.19) behaved similarly in effecting ring-closure of the mono-substituted hydrazides of this series, giving rise to *endoxytriazole-thiols* VII, IX and XI which in their turn were converted by acetylation followed by hydrolysis into *endoxythiobiazoles* VIII, X and XII by an interchange of position between the group NR of the nucleus and the sulphur atom.

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