CONSTITUTION OF THE SO-CALLED DITHIOURAZOLE OF MARTIN FREUND.

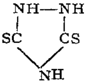
RING CLOSURE OF HYDRAZO-DITHIO-DICARBONAMIDE AND ITS MONO- AND DI-SUBSTITUTED DERIVATIVES.

PART VII. ACTION OF HEAT.
PART VIII. ACTION OF SODIUM HYDROXIDE (*CONTD.*).
PART IX. ACTION OF HYDROCHLORIC ACID (*CONTD.*).
PART X. ACTION OF ACETIC ANHYDRIDE (*CONTD.*).

By P. C. Guha and D. R. Mehta.

INTRODUCTION.

The ring closing action of various reagents, *e.g.*, carbonyl chloride, sodium hydroxide, hydrochloric acid, ferric chloride, hydrogen peroxide, iodine, hydrazine hydrate, acetic anhydride, etc., upon hydrazodithio- and monothio-dicarbonamides and their alkyl and aryl substituted derivatives has been studied by a number of workers, *viz.*, Freund, Busch, Guha, Fromm, Arndt and others with their collaborators and all the four possible types of triazoles and thiobiazoles, *viz.*,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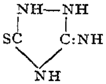
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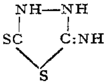
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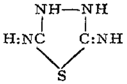
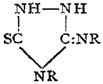

(D)

have been isolated. Freund and Wischewiansky[1] studied the action of carbonyl chloride on hydrazodithio-dicarbonamides (RHN.SC. NH.NH.CS.NHR) and attributed the triazole formula (E) to the compound formed by the elimination of a molecule of hydrogen sulphide.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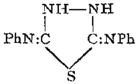
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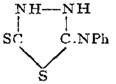
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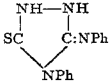
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Freund and Imgart[2] *subjected a number of hydrazides of the* above type to the action of boiling concentrated hydrochloric acid with the result that in all cases (excepting the diphenyl hydrazide which gave only the acidic product), they isolated two types of compounds, one acidic and the other basic in nature, which were regarded

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[1] *Ber.*, 1893, **26**, 2877.

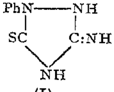
[2] *Ibid.*, 1895, **28**, 946; 1896, **29**, 859.

erroneously as dithiourazole (type A) and iminothiourazole (type B) respectively

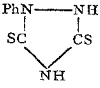
Walther[3] while trying the action of hydrazine on *sym*-diphenyl-thio-carbazide also obtained the compound F (*vide supra*) to which, he assigned the formula PhN : C : N . NH . CS . NHPh. Freund and Wischewiansky[1] considered the same substance to be, 4-N-phenyl-3-phenylimino-5-thio-tetrahydro-1 : 2 : 4-triazole (H). In their attempt to prepare a derivative of amino-carbodi-imide, NH : C : N . NH_2, by heating PhNH . CS . NH . NH . CS . NHPh with mercuric oxide, Busch and Schmidt[4] found the reaction product to consist of a mixture of diphenyliminotetrahydrothiodiazole (F) and anilino-thiol-thiodiazole (G) and they criticised the dithiourazole structure of Freund and suggested (C) as the correct formula. Guha[5, 6] definitely established that Freund's supposed 'Dithiourazoles' were all thio : iminothiobiazoles of type C, as every one of them (*i*) contained only one atom of hydrogen replaceable by Na, K or Ag, (*ii*) lost on oxidation with iodine only *one* atom of hydrogen, and not *two* (as supposed by Freund) from one molecule of the substance, and that (*iii*) one of the acetyl groups (being thiol-acetyl) of the diacetyl compound can be easily hydrolysed giving rise to a stable (connected with nitrogen) mono-acetyl derivative, (*iv*) and from different methods of preparation of acetyl-methyl and diacetyldisulphides. Busch and Schmidt[4] have also proved that the basic compounds of the composition $C_2H_2R_2N_4S$ obtained by Freund and Imgart were 3 : 5-diimino-tetrahydro-4 : 1 : 2-thiobiazoles (D).

Arndt and Milde[7] obtained by the action of alkali and acids upon the mono- and di-thiomethyl and benzyl ethers of the hydrazides, derivatives of compounds of types A, B and C. They synthesised real dithiourazole by the action of hydrazine hydrate upon methyl trithio-allophanate NH_2.CS.NH.NH.CS.SMe.

Fromm[8] by the action of phenyl hydrazine on perthiocyanic acid obtained 3-imino-5-thio-1-phenyl-tetrahydro-4 : 1 : 2-triazole (I) and 3 : 5-dithio-1-phenyl-tetrahydro-4 : 1 : 2-triazole (J).



(I)



(J)

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[3] *J. pr. Chem.*, 1906, **74**, ii, 1222.

[4] *Ber.*, 1913, **46**, 2240.

[5] *J. Amer. Chem. Soc.*, 1922, **44**, 1502.

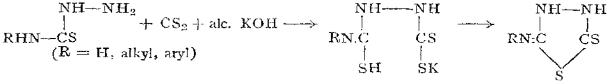
[6] *Ibid.*, 1925, **47**, 386.

[7] *Ber.*, 1921, **54**, 2089.

[8] *Annalen*, 1906, **348**, 174.

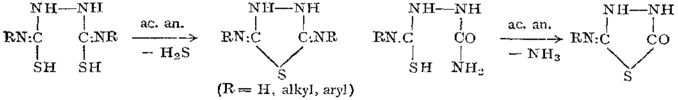
In a subsequent paper Fromm, Kayser, Briegleb and Fohrenbach[9] obtained by the action of hydrazine hydrate on phenyldithiobiuret, (*i*) 3-thio-5-phenylimino- and (*ii*) 3-imino-5-phenylimino-tetrahydro-1 : 2 : 4-triazoles. Further, by the action of hydrazine hydrate on perthiocyanic acid they obtained dithiourazole and iminothiourazole and by investigation on the substances $C_2H_3N_3S_2$ and $C_2H_4N_4S$, of Freund and Imgart[2] arrived at the same conclusion as Guha, Busch and Schmidt that these substances are not triazoles but thiodiazoles (C and D respectively).

Guha[5] and Guha and Ray[6] discovered other methods by which 3 : 5-imino : thio-tetrahydrothiobiazoles (type C) could be synthesised, the most important and of the widest applicability being the one in which thiosemicarbazide and its 4-R-substituted derivatives react with carbon disulphide in presence of alcoholic potash.

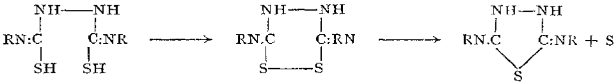


(type C)

Guha[10] made a systematic study of the ring closure of these hydrazo compounds with the aid of acetic anhydride, and obtained 3 : 5-diimino-4 : 1 : 2-thiodiazole (type D) and a large number of its mono- and di-substituted derivatives. Guha and Chakraborti[11] while studying the ring closure of differently substituted (mono and di) hydrazomonothiodicarbonamides with acetic anhydride, obtained iminothiobiazolones and in one case also an iminothioltriazole.



Fromm, Layer and Nerz[12] observed that 3 : 5-diamino-4 : 1 : 2-thiodiazoles are the main products when hydrogen peroxide, iodine, or phenyl hydrazine react with hydrazodithiodicarbonamides.



(type D)

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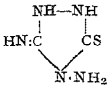
[9] *Annalen*, 1922, **426**, 313.

[10] *J. Amer. Chem. Soc.*, 1923, **45**, 1036.

[11] *J. Ind. Chem. Soc.*, 1929, **6**, 99.

[12] *Annalen*, 1923, **433**, 1.

Purgotti and Vigano[13] obtained a feebly basic product, m.p. 198°, by the action of hydrazine on hydrazodithiodicarbonamide, which they regarded as dithio-*p*-urazine (N). Arndt and Bielich[14] repeating their experiments under various conditions observed the simultaneous formation of 4-N-amino-3-imino-5-thio-4 : 1 : 2-tetrahydrotriazole (K), 4-N-amino-dithiourazole (L) and probably also the hydrazide (M).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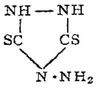
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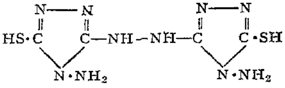
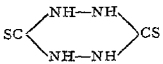

(M)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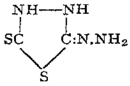
(O)

Guha and De[15] obtained an acidic compound, m.p. 202–3°, by the action of potassium ethyl xanthate upon thiocarbohydrazide, which they regarded as dithio-*p*-urazine (N) and suggested the probability of Purgotti and Vigano's compound being (O).

Guha and Sen[16] obtained by the action of urea upon 4-substituted thiosemicarbazides four types of compounds, namely, 4-R-5-keto-3-thiol-dihydro-4 : 1 : 2-triazole, 5-keto-3-R-amino-dihydro-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 Schander,[17] Arndt, Milde and Tschenscher,[18] and by Fromm and Nehring,[19] ketoaminothiobiazoles by Busch,[20] and Nirdlinger and Acree.[21] Lastly, though Schneider,[22] Marckwald,[23] Busch[20] and Nirdlinger and Acree[21] have prepared the derivatives of *endo*xy-, *endo*thio-, and *endo*imino- triazoles and thiobiazoles by

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[13] *Gaz.*, 1901, **31**, ii, 563.

[14] *Ber.*, 1923, **56**, 809.

[15] *J.C.S.*, 1924, **125**, 1215.

[16] *J. Ind. Chem. Soc.*, 1927, **4**, 43.

[17] *Ber.*, 1896, **29**, 2506.

[18] *Ibid.*, 1922, **55**, 341.

[19] *Ibid.*, 1923, **56**, 1370.

[20] *Ibid.*, 1901, **34**, 320, 2328; 1902, **35**, 973; 1904, **37**, 2333; 1909, **42**, 4763; 1911, **44**, 561, 1580.

[21] *J. Amer. Chem. Soc.*, 1922, **44**, 224.

[22] *J. pr. Chem.*, 1890, **67**, 263.

[23] *Ber.*, 1892, **25**, 3113; 1896, **29**, 2923.

methods entirely different from that of Guha and Sen,[16] the parent *endo*xytriazole was prepared for the first time by Guha and Sen.[16] Guha and Guha[24] prepared a large number of thiobiazoles and oxdiazoles by the action of various ring closing agents upon the 4R-thiosemicarbazide- and 4R-semicarbazide-dithiocarboxylates.

Different authors have attributed different melting points to apparently identical substances as can be seen from the following table.

Names of compounds	Authors and m.p.'s
(i) 4-Phenyldithio-urazole	Arndt, Milde and Tschenscher,[25] 216° Fromm,[12] 230°
(ii) 3 : 5-Imino : thio-tetrahydro-1 : 2 . 4-triazole	Arndt and Milde,[7] 303° Fromm,[9] 298°
(iii) 3-Phenylimino-5-thio-tetrahydro-1 : 2 : 4-triazole	Fromm,[9] 268° Arndt,[26] 275°
(iv) 3-Phenylimino-4-phenyl-5-thio-tetrahydro-1 : 2 : 4-triazole	Arndt,[7] 205° ; Fromm,[12] 206° ; Guha,[16] 210°
(v) 3 : 5-Imino : thio-4-N-amino-tetrahydro-1 : 2 : 4-triazole	Fromm,[12] 217° Arndt,[14] 240–42°
(vi) 3-Imino-5-thio-tetrahydro-4 : 1 : 2-thiobiazole	Freund and Imgart,[2] 245° Guha,[5] 244°, 233°, 224° Fromm,[27] 228–35°
(vii) 3-Phenylimino-5-thio-tetrahydro-4 : 1 : 2-thiobiazole	Freund and Imgart,[2] 219° ; Guha,[5] 208° , Guha and Guha,[24] 215°
(viii) 3 : 5-Di-imino-tetrahydro-4 : 1 : 2-thiobiazole	Freund and Imgart,[2] 223° Guha,[10] 210° , Fromm,[12] 210°
(ix) 3 : 5-Diphenylimino-tetrahydro-4 : 1 : 2-thiobiazole	Freund,[1] 240° Guha,[10] 247°
(x) Thiourazole	Arndt,[18] 206° ; Fromm,[19] 202°
(xi) 4-Phenyl-thiourazole	Arndt,[18] 196° ; Fromm,[19] 193° ; Guha,[16] 197°
(xii) 3-Imino-tetrahydro-4 : 1 : 2-thiobiazole-5-one	Freund[17] and Arndt,[18] 177° ; Guha,[10] 235°

All these led Guha to suspect the possibility for the existence of some sort of isomerism in these compounds.

By a careful study of the action of hydrochloric acid under different concentrations and duration of treatment, Guha and Janniah[28]

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[24] *J. Ind. Chem. Soc.*, 1927, 4, 161; 239.

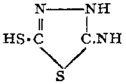
[25] *Ber.*, 1922, **55**, 341.

[26] *Ibid.*, 1922, **55**, 12.

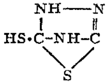
[27] *Ann.*, 1922, **426**, 313.

[28] *J. Amer. Chem. Soc.*, 1930, **52**, 4860.

succeeded in showing that hydrazodithiodicarbonamide (m.p. 223°), gives an isomeric hydrazide, m.p. 203°, yielding derivatives (acetyl, methyl ether) identical with those of the parent hydrazide. From their interconvertibility and difference in their absorption bands they concluded that the 223° variety exists in the monothiol form $NH_2.CS.NH.NH.C(SH):NH$ whilst the new variety in the dithiol form $NH:(HS)C.NH.NH.C(SH):NH$. Similar cases of isomerism have been observed with the alkyl and aryl substituted mono- and dithio-hydrazides. Imino-thiol-dihydro-thiobiazole was isolated as an intermediate product during the formation of Freund's "dithio-urazole" which was shown to be *endo*-imino-thiol-dihydro-thiobiazole (P); the latter has been found to be formed either by the prolonged action of conc. hydrochloric acid on the hydrazide of the imino-thiol-thiobiazole (C), or from both of them by acetic anhydride treatment followed by hydrolysis with conc. hydrochloric acid (*d*, 1.19).



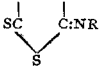
(C, m.p. 234°)



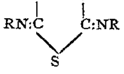
(P, m.p. 245°)

The action of 2N hydrochloric acid on mono- and di-substituted hydrazodithiodicarbonamides[29] 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-thiobiazoles (C) and *endo*iminothiolthiobiazoles (P).

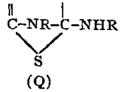
In the case of disubstituted hydrazides, hydrochloric acid (*d*, 1.16) gives the alkali-soluble R-iminothio-tetrahydro-thiobiazoles (type C) as the main product; concentrated acid (*d*, 1.19) on the other hand, yields 3: 5-di-R-imino-tetrahydro-thiobiazole (type D), with a small quantity of alkali soluble R-imino: thio-thiobiazoles. The acetyl derivative of di-R-iminothiobiazole gives on hydrolysis with hydrochloric acid (*d*, 1.16) the di-R-iminothiobiazole (type D) and with hydrochloric acid (*d*, 1.19) 3: 5-*endo*-R-imino-3R-imino-2: 3-dihydro-thiobiazole (Q).



(type C)



(type D)



(R=Ph, *o*-tolyl)

(Q)

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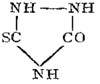
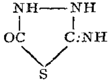
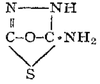
[29] Janniah and Guha, *J. Ind. Inst. Sci.*, 1933, 16A, 11.

Freund and Schander[17] by treating hydrazomonothiodicarbonamide H_2N-CS-NH-NH-CO-NH_2 with strong hydrochloric acid, obtained a compound, m.p. 177°, which they regarded as monothiourazole (R), proved later by Busch and Lotz[30] to be iminothiobiazolone (S). Guha[10] discovered that the same hydrazide as also the iminothiobiazolone (S) on being treated with acetic anhydride, followed by hydrolysis of the acetyl compound, gave an isomeric compound melting at 235°. From the difference observed in the chemical behaviour and absorption spectra of these two substances (m.p.'s 177° and 235°) Guha and Janniah[29] attributed the *endo*-structure (T) to the latter.


(R)


(S)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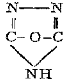
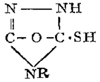
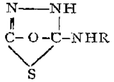

(U)

In a later paper Guha and Janniah[29] found that the isomeric form of hydrazomonothiocarbonamide could not be obtained, owing to ready decomposition; but isomers of the substituted hydrazides had been isolated. Besides iminothiobiazolone m.p. 177°, the unsubstituted hydrazide yielded 3 : 5-*endo*xytriazole, m.p. 255° (V), and 3 : 5-*endo*xy-3-aminothiobiazole, m.p. 235°, 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 *endo*xytriazole-thiols (V) which in their turn were converted by acetylation followed by hydrolysis into *endo*xythiobiazoles (W) by an interchange of position between the group (:NR) and the sulphur atom.


(V)


(W)

THEORETICAL.

Although it is well known that hydrazodithiodicarbonamide and most of its mono- and di-substituted derivatives suffer decomposition at their fusion temperature, no record seems to be available in chemical literature about any systematic study of the products left after fusion excepting a casual observation made by Busch and Schmidt[4] that the diphenyl substituted hydrazide PhNH.CS.NH.NH.CS.NHPh gives rise to diphenylimino-tetrahydrothiodiazole on fusion.

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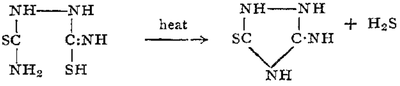
[30] *J. pr. Chem.*, 1914, **90**, ii, **257**.

So, a thorough and systematic study of the behaviour of these hydrazides on heating was undertaken, in the hope that it might furnish a convenient method for the preparation of one or more of the various types of thiodiazole and triazole derivatives known to be formed by the action of different ring closing agents. This expectation, as will be seen, has been amply realised, besides a comparative study of the yields of the products as obtained from the hydrazides on treatment with different ring closing agents has also proved to be of considerable interest.

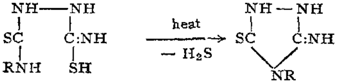
Hydrazodithiodicarbonamide (unsubstituted) when kept for ten minutes at 210° C. gives 3:5-imino:thio-tetrahydro-1:2:4-triazole (I) the reaction proceeding evidently as follows:



(I)

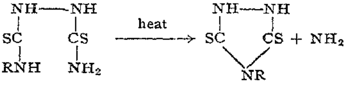
Iminothio-tetrahydrotriazole and its substitution products have been prepared by (i) Arndt and Milde,[7] Arndt, Milde and Tschenscher[18] and by Fromm[12] by the action of alkali on the hydrazodithiodicarbonamide; (ii) by Fromm[9] by the action of hydrazine hydrate upon perthiocyanic acid; (iii) by Arndt[26] and Fromm[9] by the action of hydrazine on phenyldithiobiuret; (iv) by Guha and Sen[16] by the action of urea on 4-R-thiosemicarbazides and (v) by Guha and Chakraborty[11] by the action of acetic anhydride on aryl-hydrazo-monothiodicarbonamide.

Mono-substituted hydrazides give 4-N-aryl-3:5-iminothio-tetrahydro-4:1:2-triazoles (II, R = Ph; III, R = *o*-tolyl; IV, R = *p*-tolyl) by the loss of hydrogen sulphide.



(II, III, IV)

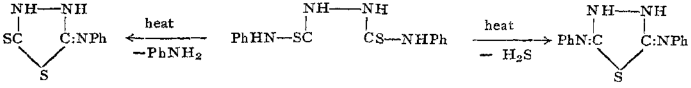
If the ring-closing action of alkali upon mono-substituted hydrazides is compared with that of heat, it is found, that two compounds, *viz.*, 4-R-3:5-dithio-4:1:2-triazoles and 3-imino-5-thio-tetrahydro-4-R-4:1:2-triazoles are obtained with alkali; whereas, only compounds of the latter type are obtained by the action of heat. Identity of the compound (II) obtained by heat from the mono-phenyl substituted hydrazide (Ph NH.CS.NH.NH.CS.NH_2) has been established with that obtained by alkali treatment. The identities of the compounds III and IV obtained for the first time from *o*-tolyl and *p*-tolyl mono-substituted hydrazides by alkali treatment as also by fusion have been established. 4-*o*-tolyl-3 : 5-dithio-tetrahydro-4 : 1 : 2-triazole (V) and 4-(*p*)-tolyl-3 : 5-dithio-tetrahydro-4 : 1 : 2-triazole (VI) have also been isolated for the first time by reacting the corresponding mono-substituted hydrazides with alkali.



(V, VI)

3 : 5-dithio-tetrahydro-1 : 2 : 4-triazole (dithiourazole) and its derivatives have been made (i) by Arndt and Milde[7] by the action of hydrazine hydrate upon methyltrithioallophanate and (ii) by Fromm,[9] by the action of the same reagent upon perthiocyanic acid, (iii) by the action of ferric chloride upon phenyl-hydrazodithiodicarbonamide by Arndt,[12] (iv) by the action of 2N.NaOH upon Ph NH.CS.NH.NH CS.NH_2 by Arndt,[18] etc.

The action of heat on the diphenyl-substituted hydrazide Ph NH-CS.NH.NH.CS.NH Ph results in the formation of two compounds, one (VII) soluble and the other (VIII) insoluble in alkali, the former formed by the loss of a molecule of aniline and the latter by the loss of a molecule of H_2S respectively.

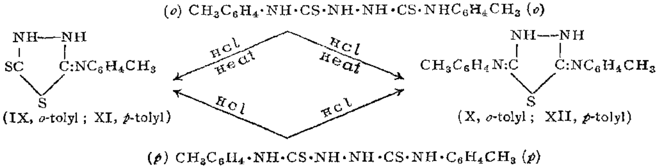


(VII)

(VIII)

Freund and Imgrat[2] observed the formation of only one product of acidic nature (VII) by the action of strong hydrochloric acid upon the diphenyl-substituted hydrazide, whereas Janniah and Guha[29] have proved the formation of two compounds, one soluble in alkali (VII) and another insoluble (VIII); they have further observed that the former 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 the alkali-insoluble compound is obtained as the main product. It was thought worthwhile to confirm their results by extending the work further and studying the action of hydrochloric acid upon some more diaryl-substituted hydrazides. The action of concentrated hydrochloric acid has now been tried upon diphenyl, *o*-ditolyl and *p*-ditolyl-substituted hydrazides.

The compounds (VII and VIII) now obtained by the action of heat on the diphenyl hydrazide (PhNH.CS.NH.NH.CS.NHPh) have been proved to be identical with the corresponding compounds obtained by boiling the hydrazide with hydrochloric acid of different concentrations according to the method of Janniah and Guha.[29] The corresponding di-*o*- and di-*p*-tolyl hydrazides have been subjected to the action of concentrated hydrochloric acid and heat. While the *o*-ditolyl-substituted hydrazide yields both of the products (IX) and (X) in both ways, the *p*-ditolyl-substituted hydrazide gives only the alkali-insoluble compound (XII) by the action of heat, while it gives only the acidic product (XI) on treatment with hydrochloric acid.



(IX, *o*-tolyl ; XI, *p*-tolyl)

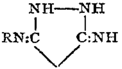
(X, *o*-tolyl ; XII, *p*-tolyl)

The *o*-tolyl compound (X) forms an azo compound on oxidation. The following derivatives have now been prepared from 3-thio-5-*o*-tolylimino-tetrahydro-4 : 1 : 2-thiobiazole (IX), *viz.*, disulphide, methyl, benzyl, methyl : acetyl (also acetyl : methyl), diacetyl, monoacetyl, acetyl : benzyl (also benzyl : acetyl) ; the formation of these derivatives being in perfect agreement with the formula as established by Guha.[5]

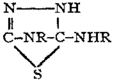
o-Ditolyl-substituted hydrazide gives with concentrated hydrochloric acid mainly the acidic compound (IX), with a very small quantity of the compound (X). The acidic compound after repeated crystallisation melts at 214° (*cf.* Janniah and Guha,[29] m.p. 195°).

One word may be said with regard to the comparative yields obtained by the two methods. Hydrochloric acid and heat give almost equal yields of 3-thio-5-phenylimino-tetrahydro-4 : 1 : 2-thiodiazole (VII) from the diphenyl-substituted hydrazide, the heat reaction favours the formation of 3 : 5-diphenylimino-tetrahydro-4 : 1 : 2-thiodiazole (VIII). In the case of di-*o*-tolyl hydrazide, the hydrochloric acid reaction favours the formation of the compound of the former type and gives only a very poor yield of the compound of the latter type, of which a better yield is obtained by the action of heat. In the case of the di-*p*-tolyl hydrazide, the hydrochloric acid reaction does not give the alkali-insoluble compound at all, while the acidic compound is not formed by the action of heat. It seems in general that hydrochloric acid reactions favour the formation of acidic compounds whereas, the heat reactions favour the formation of alkali insoluble products.

It is interesting to note that acetic anhydride brings about ring closure[10, 11, 29] of hydrazodithiodicarbonamide and its mono- and di-substituted compounds yielding acetyl-derivatives of di-R-imino-tetrahydrothiobiazoles (R = H, alkyl, aryl), which when hydrolysed with hydrochloric acid of different concentrations yield isomeric R-imino-thiodiazoles.[29] To throw some further light on this phenomenon, the action of acetic anhydride has now been studied with *o*- and *p*- mono- and di-tolyl hydrazodithiodicarbonamides. Mono-*o*- and *p*-tolyl-hydrazides give on treatment with acetic anhydride followed by hydrolysis, 5-tolylimino-3-imino-tetrahydrothiodiazoles (XIII, R = *o*-tolyl; XIV, R = *p*-tolyl). The di-*o*-tolyl-substituted hydrazide gives, on similar treatment, a compound m.p. 223° (the hydrolysing agent being concentrated hydrochloric acid) which is not identical with the compound (X) obtained by the action of hydrochloric acid and heat (m.p. 217°), although the latter product as obtained by the action of HCl and heat are identical.



(XIII, XIV)



(XV)

The compositions of compound (X) (m.p. 217°) and (XV) (m.p. 223°) are identical. The compound (X) as obtained by the action of hydrochloric acid and heat, gives on acetylation followed by hydrolysis, the compound (XV), m.p. 223°. The new compound (XV) gives an acetyl derivative identical with that derived from compound (X). In the light of the above facts, it is proposed to attribute the structure 2 : 3-dihydro-3-*o*-tolylimino-3 : 5-*endo*-*o*-tolylimino-4 : 1 : 2-thiobiazole (XV) to the new compound.

In the case of di-*p*-tolyl hydrazodithiodicarbonamide, it is rather unexpected that the final product now obtained by the hydrolysis of the acetyl compound is found to be identical with that obtained by the action of heat and hydrochloric acid (XII).

EXPERIMENTAL.

PART VII. ACTION OF HEAT.

Action of heat upon hydrazodithiodicarbonamide: Formation of 3, 5-*imino* : *thio-tetrahydro*-1 : 2 : 4-*triazole* (I).—Hydrazodithiodicarbonamide (15 g.) was placed in a small conical flask and heated in an oil-bath between 210° and 215° for about 10 to 15 minutes. After cool ing, the contents were treated with 2N sodium hydroxide solution when almost the whole quantity went into solution. It was the filtered, acidified with concentrated hydrochloric acid and the precipi tate repeatedly crystallised from hot water using animal charcoal The colourless powder melted at 298°.5 (yield, 2 g.). Mixed m.p of this substance with that obtained by the action of hydrazine hydrat on perthiocyanic acid (*Annalen,* 1922, **426**, 313) showed no depres sion.

Acetyl derivative was prepared by heating the compound (I) (1 g.) with acetic anhydride (7 c.c.) under reflux for about 10 minute when a clear solution was obtained. It was then poured into wate (300 c.c.) and stirred well and the white insoluble precipitate crystallised from hot water, m.p. 325° (decomp.).

Action of heat upon monophenyl-hydrazodithiodicarbonamide: Formation of 4-phenyl-3:5-imino:thio-tetrahydro-1:2:4-triazol (II).—The hydrazide (10 g.) was heated at a temperature between 180° and 185° during about 15 minutes. The contents of the flask after cooling were dissolved in 2N sodium hydroxide solution, filtered and acidified with hydrochloric acid. The precipitate was purified by dissolving in a large quantity of dilute ammonia, reprecipitating with hydrochloric acid and finally crystallising from alcohol in colourless needles, m.p. 265°. Mixed m.p. with Arndt and Milde's compound (*Ber.,* **55**, 341) showed no depression. The identity was further established by preparing acetyl derivatives from samples obtained by the two different methods, mixed m.p. remaining undepressed (Found: N, 26.32; S, 15.43. $C_8H_8N_4S$ requires N, 26.66; S, 15.24 per cent.).

Acetyl derivative of (II).—The above compound (2 g.) together with a little fused sodium acetate was heated with acetic anhydride (7 c.c.) under reflux during about half an hour. It was poured into water and stirred well, till the liquid layer at the bottom had solidified. crystallised from benzene in colourless needles, m.p. 163°–64°.

*Action of heat upon mono-*o*-tolylhydrazodithiodicarbonamide: Formation of 4-*o*-tolyl-3:5-imino:thio-tetrahydro-1:2:4-triazole* (III).—The hydrazide (10 g.) was heated at 180–85° for about 15 minutes. The cold melt was worked up as before, and crystallised from alcohol in colourless small cubes, m.p. 231°. It is insoluble in N/2 sodium carbonate, but soluble in 2N caustic alkali from which it can be reprecipitated unchanged. It contains a molecule of water of crystallisation. It is moderately soluble in almost all organic solvents (Found: N, 24.85; S, 14.5. $C_9H_{10}N_4S,H_2O$ requires N, 25.0; S, 14.3 per cent.).

Identity of (III) has been established with that obtained by the action of 2N sodium hydroxide solution (described later, p. 56) on the above hydrazide, by taking the mixed melting point and preparing different derivatives.

The *acetyl derivative* crystallised in beautiful colourless leaflets from alcohol, m.p. 205° (Found: N, 22.9. $C_{11}H_{12}ON_4S$ requires N, 22.59 per cent.).

The methyl derivative.—Compound (III) was dissolved in 2N sodium hydroxide solution, filtered and dimethyl sulphate added to it drop by drop under shaking and avoiding excess. A thick liquid layer separated at the bottom, which solidified on cooling. It crystallised from water in colourless prisms, m.p. 142°. It is very soluble in alcohol, difficultly soluble in cold but easily in hot water.

*Action of heat upon mono-*p*-tolylhydrazodithiodicarbonamide: Formation of* 4-p*-tolyl-*3 : 5*-imino* : *thio-tetrahydro-*1 : 2 : 4*-triazole* (IV).—The hydrazide (5 g.) was kept at 180° for about 10 minutes. The cold melt almost completely dissolved in 2N sodium hydroxide solution, with a small residue which could not be purified and hence neglected. The filtrate on acidification with concentrated hydrochloric acid gave a yellow precipitate, which was purified by reprecipitating with concentrated hydrochloric acid from its solution in dilute ammonia and was finally crystallised from alcohol in colourless cubes, m.p. 277° (yield, 0.8 g.). It is moderately soluble in almost all organic solvents but insoluble in water.

Identity of this compound (IV) was established with that obtained by the action of 2N sodium hydroxide on the above hydrazide (described later, p. 57) by taking the mixed m.p. and preparing acetyl and methyl derivatives from both.

The *acetyl derivative* crystallised from alcohol in colourless needles, m.p. 160°.

The *methyl derivative* was prepared in the usual way, and crystallised from hot water, m.p. 142°.

Action of heat upon diphenylhydrazodithiodicarbonamide: Formation of 5*-phenylimino-*3*-thio-tetrahydro-*4 : 1 : 2*-thiodiazole* (VII) *and* 3 : 5*-diphenylimino-tetrahydro-*4 : 2 : 1*-thiodiazole* (VIII). The hydrazide (10 g.) was heated as before in an oil-bath, at 180°, *i.e.*, a few degrees below its melting point, for 10 to 15 minutes. The cold melt on treatment with 2N sodium hydroxide solution dissolved partially and was filtered. The alkaline filtrate gave on acidification with concentrated hydrochloric acid a precipitate which crystallised from alcohol in beautiful yellow needles, m.p. 219°. The mixed m.p. of this compound (VII) with that, obtained by the action of concentrated hydrochloric acid[29] on the above hydrazide, remained undepressed.

Isolation of compound (VIII).—The alkali-insoluble residue obtained above, after being thoroughly washed with water, was crystallised from a large quantity of alcohol in shining colourless leaflets, m.p. 248°. Identity of this substance with that obtained by the action of concentrated hydrochloric acid on the hydrazide (*J. Ind. Inst. Sci.*, 1933, **16A**, 16) was established by mixed melting point (undepressed). The acetyl derivative prepared from samples obtained by both the methods crystallised in colourless columns, m.p. 224°.

Curiously enough, the above diphenyl hydrazide when heated above 200° for about 15 minutes and treated as in the foregoing experiments, gives an alkali-insoluble compound m.p. 232–33° (Found: N, 21.0 per cent.) crystallising in prisms from alcohol, and an alkali-soluble product (purified by converting it to the acetyl derivative followed by hydrolysis) melting at 206°. The acetyl derivative crystallised from alcohol in colourless needles, m.p. 174° (Found: N, 18.6 per cent.). The yield being extremely poor, no further work could be done with these compounds.

*Action of heat upon di-*o*-tolyl-hydrazodithiodicarbonamide: Formation of* 5-o-*tolyl*-3: 5-*thio*: *imino-tetrahydro*-4: 1: 2-*thiodiazole* (IX) *and* 3: 5-*di*-o-*tolylimino-tetrahydro*-4: 1: 2-*thiodiazole* (X).—The hydrazide (10 g.) was heated at 170° for 15 minutes and worked up as in the case of the diphenyl substituted hydrazide. The alkaline filtrate on acidification gave a white precipitate which, after being washed with water, was crystallised from dilute alcohol in microscopic needles, m p. 213–14° (yield, 5 g.). The same compound was also obtained by the action of concentrated hydrochloric acid on the di-*o*-tolylhydrazide and the mixed m.p. of the samples obtained by both of these methods remained undepressed (Found: N, 18.85. $C_9H_9N_3S_2$ requires N, 18.83 per cent.).

The *disulphide of* (IX) was prepared by adding drop by drop a 2.5 per cent. solution of iodine to the compound (1 mol.) dissolved in aqueous potash (1 mol.). The yellow precipitate, after being washed with water and a little alcohol, was crystallised from a large quantity of alcohol in glistening yellow leaflets, m.p. 200° (Found: N, 18.5. $C_{18}H_{16}N_6S_4$ requires N, 18.9 per cent.).

The *methyl derivative* was prepared by heating under reflux a mixture of compound IX (1 mol.) dissolved in methyl alcoholic potash (1 mol.) and an excess of methyl iodide, for about an hour on a water-bath. The reaction mixture was evaporated to dryness and the residue after being washed with water crystallised from alcohol in beautiful long colourless needles, m.p. 158° (yield, 2.7 g. from 4 g. of compound IX) (Found: N, 17.8. $C_{10}H_{11}N_3S_2$ requires N, 17.7 per cent.).

The *benzyl derivative* was obtained by heating under reflux a mixture of the thiol compound (1 mol.), aqueous potash (1 mol.) and benzyl chloride (1 mol.) dissolved in alcohol for about 2 hours. After the removal of some alcohol by evaporation, and on addition of water to it, a white precipitate was obtained which crystallised from alcohol, m.p. 112–13° (yield 1.5 g. from 4 g. of compound IX).

The methyl-acetyl derivative.—The methyl derivative (1 g.) was heated with acetic anhydride (5 g.) for about 10 minutes and then poured into a large volume of water. The heavy layer formed at the bottom, solidified after about 3 hours and after being carefully washed with water, was crystallised from alcohol in colourless plates, m.p. 123°. The same acetyl-methyl derivative was obtained (as established by mixed melting point) by methylation of the mono-acetyl derivative (to be described below).

The *diacetyl derivative* was prepared by heating compound (IX) (2 g.) under reflux with acetic anhydride (5 g.). After the substance had gone into solution, it was heated gently for about 3 to 4 minutes, and then poured into a large volume of water under stirring. The separated solid was then filtered, washed with water, and crystallised from alcohol in glistening golden yellow plates, m.p. 145° (Found: N, 13.63. $C_{13}H_{13}O_2N_3S_2$ requires N, 13.67 per cent.).

The *monoacetyl derivative* was obtained as in the foregoing experiment by prolonging the heating for ten minutes more, when a solid began to separate. After 5 minutes' more heating, some water was added to the liquid, and the reaction product allowed to cool. The separated solid was filtered, washed free from acetic acid and crystallised from a large quantity of alcohol in colourless needles, m.p. 249° (Found: N, 15.2. $C_{11}H_{10}ON_3S_2$ requires N, 15.8 per cent.).

Conversion of the di- into the mono-acetyl derivative was effected by repeatedly recrystallising the former from dilute alcohol. The same change can also be effected by heating the diacetyl compound for 10 minutes with dilute acetic acid.

The *acetyl-benzyl derivative* was obtained from the above monoacetyl derivative on treatment with benzyl chloride in presence of alkali. The product crystallised from alcohol in colourless needles, m.p. 93°.

The identical *benzyl-acetyl derivative* was also obtained by acetylating the above benzyl derivative.

Isolation of 3: 5-*di*-o-*tolylimino-tetrahydro*-4: 1: 2-*thiodiazole* (X).—The alkali-insoluble residue obtained after treating the cold melt with 2N sodium hydroxide solution, was well washed with water and crystallised from a large quantity of alcohol in colourless leaflets, m.p. 217° (yield, 0.6 g.). Identity of this compound with that obtained by the action of hydrochloric acid[29] was established by taking their mixed melting point as well as by the preparation of an identical acetyl derivative from both.

The *acetyl derivative* crystallised from alcohol, in colourless needles, m.p. 251°.

Action of heat upon di-p-*tolyl-hydrazodithiodicarbonamide*: *Formation of* 3: 5-*di*-p-*tolylimino-tetrahydro*-4: 1: 2-*thiodiazole* (XII).—The hydrazide (10 g.) was heated at 185° for about 15 minutes and after cooling, was treated with 2N sodium hydroxide solution, which dissolved only a very small quantity, leaving the major portion insoluble. The filtered liquid on acidification with hydrochloric acid gave a precipitate which was too small in quantity for purification and hence was neglected.

The alkali-insoluble residue was washed with water and crystallised from a large quantity of alcohol in silky leaflets, m.p. 246–47°. Its identity was established with that obtained by acetylating the hydrazide and subsequent deacetylation.[10]

The *acetyl derivative* was crystallised from alcohol, m.p. 166–67°.

The *azo-derivative* was prepared by dissolving compound (XII) (2 g.) in glacial acetic acid and adding an excess of a concentrated solution of permanganate. The precipitate after being washed with water was crystallised from alcohol in beautiful red needles, m.p. 167°.

PART VIII. ACTION OF SODIUM HYDROXIDE.

Action of sodium hydroxide on mono-o-*tolyl-hydrazodithiodicarbonamide*: *Formation of* 4-o-*tolyl*-3: 5-*dithio*-1: 2: 4-*triazole* (V).—The hydrazide (15 g.) was boiled with 2N sodium hydroxide solution (100 c.c.) for about an hour and acidified after cooling with concentrated hydrochloric acid when hydrogen sulphide evolved. The precipitate after being washed with water, was treated with N/2 sodium carbonate solution and filtered. The sodium carbonate solution gave, on acidification, a solid which after being purified by precipitation from ammonia solution was crystallised from alcohol, care being taken not to expose the substance to air in which it gets spontaneously oxidised. It melts at 223° (yield, 3.5 g.).

The sodium carbonate insoluble portion was crystallised from alcohol. It comes out as needles or sometimes as small cubes, m.p. 231° (yield, 2.4 g.). It is identical with compound (III, p. 53).

Disulphide of compound (V) was prepared by adding iodine solution to a solution of the substance in aqueous potassium hydroxide. After washing with water, alcohol, benzene and ether, it was obtained as a yellow powder, m.p. 245° (Found: N, 18.4. $C_{18}H_{16}N_6S_4$ requires N, 18.9 per cent.).

The *dimethyl derivative* was prepared by dissolving the compound in dilute ammonia and adding dimethyl sulphate to it when heat was evolved. The liquid layer at the bottom solidifies on cooling and crystallised from dilute alcohol in needles, m.p. 178°. It is very soluble in alcohol but difficultly so in water.

Action of 2N *sodium hydroxide solution on mono*-p-*tolyl-hydrazo-dithiodicarbonamide*: *Formation of* 4-p-*tolyl*-3 : 5-*dithio*-1 : 2 : 4-*triazole* (VI).—The hydrazide (10 g.) was treated similarly with sodium hydroxide solution as in the case of the *o*-tolyl hydrazide and two compounds obtained, *viz.*, (i) soluble in N/2 sodium carbonate and easily soluble in dilute ammonia; and (ii) insoluble in N/2 sodium carbonate and difficultly soluble in dilute ammonia; (i) was crystallised from alcohol (avoiding exposure to air) in colourless cubes (VI), m.p. 213° (yield, 1.4 g.).

Compound (ii) after being washed with water and dilute ammonia was crystallised from alcohol, m.p. 277° (yield, 2 g.). It is identical with compound (IV).

The *disulphide* of compound (VI) is insoluble in all ordinary organic solvents, excepting alcohol in which it is sparingly soluble, yellow powder, m.p. 227° (decomp.). (Found: N, 18.3. $C_{18}H_{16}N_6S_4$ requires N, 18.9 per cent.).

Dimethyl derivative of compound (VI) comes out from dilute alcohol in long needles, m.p. 140°.

PART IX. ACTION OF HYDROCHLORIC ACID.

Action of concentrated hydrochloric acid on di-o-*tolyl-hydrazo-dithiodicarbonamide: Formation of compounds* (IX) and (X).—The hydrazide (10 g.) was heated with concentrated hydrochloric acid (*d*, 1.19; 30 c.c.) for half-an-hour during which a solid separated out. Most of the solid dissolved in 2N sodium hydroxide solution leaving a small residue which, after being washed with water, crystallised from alcohol in colourless leaflets, m.p. 217° (X).

The alkaline filtrate on acidification with concentrated hydrochloric acid, gave a precipitate which crystallised from dilute alcohol in microscopic needles, m.p. 213–14° (IX). These two compounds were identical with the corresponding compounds obtained by the action of heat.

*Action of concentrated hydrochloric acid on di-*p*-tolyl-hydrazodithiodicarbonamide: Formation of 5-*p*-tolylimino-3-thio-tetrahydro-4:1:2-thiodiazole* (XI).—The clear solution obtained on treatment of the reaction product with 2N sodium hydroxide solution was acidified, filtered and the precipitate, after being washed with water, crystallised from dilute alcohol in thin, long, thread-like crystals, m.p. 217–18°. Guha and Ray[6] obtained this compound, m.p. 219°, by the action of CS_2 upon *p*-tolyl-thiosemicarbazide.

The *disulphide* melted at 230–31°; Guha and Ray give m.p. 232°.

PART X. ACTION OF ACETIC ANHYDRIDE.

*Action of acetic anhydride on mono-*o*-tolyl-hydrazodithiodicarbonamide: Formation of 5-*o*-tolylimino-tetrahydro-4:1:2-thiodiazole* (XIII).—The hydrazide (5 g.) was heated with acetic anhydride under reflux for about 15 minutes and the liquid poured into a large volume of water under stirring. The separated solid crystallised from alcohol in colourless needles, m.p. 264°.

Hydrolysis of the above acetyl compound was effected by gently boiling it (2 g.) with concentrated hydrochloric acid (10 to 15 c.c.); the solution, when cooled, yielded the hydrochloride as beautiful colourless needles from which the base was liberated by sodium carbonate. The precipitate was filtered, washed and crystallised from dilute alcohol, m.p. 206–7° (Found: N, 26.85. $C_9H_{10}N_4S$ requires N, 27.18 per cent.).

*Action of acetic anhydride on mono-*p*-tolyl-hydrazodithiodicarbonamide: Formation of 5-*p*-tolylimino-3-imino-tetrahydro-4:1:2-thiodiazole* (XIV).—The acetyl derivative comes out directly in the reaction with acetic anhydride as colourless leaflets, m.p. 298°, and is insoluble in almost all ordinary organic solvents.

Hydrolysis of the above compound was effected by boiling the acetyl derivative (2 g.) with 5N hydrochloric acid for about 15 minutes, the clear solution thus obtained gave a solid on cooling. This (the hydrochloride) was filtered, washed with water and crystallised from dilute alcohol in thin thread-like crystals, m.p. 188° (Found: N, 22.9. $C_9H_{10}N_4S$, HCl requires N, 23.09 per cent.). It is very soluble in alcohol. With sodium carbonate, it gave a base, which crystallised from alcohol in colourless leaflets, m.p. 203° (Found: N, 27.3. $C_9H_{10}N_4S$ requires N, 27.1 per cent.).

*Action of acetic anhydride on di-*o*-tolyl-hydrazodithiodicarbonamide: Formation of 2:3-dihydro-3-tolylamino-3:5-endo-*o*-tolylimino-4:1:2-thiobiazole* (XV).—The acetyl derivative was crystallised from alcohol, m.p. 250–51°, the mixed m.p. with the acetyl derivative of compound (X) remains undepressed.

Hydrolysis of the acetyl compound was effected by boiling with concentrated hydrochloric acid (*d*, 1.19) when a compound melting at 223° and crystallisable from alcohol was obtained. Compound (X) (m.p. 217°) also on acetylation followed by hydrolysis gave this endo-compound, m.p. 223° (Found: N, 18.7; S, 10.9. $C_{18}H_{16}N_4S$ requires N, 18.9; S, 10.8 per cent.).

*Action of acetic anhydride on di-*p*-tolyl-hydrazodithiodicarbonamide: Formation of compound* (XII).—The hydrazide (2 g.) was gently boiled with acetic anhydride (15 c.c.) and the solution, after about 10 more minutes' heating, was poured into a large volume of water. The pasty mass obtained, did not solidify even after standing for four days; but an ethereal solution, after being shaken with dilute sodium carbonate solution and the ether on being allowed to evaporate slowly, gave colourless crystals, m.p. 166–67°, mixed m.p. taken with the acetyl derivative of compound (XII) obtained in the heat reaction, remained undepressed.

Hydrolysis of the above acetyl derivative (1 g.) was effected by heating it with concentrated hydrochloric acid (10–15 c.c.). The solid soon dissolved, but after a time, the solution became turbid, and on prolonged boiling, a pasty mass separated. The semisolid obtained after cooling was purified by dissolving it in the minimum quantity of alcohol and adding ether in large excess. The white powder thus obtained was finally crystallised from alcohol in colourless shining leaflets, m.p. 246°. Identity of this product with compound (XII) obtained in the heat reaction was established by mixed melting point.

Hydrolysis of the acetyl compound with 5N hydrochloric acid gave the same product in a purer form.

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