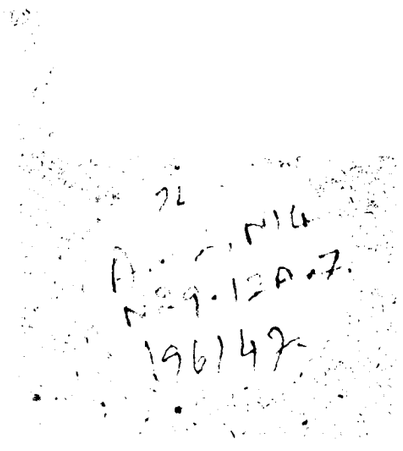
Journal of the IIs.

XIIA.

7.

1929.



Price, Rs. 1-4.] [Vol. 12A, Part VII, pp. 79 to 104.

JOURNAL

OF THE

Indian Institute of Science.

CONTENTS.

JOURNAL

OF THE

INDIAN INSTITUTE OF SCIENCE

Parts I—XXI.	VOLUME I.—(1914-18).
Parts I—XV.	VOLUME II.—(1918-19).
Parts I—IX.	VOLUME III.—(1920).
Parts I—XVI.	VOLUME IV.—(1921).
Parts I—XIV.	VOLUME V.—(1922).
Parts I—XIII.	VOLUME VI.—(1923).
Parts I—XV.	VOLUME VII.—(1924).
Parts I—XVI.	VOLUME VIII (A)—(1925).
	VOLUME VIII (B)—1925.
Parts I—II.	
Parts I—X.	VOLUME IX (A)—1926.
Parts I—V.	VOLUME IX (B)—1926.
Parts I—X.	VOLUME X (A)—1927.

VOLUME X (B)—1927.

Part I.—Tests on Suspension Insulators after Ten Years' Service. By A. S. Venkateswaran and U. Ganguly. Price, Re. 1.

Part II.—The Measurement of Voltage Gradient on a String of Suspension Insulators. By G. Yoganandam and R. K. Sen. Price, Re. 1.

Part III.—Intensity Variations of Madras (Fort) Radio Station. By K. Sreenivasan. Price, As. 8.

Part IV.—Suspension Insulator Testing. By G. Yoganandam. Price, As. 8.

VOLUME XI (A)—1928.

Part I.—I. Studies on Invertase, Part I. Preparation and Purification of the Enzyme. By B. N. Sastri and Roland V. Norris. II. Note on a Simple Method for concentrating Enzyme Solutions. By B. N. Sastri. Price, Re. 1.

Part II.—The Bleaching of Lac. By M. Venugopalan. Price, As. 8.

Part III.—Contributions to the Study of Spike-Disease of Sandal (*Santalum Album*, Linn.). Part I. Diastatic Activity of the Leaves. By M. Sreenivasaya and B. N. Sastri. Price, As. 12.

Part IV.—A Micro-Method for the Determination of Enzyme Activity. By B. N. Sastri and M. Sreenivasaya. Price, As. 12

Part V.—The Dielectric Constants of Ammonia, Phosphine and Arsine. By H. E. Watson. Price, Re. 1.

Price, Rs. 1-4.] [*Vol. 12A, Part VII, pp. 79 to 104.*

JOURNAL

OF THE

Indian Institute of Science.

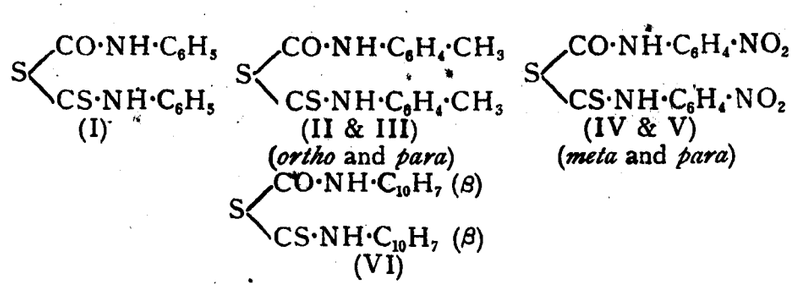
CONTENTS.

I.—FORMATION OF HETEROCYCLIC COMPOUNDS FROM DIETHYLXANTHIC FORMIC ESTER.[1]

By Praphulla Chandra Guha and Devendra Nath Datta.

Diethylxanthic formic ester, $CO_2Et{\cdot}S{\cdot}CS{\cdot}OEt$, was prepared by Holmberg (*J. pr. Chem.*, 1905, **71**, 264) by the action of chlorocarbonic ester upon potassium ethyl xanthate. Similar compounds, *viz.*, diethylxanthic acetic ester and ethylxanthic propionic acid and their calcium, barium and sodium salts had also been prepared by the same author. This appears to be all about such di-esters and their reactions as studied up to this time. Ethylxanthic formic ester contains two active ester groups, so it was thought advisable to utilise this compound as a reagent for the construction of heterocyclic compounds. With this object in view its action upon bases like amines, hydrazines, diamines, semi- and thiosemicarbazides has been studied, and as will be seen the object has been amply realised.

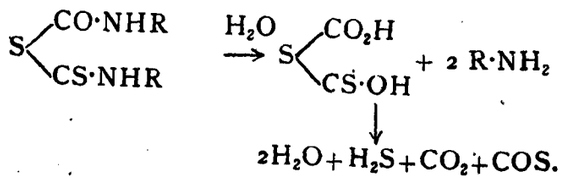
The primary amines, *e.g.*, aniline, *o*-and *p*-toluidines, *m*- and *p*-nitranilines and *β*-naphthylamine react readily with the di-ester to yield the corresponding thiodicarbo-monothiodiarylamides and thus the following compounds (I–VI) have been obtained :



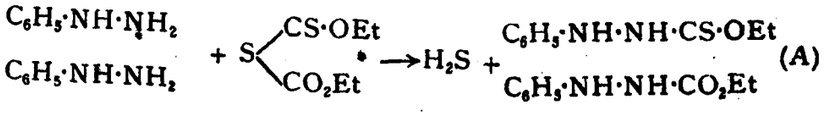
The diarylamides form diacetyl derivatives and instead of disulphides by the oxidising action of ferric chloride, yield simple iron salts and are indifferent to the action of iodine and potassium ferricyanide. They are decomposed on being boiled with strong hydrochloric acid

[1] Reprinted from the *Journal of the Indian Chemical Society*, 1929, **6**, 65.

into carbon dioxide, carbon oxysulphide, sulphuretted hydrogen and arylamines, thus :



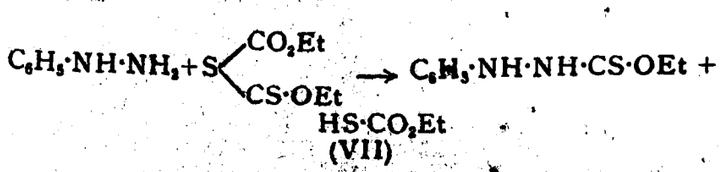
It was expected by analogy with the action of arylamines that two molecules of phenylhydrazine would react with one molecule of the ester to yield a diphenylhydrazide. But the compound actually isolated is monothiophenylcarbazinic ester, $C_6H_5{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}OEt$. So, it was assumed that the reaction had proceeded thus :—



and it is well known that acidyl sulphides like $S(CO{\cdot}CH_3)_2$ and $S(CO{\cdot}C_6H_5)_2$ react with ammonia, amines, hydrazines etc., to yield amides and hydrazides thus :

$$2NH_3+S(CO{\cdot}R)_2=H_2S+2R{\cdot}CO{\cdot}NH_2$$

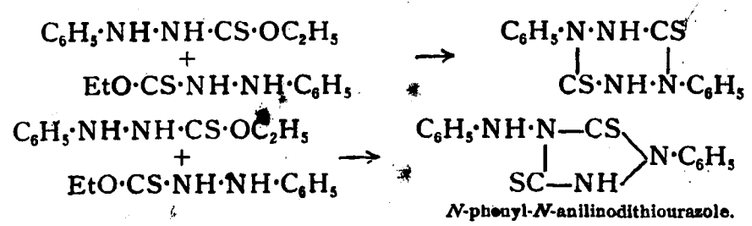
The explanation as to the course of the reaction expressed in equation (*A*) appears to require some modification as the other product, *viz.*, $C_6H_5{\cdot}NH{\cdot}NH{\cdot}CO_2Et$, could not be traced and also because of the fact that carbon dioxide was proved to be one product. The equation which can explain all these facts appears to be as given below :



The thiocarbonic ester being unstable is hydrolysed into alcohol, carbon dioxide and sulphuretted hydrogen.

By analogy with the formation of diphenylurazine by the action of heat upon phenylcarbazinic ester (*Ber.*, 1888, **21**, 2329; *Annalen*, 1891, **263**, 282; *Ber.*, 1896, **29**, 829) it was expected that phenylcarbazinic

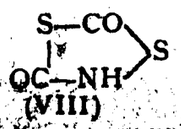
monothio-ester, $C_6H_5{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}OC_2H_5$, would yield diphenyldithio-*β*-urazine or *N*-phenyl-*N*-anilinodithiourazole, thus :



But the reaction was very complicated and yielded only a tarry mass. At 140–150° the ester was only partially decomposed and mostly recovered ; at still lower temperatures (110–115°) the ester was found to remain unchanged.

The action of aqueous potassium hydroxide (20 per cent.) was next studied and it was found that the ester is decomposed into phenylhydrazine, alcohol and potassium thiocarbonate from the last of which sulphuretted hydrogen was evolved during acidification.

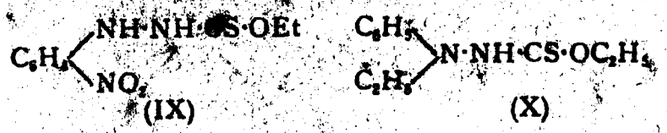
The action of strong hydrochloric acid upon the ester, $C_6H_5{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}OEt$, however, led to a heterocyclic five-membered compound (VIII) containing two sulphur atoms in the ring,



(VIII)

That the two sulphur atoms in compound (VIII) form members of the ring is proved by the fact that they can neither be desulphurised with mercuric oxide nor can they yield disulphide with iodine.

The action of *p*-nitrophenylhydrazine and *unsym*-phenylethylhydrazine was likewise studied ; they yielded the corresponding monothiocarbazinic esters (IX) and (X) as in the case of phenylhydrazine.



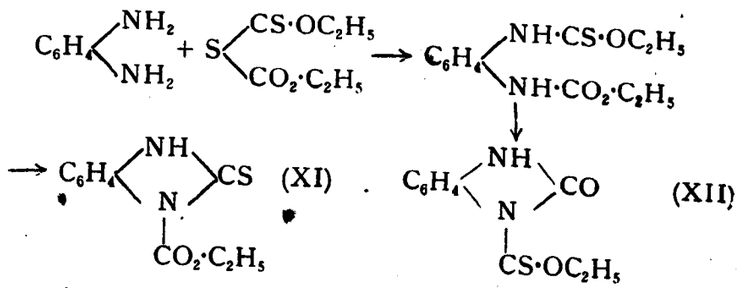
(IX) (X)

The compound (VIII) was also obtained from (IX) and (X) on treatment with hydrochloric acid.

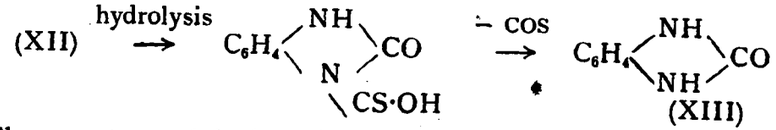
Action of Diamines.

The reaction of *o*-phenylenediamine with the ester is interesting and is attended with the formation of three compounds, *viz.*, (XI), (XII) and (XIII).

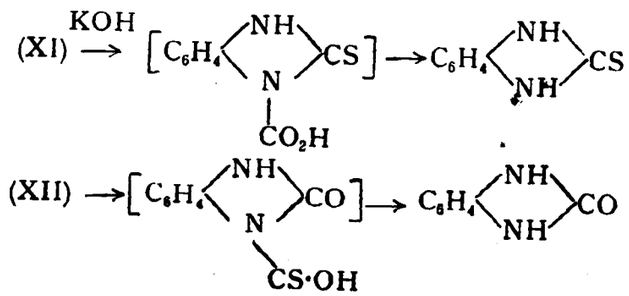
Firstly *o*-phenylene monothiodiurethane[1] is formed which under the conditions of the experiment suffers internal condensation in two different ways yielding *N*-carbethoxyphenylene thiourea (XI) and *N*-thiocarbethoxyphenylene urea (XII) thus:



The formation of phenylene urea (XIII) can be explained on the assumption that compound (XII) is first hydrolysed and then loses a molecule of carbon oxysulphide.

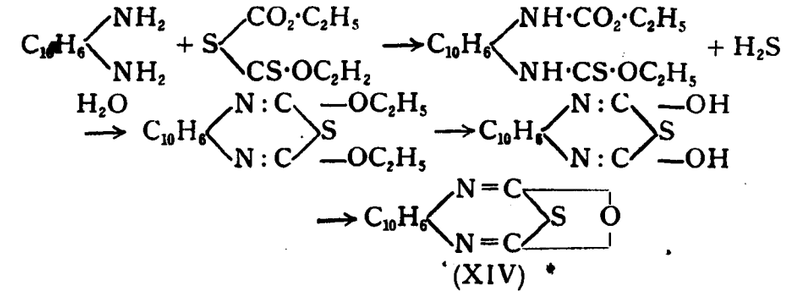


The correctness of the formulae (XI) and (XII) has been established by the facts gathered from a study of the action of potassium hydroxide solution (20 per cent.) upon them when phenylene thiourea and phenylene urea are obtained respectively from (XI) and (XII), thus:



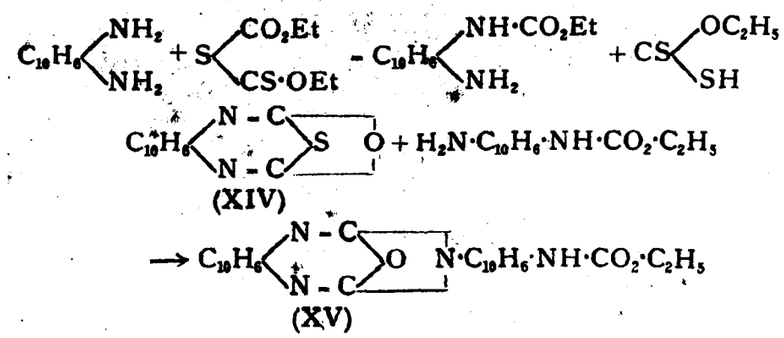
[1] A compound of the type of (XVI) has actually been isolated with ethylenediamine.

The action of 1 : 2-naphthylenediamine has also been studied but its behaviour with the di-ester appears to be a little peculiar[1] in so far as the two products finally isolated are quite different from compounds (XI, XII and XIII). Two compounds, 4 : 5-naphthylene-2 : 7-endoxy-1 : 3 : 6-thioheptadiazine (XIV) and 1-carbethoxyamino-naphthyl-4 : 5-naphthylene-2 : 7-endoxy-1 : 3 : 6-heptatriazine (XV) are formed in this case; the formation of (XIV) can be best explained thus:



That the sulphur atom of compound (XIV) is a member of the ring is proved by the fact that it cannot be desulphurised on treatment with mercuric oxide; moreover the absence of any group like (NH—CO) or (NH—CS) is proved by the fact that the compound is insoluble in alkali (compare compounds XI–XIII which are all soluble in alkali).

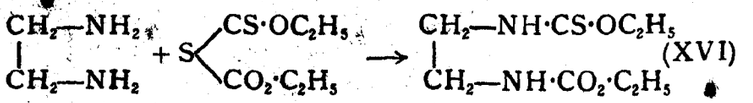
As regards the formation of the heptatriazine compound, it appears to be essential to assume, first of all, the formation of 1-amino-2-carbethoxyamino-naphthalene, $NH_2 \cdot C_{10}H_6 \cdot NH \cdot CO_2Et$, which in its turn acting upon (XIV) produces compound (XV).



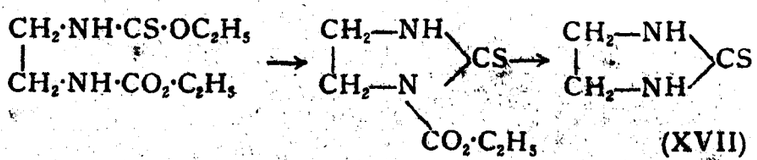
[1] It will be seen that the experiments with phenylene- and naphthylenediamines have not been conducted under identical conditions (*vide Experimental*).

Such replacement of sulphur by a nitrogen atom by the action of ammonia and amines is well known in heterocyclic chemistry.

The action of one diamine of the aliphatic series, *viz.*, ethylenediamine has also been studied when ethylene monothiodiurethane (XVI) and ethylene thiourea (XVII) are simultaneously formed thus :



(XVI)



(XVII)

The above equation regarding the formation of (XVII) from (XVI) has been further confirmed from a study of the action of hydrochloric acid upon (XVI) when ethylene thiourea is obtained (compare the formation of phenylene thiourea from *N*-carbethoxyphenylene thiourea).

Phenylene and ethylene thiourea could up to this time be obtained only by heating *o*-phenylene disulphocyanide (Lellmann, *Annalen*, 1888, 221, 8) and the thiocarbamic acid derivative obtained from ethylenediamine and carbon disulphide (Hofmann, *Ber.*, 1872, 5, 242) at the temperature of boiling water.

Action of semi- and thiosemicarbazides.

Semicarbazide reacts with the di-ester to yield semicarbazide monothiocarboxylic ethyl ester, $NH_2—CO—NH—NH—CS·OC_2H_5$ (XVIII). It is interesting to note that the behaviour of thiosemicarbazide and 4-arylthiosemicarbazides towards the di-ester is different from that of semicarbazide. Semicarbazide yields the corresponding monothiocarbonic ester, whereas thiosemicarbazide and 4-arylthiosemicarbazides yield their carbonic esters.

$NH_2·CO·NH·NH_2 \longrightarrow NH_2·CO·NH·NH·CS·OC_2H_5$ (XVIII)

$NH_2·CS·NH·NH_2 \longrightarrow NH_2·CS·NH·NH·CO_2C_2H_5$ (XIX)

$C_6H_5·NH·CS·NH·NH_2 \longrightarrow C_6H_5·NH·CS·NH·NH·CO_2C_2H_5$ (XX)

p-$C_7H_7·NH·CS·NH·NH_2 \longrightarrow p$-$C_7H_7·NH·CS·NH·NH·CO_2Et$ (XXI)

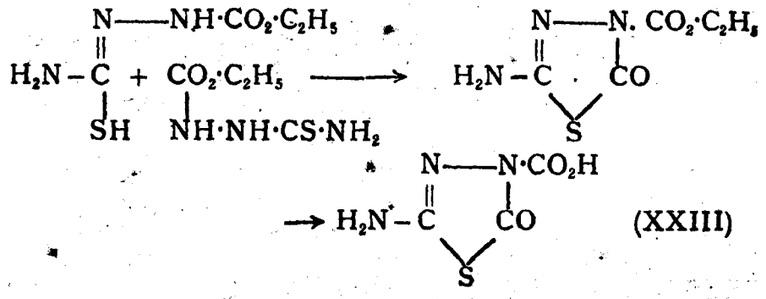
$C_{10}H_7·NH·CS·NH·NH_2 \longrightarrow C_{10}H_7·NH·CS·NH·NH·CO_2C_2H_5$ (XXII)

It is probable that in each case both types of compounds (*viz.*, carbonic ester and thiocarbonic ester) are simultaneously formed, of

which one preponderates. From a survey of the compounds (XVIII–XXII) a generalisation appears possible. The remote (NH_2—CO) group of semicarbazide, being more negative in character as compared with the ($NH_2·CS$) group of thiosemicarbazide, facilitates the formation of $NH_2·CO·NH·NH·CS·OEt$; whereas the $NH_2·CS$ group of thiosemicarbazide being less negative, facilitates the formation of $NH_2·CS·NH·NH·CO_2·C_2H_5$.

The action of strong hydrochloric acid upon the semicarbazide and thiosemicarbazide compounds (XVIII and XIX) is also quite interesting ; the former is decomposed into alcohol, carbon oxysulphide and semicarbazide ; whereas the latter yields 2-amino-4-carboxylic-5 keto-4 : 5-dihydro-1 : 3 : 4-thiodiazole (XXIII), thus :

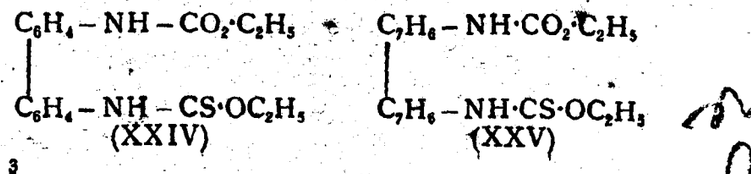
$$NH_2·CO·NH·NH·CS·OC_2H_5 \longrightarrow NH_2CO·NH·NH_2 + H_2O + COS + C_2H_5·OH$$



(XXIII)

It liberates carbon dioxide from sodium bicarbonate and is readily soluble in sodium carbonate showing the presence of a carboxylic group ; it does not form mercaptides with mercuric chloride and lead acetate, does not form disulphide with iodine, nor can it be desulphurised by treatment with mercuric oxide. All these reactions go to show that the sulphur atom is present not in the 'SH' form, nor in the thioketonic form, 'CS,' but as a member of the ring. It forms a benzylidene derivative with benzaldehyde which shows that it contains an amino-group.

Benzidine and tolidine form with the di-ester p : p'-diphenyl-monothiodiurethane (XXIV) and p : p'-ditolyl-monothiodiurethane (XXV).



(XXIV) (XXV)

EXPERIMENTAL.

THIODICARBO-MONOTHIODIPHENYLAMIDE (I).

Diethylxanthic formic ester (4 g.) dissolved in a small quantity of alcohol was cooled to 0° in an ice-bath and aniline (3·8 g.) gradually added. Heat was developed during the reaction with liberation of a small amount of sulphuretted hydrogen. For completion of the reaction the mixture was allowed to stand for two to three hours. It was then shaken with dilute hydrochloric acid to remove excess of aniline. A solid separated at this stage which was filtered, washed with water and crystallised from dilute alcohol, m.p. 63–64°. The substance is soluble in dilute alkali but insoluble in dilute acid. On being boiled with concentrated hydrochloric acid it decomposes into carbon dioxide, carbon oxysulphide and aniline hydrochloride (Found: N, 9·82. $C_{14}H_{12}ON_2S_2$ requires N, 9·71 per cent.).

Behaviour towards Oxidising Agents.

The substance was heated with excess of ferric chloride under reflux for about two hours and allowed to cool. The crystalline green solid was repeatedly washed with ether to remove ferric chloride (neither water nor alcohol should be used for washing, for in the former case a tarry matter is formed whilst in the latter the substance passes into solution). The residue was crystallised from dilute alcohol. The substance is insoluble in alkali but the original substance is soluble in alkali. The test for iron was made by burning the substance. A brown residue always remained which responded to the usual tests for iron. So the substance is not oxidised by ferric chloride but only its iron salt is formed. The substance was found to be quite indifferent to the oxidising action of iodine and potassium ferricyanide.

Thiodicarbo-monothiodi-o-*tolylamide* (II).

An alcoholic solution of *o*-toluidine (2·2 g.) was gradually added to an alcoholic solution of the ester (2 g.). As the reaction proceeded with development of heat, it had to be moderated by cooling. A small quantity of sulphuretted hydrogen was evolved during the reaction. The mixture was allowed to stand at the room temperature for two to three hours, then diluted with water and shaken with dilute hydrochloric acid to remove excess of *o*-toluidine. A solid separated at this stage which after filtration and washing was crystallised from absolute alcohol, m. p. 205° (Found: N, 8·91. $C_{16}H_{16}ON_2S_2$ requires, N, 8·86 per cent.).

Thiodicarbo-monothiodi-p-*tolylamide* (III) was obtained in a similar manner. It crystallised from dilute alcohol, m. p. 85°, is soluble in dilute alkali but insoluble in dilute acid (Found: N, 8·52; S, 20·81. $C_{16}H_{16}ON_2S_2$ requires N, 8·86; S, 20·25 per cent.).

Thiodicarbo-monothiodi-m-*nitranilide* (IV).

m-Nitraniline (1·5 g.) was added to the ester (2 g.) dissolved in alcohol. As the reaction took place with development of heat, the mixture was cooled with ice water; traces of sulphuretted hydrogen were detected. The mixture was allowed to stand at the ordinary temperature for two to three hours, diluted with water and shaken repeatedly with warm dilute hydrochloric acid to remove excess of *m*-nitraniline. The crystalline solid was filtered and recrystallised from dilute alcohol, m. p. 105°; it is soluble in dilute alkali but insoluble in dilute acid (Found: N, 14·52. $C_{14}H_{10}O_5N_4S_2$ requires N, 14·81 per cent.).

The *diacetyl* derivative was obtained by heating the substance for a short time with an excess of acetic anhydride and crystallised from alcohol, m. p. 114–115° (Found: N, 12·42. $C_{18}H_{14}O_7N_4S_2$ requires N, 12·12 per cent.).

Thiodicarbo-monothiodi-p-*nitranilide* (V).

The method of preparation and purification was the same as in the case of the previous compound. It melts at 95–96°, and is soluble in dilute alkali but insoluble in acid (Found: N, 14·65. $C_{14}H_{10}O_5N_4S_2$ requires N, 14·81 per cent.).

Thiodicarbo-monothiodi-β-naphthylamide (VI) obtained in a similar manner melts at 90°. It is insoluble in acid but soluble in alkali (Found: N, 7·05. $C_{22}H_{16}ON_2S_2$ requires N, 7·21 per cent.).

Monothiophenylcarbazinic ester (VII).

An alcoholic solution of phenylhydrazine (2·2 g.) was gradually added to the ester (2 g.) dissolved in alcohol under ice cooling when the reaction proceeded with evolution of sulphuretted hydrogen. For completion of the reaction the mixture was allowed to stand at the room temperature for two to three hours and then heated under reflux on a water-bath for half an hour more. The cold solution was then shaken with dilute hydrochloric acid to remove excess of phenylhydrazine. A solid separated which was crystallised from dilute alcohol, m. p. 73–74°. It is soluble in alkali but insoluble in acid (Found: N, 14·41. $C_9H_{12}ON_2S$ requires N, 14·28 per cent.). The filtrate from the above carbazinic ester on evaporation gave phenylhydrazine hydrochloride.

Conversion of (VII) *into* (VIII).

The ester was heated under reflux with concentrated hydrochloric acid for half an hour when a clear solution was obtained, and on cooling yielded a precipitate which was filtered, washed and crystallised from water, m.p. 135°. The substance is soluble in alkali and can be precipitated with acid. It does not give any disulphide with iodine and cannot be desulphurised with mercuric oxide (Found: N, 10·2. $C_2HO_2NS_2$ requires N, 10·37 per cent.).

Action of Heat upon Monothiophenylcarbazinic ester.

About 5 gms. of the ester were heated in an oil-bath at 230–240° for 3–4 hours when sulphuretted hydrogen was profusely evolved. A tarry mass was obtained on cooling, very soluble in ether, acetone and benzene but slightly less soluble in alcohol; it was treated with alcohol when a very small amount of solid insufficient for purification separated. The reaction was repeated at 140–150°, the period of heating remaining the same. In this case also a good quantity of tar was formed and a small quantity of the unchanged substance only could be recovered. At a still lower temperature (110–115°) for fourteen hours the whole was found to remain unchanged.

Action of Potassium Hydroxide on (VII).

The ester was heated with aqueous caustic potash (20 per cent.) under reflux for about 45 minutes. The clear solution was then allowed to cool and acidified with dilute hydrochloric acid which liberated sulphuretted hydrogen profusely and a solid containing sulphur. The substance was freed from sulphur by extracting with benzene in which the substance is very soluble. On evaporation of benzene, a solid was obtained which on examination was found to be nothing but the unchanged substance. The original filtrate contained phenylhydrazine. Evidently the monothiophenylcarbazinic ester is decomposed into phenylhydrazine, alcohol, and potassium thiocarbonate from the last of which sulphuretted hydrogen is evolved during acidification.

p-*Nitrophenylcarbazinic Monothio-ethyl ester* (IX).

p-Nitrophenylhydrazine under conditions similar to phenylhydrazine gives a similar type of compound. After crystallisation from alcohol it melts at 108–109°; is soluble in alkali but insoluble in acid (Found: N, 17·61. $C_9H_{11}O_3N_3S$ requires N, 17·5 per cent.).

Conversion of (IX) *into* (VIII).

p-Nitrophenylcarbazinic monothio-ethyl ester was heated under reflux with concentrated hydrochloric acid for half an hour when the whole of it passed into solution. The solution was then allowed to cool when a solid separated. The mixture was then diluted with water when a part of the solid passed into solution. The residue was filtered, washed with cold water and crystallised from boiling water, m.p. 135°. The substance on analysis was found to be identical with compound (VIII). (Found: N, 10·50 per cent.).

Ethyl Monothio-ethylphenylcarbazinic ester (X).

This was obtained similarly to the foregoing compound; crystallised from alcohol it melted at 242° (Found: N, 12·32. $C_{11}H_{16}ON_2S$ requires N, 12·50 per cent.).

Action of o-Phenylenediamine on Diethylxanthic formic ester: Formation of (XI), (XII) *and* (XIII).

An alcoholic solution of *o*-phenylenediamine (2 g.) was gradually added to the ester (4 g.) cooled to 0°. During the reaction, heat was developed and sulphuretted hydrogen liberated. The reaction mixture was allowed to stand at the ordinary temperature for two to three hours to complete the reaction. A solid (XI) separated at this stage which was filtered and crystallised from water, m.p. 93–94°; it is soluble in dilute acid and dilute caustic alkali but insoluble in dilute ammonia (Found: N, 11·77. $C_{10}H_{10}O_2N_2S$ requires N, 12·10 per cent.).

Through the filtrate from compound (XI) steam was passed for three to four hours to remove some oily matter; on cooling a solid (XIII) separated which was soluble in dilute alkali but insoluble in dilute acid and even in strong acid. It was crystallised from alcohol, m.p. 306° (Found: N, 21·20. $C_7H_6ON_2$ requires N, 20·89 per cent.). The compound is phenylene urea (m.p. 305°–307°).

The reaction of *o*-phenylenediamine with the ester was also conducted at the ordinary temperature without solvent. A solid separated and was shaken with dilute hydrochloric acid to remove excess of *o*-phenylenediamine. The solid portion insoluble in hydrochloric acid (XII) was filtered, washed and crystallised from dilute alcohol; m.p. 122–123°. The compound (XII) is soluble in dilute alkali (Found: N, 11·83. $C_{10}H_{12}O_2N_2S$ requires N, 12·10 per cent.).

To the filtrate from (XII) dilute ammonia was added; the precipitate on crystallisation from water melted at 93° and was found to be identical with compound (XI).

Action of Potassium Hydroxide upon (XI).

N-Carbethoxy-*o*-phenylene thiourea was heated with the alkali solution (20 per cent.) for half an hour under reflux. The solution was

then allowed to cool and acidified with dilute hydrochloric acid; the precipitate wasfiltered, washed with water and crystallised from dilute alcohol, m.p. 301–302°. It gives with iodine a disulphide which melts at 230°. The compound has all the properties of phenylene thiourea. The melting point of phenylene thiourea is given in Richter as 298° and in Meyer and Jacobson 292–293°. The melting point of the disulphide is given in literature as 230° (Found: N, 18·56. $C_7H_6N_2S$ requires, N, 18·66 per cent.).

Action of Potassium Hydroxide upon (XII).

N-Thiocarbethoxy-*o*-phenylene urea was heated with potassium hydroxide solution (20 per cent.) for half an hour. The solution was allowed to cool and acidified with dilute hydrochloric acid, when sulphuretted hydrogen was evolved and a white precipitate mixed with sulphur was obtained. This was freed from sulphur by dissolution in warm alcohol; on concentration of the alcoholic solution a crystalline compound (m.p. 305°) was obtained identical with phenylene urea (Found: N, 20·68. $C_7H_6N_2O$ requires N, 20·89 per cent.).

Action of 1 : 2-*Naphthylenediamine on Diethylxanthic formic ester: Formation of* (XIV) *and* (XV.)

1 : 2-Naphthylenediamine (1·5 g.) was added to the ester (2 g.) under ice cooling. The reaction took place with development of heat and evolution of hydrogen sulphide. After fifteen minutes the mixture was diluted with alcohol and allowed to stand at the ordinary temperature for three to four hours during which a solid substance gradually accumulated which was filtered and crystallised from pyridine; m.p. 250°. It is insoluble in both dilute acid and dilute alkali. It is not desulphurised when heated with freshly prepared yellow mercuric oxide (Found: N, 12·21; S, 13·62 $C_{13}H_9ON_2S$ requires N, 12·38 and S, 14·15 per cent.). The filtrate from (XIV) was evaporated to dryness when a small quantity of the same substance was obtained.

The action of naphthylenediamine on the ester was tried again at a higher temperature. The reaction, as before, was first of all conducted under ice cooling in alcoholic suspension; and after an hour the mixture was heated under reflux for two hours when the reaction was completed. The solution was then cooled and the solid (XV) formed was filtered and crystallised from pyridine. The substance is soluble in no other ordinary organic solvents. It is insoluble in dilute acid and alkali; m.p. 304° (Found: N, 13·52, $C_{13}H_{10}O_2N_4$ requires N, 13·27 per cent.).

Ethylene monothio-diurethane (XVI) *and Ethylene thiourea* (XVII).

To an alcoholic solution of the ester (8 g.) ethylenediamine (2·4 g.) was gradually added under ice cooling; the reaction took place at once with liberation of heat and evolution of hydrogen sulphide. The reaction mixture was allowed to stand for two to three hours and then diluted with water when an oil separated. The dilute solution was shaken with hydrochloric acid to remove excess of ethylenediamine. At this stage the oil solidified. The solid (XVI) was separated by filtration and crystallised from dilute alcohol, m.p. 110–111°. It is insoluble in dilute acid and dilute alkali (Found: N, 12·56. $C_8H_{16}O_3N_2S$ requires N, 12·72 per cent.). To the acid filtrate from (XVI) dilute ammonia was added as in the case of the reaction with *o*-phenylenediamine but nothing was obtained.

The action of ethylenediamine on the ester was conducted without solvent and at the ordinary temperature. The solid (XVII) which separated was filtered from oil and crystallised from dilute alcohol; m.p. 193–194°. It is soluble in alkali but could be precipitated with dilute acid. It forms a mercaptide, a disulphide and a lead salt with mercuric chloride, iodine and lead acetate respectively. It gives a hydrochloride melting at 304–305° (Found: N, 27·22. $C_3H_6N_2S$ requires N, 27·45 per cent.).

To the oily filtrate from (XVII) dilute alcohol was added when it readily passed into solution which, on being diluted with water, yielded a solid substance; this was crystallised from alcohol, m.p. 110–111°, and found to be identical with compound (XVI).

The hydrazide was covered with acetic anhydride in presence of a little powdered fused sodium acetate and gently heated to boiling for about five minutes; the turbid solution was poured into water through a filter. The separated oil was stirred vigorously for ten minutes with hot water and within an hour or so the oil solidified, being freed from tar by washing successively with acetone, ether and benzene. It was then crystallised twice from boiling pyridine; m.p. 293°. The compound contains no sulphur, is insoluble in acid and alkali and in all solvents excepting boiling pyridine (Found: N, 9·18 per cent.). It is therefore *sym*-α : α′-dinaphthyl urea (Cal. N, 8·97 per cent.).

Action of Potassium Hydroxide on Ethylene monothio-diurethane.

Ethylene monothio-diurethane was mixed with caustic potash (20 per cent.) and allowed to stand at the ordinary temperature for twenty-four hours. It was then heated at 60–70° under reflux for two hours when a clear solution was obtained. The solution was then allowed to cool and acidified with dilute hydrochloric acid when hydrogen sulphide was evolved and a small quantity of sulphur separated. The solution was filtered from sulphur and the filtrate evaporated to dryness. The solid residue was extracted with absolute alcohol and from the alcoholic solution on cooling ethylene thiourea was obtained on dilution with water.

Semicarbazide monothiocarboxylic ester (XVIII).—Semicarbazide hydrochloride (4·5 g.) dissolved in the least quantity of water was treated with anhydrous sodium carbonate (2 g.) to liberate the free base. The solution was diluted with alcohol and added to the required quantity of the ester. Reaction began in the cold with development of some heat and liberation of hydrogen sulphide. The mixture was allowed to stand for about two hours at the ordinary temperature and then heated under reflux for half an hour; needle-shaped crystals were found to have been formed overnight, which after filtration were crystallised from water, m.p. 161°. It is soluble in dilute acid and dilute alkali. On being boiled with strong hydrochloric acid it is decomposed into alcohol, carbon oxysulphide and semicarbazide hydrochloride (Found: N, 26·20. $C_4H_9O_2N_3S$ requires N, 25·76 per cent.).

Thiosemicarbazide carboxylic ester (XIX).—An alcoholic solution of the ester (2 g.) and thiosemicarbazide (2 g.) were heated for an hour under reflux when a clear solution was obtained. Hydrogen sulphide was evolved during the reaction. On allowing the solution to cool a solid separated which after filtration was crystallised from water, m.p. 155°–56°. The substance is soluble in dilute alkali but insoluble in dilute acid (Found: N, 25·86. $C_4H_9O_2N_3S$ requires N, 25·76 per cent.). The filtrate from (XIX) was evaporated to dryness and a second crop of the substance obtained.

Action of Hydrochloric Acid on Thiosemicarbazide carboxylic ester: Formation of (XXIII).—Thiosemicarbazide carboxylic ester was heated with strong hydrochloric acid for half an hour when it passed into solution; this was diluted with water and evaporated to dryness. The white crystalline solid (XXIII) thus obtained was recrystallised from water. It shrinks at 179° and melts at 189°. The substance is chlorine-free and liberates carbon dioxide from sodium bicarbonate. Though it contains sulphur it does not give a mercaptide or a disulphide with mercuric chloride and iodine respectively. It is not desulphurised when boiled with freshly prepared yellow mercuric oxide, so the sulphur atom is present in the ring. It gives a benzylidene derivative which melts at 158–159° (Found: N, 24·89. $C_3H_3O_3N_3S$ requires N, 25·40 per cent.).

4-Phenylthiosemicarbazide carboxylic ester (XX and XXI).—To 2 gms. of the ester, 4-phenylthiosemicarbazide (3·5 gms.) was added. The reaction took place with evolution of hydrogen sulphide and rise of temperature. After allowing the mixture to stand for two hours it was diluted with alcohol and then heated under reflux for about half an hour. The solid was filtered and crystallised from alcohol; m.p. 149–150°. It is soluble in dilute alkali and can be precipitated by dilute acid (Found: N, 17·23; S, 12·85. $C_{10}H_{13}O_2N_3S$ requires N, 17·57; S, 13·38 per cent.).

4-para-*Tolylthiosemicarbazide carboxylic ester* (XXI).—In a manner similar to the preceding reaction *p*-tolylthiosemicarbazide was condensed with the ester. The product was crystallised from a mixture of pyridine and water; m.p. 183–184°. It is insoluble in dilute acid but soluble in alkali (Found: N, 16·74. $C_{11}H_{15}O_2N_3S$ requires N, 16·53 per cent.).

β-Naphthylthiosemicarbazide carboxylic ester (XXII) was obtained in a similar manner from β-naphthylthiosemicarbazide (4 g.) and the ester (2 g.). The product was crystallised from pyridine; m. p. 287–288°. It is soluble in alkali but can be precipitated with acid (Found: N, 14·71. $C_{14}H_{15}O_2N_3S$ requires N, 14·52 per cent.).

Hydrazodicarbonamide (XI) *and acetic anhydride: Formation of* sym-*Diacetylhydrazine.*

Hydrazodicarbonamide (10 g.) prepared according to the method of Thiele (*Annalen*, 1892, **271**, 127) was heated with 30–40 c.c. of pure acetic anhydride in a sealed tube at 200° in an oil-bath for two hours when all dissolved. On opening the tube carbon dioxide escaped under great pressure. The solution was filtered from a small quantity of hydrazodicarbonamide and steam passed for four hours to remove acetic acid. The solution was then evaporated to a brown syrup on the water-bath, dissolved in acetone and boiled under reflux for thirty minutes with animal charcoal. After filtration and concentration,

II.—RING CLOSURE OF HYDRAZO-MONOTHIODICARBONAMIDES WITH ACETIC ANHYDRIDE: FORMATION OF IMINOTHIOBIAZOLONES AND IMINOTHIOLTRIAZOLES.[1]

By Praphulla Chandra Guha and Tarani Kanta Chakraborty.

The ring-closing action of acetic anhydride upon hydrazo-dithiodicarbonamide and its substituted derivatives has been studied by one of us (Guha, *J. Amer. Chem. Soc.*, 1923, **45**, 1036) where it has been shown that the reaction takes place with elimination of sulphuretted hydrogen yielding 2 : 5-diamino-1 : 3 : 4-thiodiazoles. In the present paper, the ring-closure of the following substituted hydrazodicarbonamides with acetic anhydride has been studied of which I-VII are substituted in the thiocarbonamide group, VIII and X are substituted in the carbonamide group, IX is substituted both ways and XI is an unsubstituted dicarbonamide.

$CH_3{\cdot}NH{\cdot}CS{-}NH{-}NH{-}CO{-}NH_2$ (I)

$C_3H_5{\cdot}NH{-}CS{-}NH{-}NH{-}CO{-}NH_2$ (II)

$C_6H_5{\cdot}NH{-}CS{-}NH{-}NH{-}CO{-}NH_2$ (III)

$o\text{-}CH_3{\cdot}C_6H_4{-}NH{-}CS{-}NH{-}NH{-}CO{-}NH_2$ (IV)

$p\text{-}CH_3{\cdot}C_6H_4{-}NH{-}CS{-}NH{-}NH{-}CO{-}NH_2$ (V)

$(CH_3)_2C_6H_3{\cdot}NH{-}CS{-}NH{-}NH{-}CO{-}NH_2$ (VI)

$\beta\text{-}C_{10}H_7{-}NH{-}CS{-}NH{-}NH{-}CO{-}NH_2$ (VII)

$NH_2{-}CS{-}NH{-}NH{-}CO{-}NHPh$ (VIII)

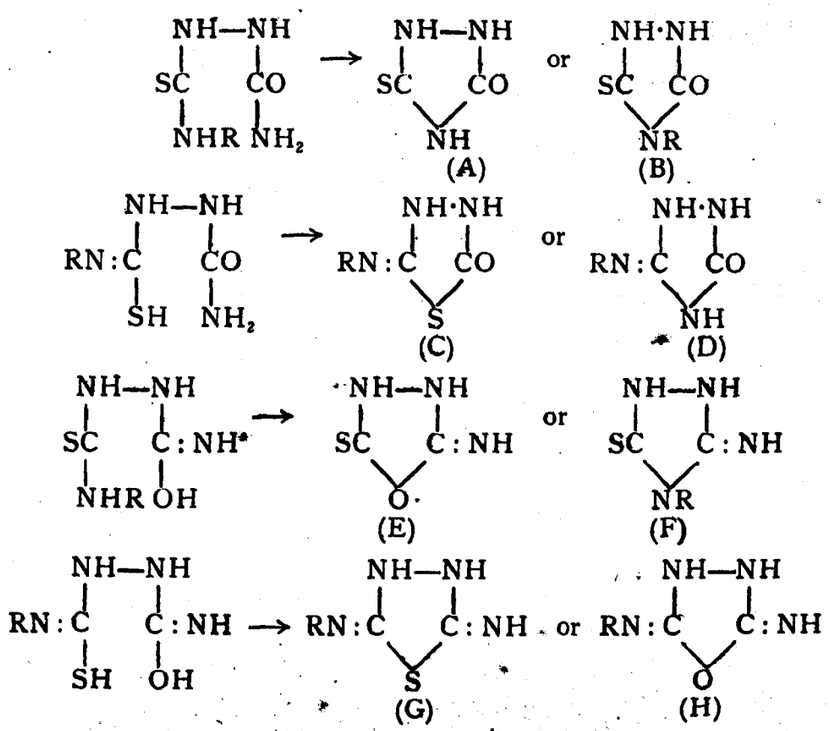
$NHPh{-}CS{-}NH{-}NH{-}CO{-}NHPh$ (IX)

$NH_2{-}CS{-}NH{-}NH{-}CO{-}NH{\cdot}C_{10}H_7(\alpha)$ (X)

$NH_2{-}CO{-}NH{-}NH{-}CO{-}NH_2$ (XI)

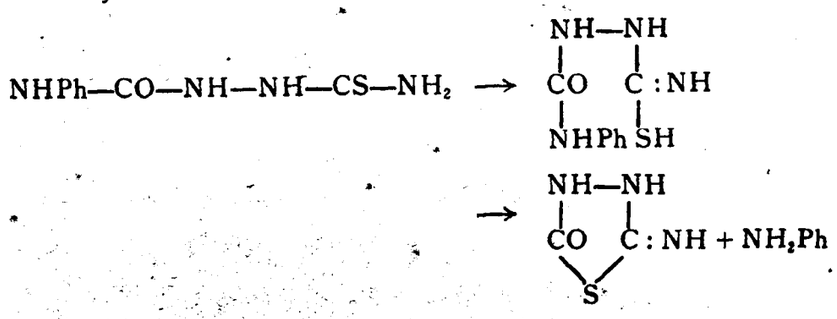
[1] Reprinted from the *Journal of the Indian Chemical Society*, 1929, **6**, 99.

Monosubstituted hydrazo-monothiodicarbonamides of the type $NHR{-}CS{-}NH{-}NH{-}CO{-}NH_2$ might react in the following four different ways to yield one or more cycloids of the type *A* to H.

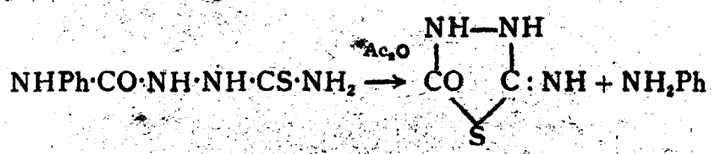


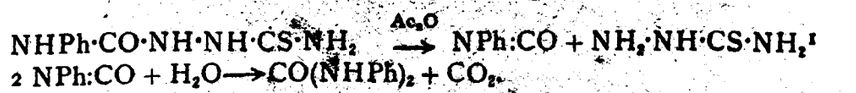
But the compounds actually isolated correspond to the general formula $C_2H_2RON_3S$ and so cannot possess the structure represented by formulae A, D, E, F, G or H, F and G being free from oxygen, D and H being free from sulphur, A and E being free from the group R. So the formula must be B or C, and as the compounds are not mercaptans only C meets all the points. The acetyl derivatives of the substituted iminothiobiazolones are invariably obtained from the hydrazides I–VI which on deacetylation give the free R-iminothiobiazolones. Besides the formation of the acetyl-R-iminothiobiazolones, indication is given as to the formation of other products and the actual isolation of more than one has been possible with the hydrazides II, III and V. It is worth mentioning that one product from the hydrazide V happens to be an iminothioltriazole of type F. The hydrazide VII is completely decomposed with the regeneration of β-naphthyl *iso*thiocyanate almost in a quantitative yield.

The hydrazide VIII under mild treatment gives mono- and diacetyl derivatives of iminothiobiazolone. The ring closure is evidently effected with elimination of aniline, thus :—



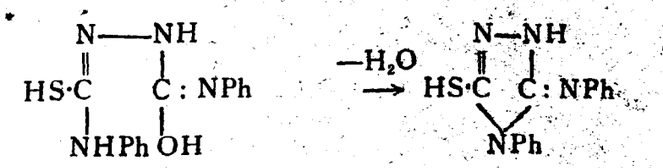
When boiled with acetic anhydride over a free flame, the hydrazide is decomposed yielding diphenylurea, acetanilide, a trace of mono-acetyliminothiobiazolone and two compounds melting at 92–93° and 115° respectively. The formation of acetyliminothiobiazolone, diphenylurea and acetanilide can be explained thus :—





The formation of unsubstituted iminothiobiazolone in the present instance and of substituted iminothiobiazolones with the hydrazides containing substituted thiocarbonamide groupings is significant.

The behaviour of the *sym*-disubstituted hydrazide, NHPh·CS·NH·NH·CO·NHPh appears to be peculiar, as instead of yielding the expected iminothiobiazolone derivatives, it gives 1-*N*-phenyl-2-phenylimino-5-thiol-dihydro- 1 : 3 : 4-triazole, thus :—



[1] The analytical values of the compound, m.p. 92–93°, agree fairly well with those of diacetyl thiosemicarbazide (Calc. N, 24·28 ; S, 18·5. Found : N, 24·70 ; S, 18·67 per cent.).

When boiled with acetic anhydride, the hydrazide yields diphenylurea as the main product. The hydrazide IX, like VII, is easily decomposed and the α-napthyl *iso*cyanate so formed reacts readily with water to give di-α-napthylcarbamide.

Hydrazodicarbonamide (XI) is unaffected even when boiled with acetic anhydride for several days, but when the mixture is heated in a sealed tube at 200° is decomposed into various products amongst which carbon dioxide and *sym*-diacetylhydrazine have been identified.

EXPERIMENTAL.

Hydrazodicarbo-monothiomethylamide (I).

Semicarbazide hydrochloride (5·6 g.) was dissolved in the least quantity of water and sodium carbonate (2·7 g.) added. Molecular proportion of methyl mustard oil dissolved in the least quantity of alcohol was added and the mixture was warmed. Within a minute or two the hydrazide separated, and was crystallised from alcohol, melting at 212° ; the yield was quantitative (Found : N, 37·62. $C_3H_8ON_4S$ requires N, 37·84 per cent.).

2-Methylimino-4-acetyl-5-keto-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole.

The substance was heated with excess of ferric chloride under reflux for about two hours and allowed to cool. The crystalline green solid was repeatedly washed with ether to remove ferric chloride (neither water nor alcohol should be used for washing, for in the former case a tarry matter is formed whilst in the latter the substance passes into solution). The residue was crystallised from dilute alcohol. The substance is insoluble in alkali but the original substance is soluble in alkali. The test for iron was made by burning the substance. A brown residue always remained which responded to the usual tests for iron. So the substance is not oxidised by ferric chloride but only its iron salt is formed. The substance was found to be quite indifferent to the oxidising action of iodine and potassium ferricyanide.

when crystals of the hydrazide began to separate as shining plates. The reaction was complete within ten minutes. The hydrazide was purified by crystallisation from alcohol; m.p. 202° (Found; N, 32·52. $C_5H_{10}ON_4S$ requires N, 32·18 per cent.).

2-Allylimino-3-acetyl-5-keto-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole.

A few grams of the hydrazide were just covered with acetic anhydride and heated under reflux over a small free flame until a clear solution was obtained. On pouring the solution into water, an oil separated which solidified on keeping under water for a few days. The yield of the solid was very small and the presence of a considerable quantity of mustard oil was detected, showing that the major portion of the hydrazide had undergone decomposition. The solid was washed with ether and crystallised from alcohol; m.p. 137°. The yield was so small that no further investigation of the substance was possible.

The experiment was repeated by heating the hydrazide with acetic anhydride on a water-bath instead of over a free flame; the resulting oil soon solidified yielding a much greater quantity of the substance. It was washed with ether, and on attempting crystallisation from rectified spirit was found to be a mixture of two substances. The solid was dissolved by heating with 60 per cent. alcohol and filtered while hot. The filtrate yielded on cooling a crystalline substance, representing about 90 per cent. It was again crystallised from rectified spirit; m.p. 171° (Found: N, 21·33; S, 15·65. The monoacetyl compound, $C_7H_9O_2N_3S$ requires N, 21·11; S, 16·08 per cent.).

The substance dissolves in cold dilute alkali but is not acted on by oxidising agents such as iodine solution or hydrogen peroxide. It was deacetylated by heating with moderately strong hydrochloric acid when it dissolved, yielding on concentration crystals of the free thiodiazole; m.p. 210° (Found: N, 26·83. $C_3H_7ON_3S$ requires N, 26·75 per cent.).

The mother-liquor was concentrated on a water-bath to very small bulk, filtered and allowed to cool when a white crystalline substance separated, m.p. 269°, and sparingly soluble in cold alkali, but more in hot, giving the smell of *iso*cyanide. The yield was only 0·05 g. and so it could not be analysed.

Hydrazomonothiophenyldicarbonamide (III) *and acetic anhydride. Formation of 2-Phenylimino-3-acetyl-5-keto-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole and 2-Phenylimino-3 : 4-diacetyl-5-keto-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole.*

The hydrazide, $NH_2{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NHPh$, prepared according to the method of Arndt, Milde and Tschenscher (*Ber.*, 1922, **55**, 349)

was heated over a small flame with acetic anhydride sufficient to cover it, in presence of a little well powdered fused sodium acetate. The clear solution thus obtained was poured into water when an oil with a strong smell of phenyl mustard oil separated and solidified on keeping under water for a few days. The yellow solid was washed successively with rectified spirit and ether, dissolved in boiling dilute alcohol, the solution filtered and the filtrate allowed to stand for some time while a good quantity of crystals separated. They were filtered, and the mother-liquor on concentration gave another crop of crystals of different shape and appearance from the former. The two portions were separately collected and gave different and fairly sharp melting points (210–211°) and (171–172°) respectively. After recrystallisation from dilute alcohol, the first portion melted at 213° and was the diacetyl compound (Found: N, 15·47. $C_{12}H_{11}O_3N_3S$ requires N, 15 per cent.). The second portion melted at 173° and was the monoacetyl compound (Found: N, 18·01. $C_{10}H_9O_2N_3S$ requires N, 17·95 per cent.).

2-Phenylimino-5-ketotetrahydro-1 : 3 : 4-thiodiazole.

The above acetyl compounds were separately hydrolysed with strong hydrochloric acid. A crystalline white precipitate was slowly produced from each solution on adding water and was crystallised from dilute alcohol, melting at 206°. It slowly dissolves in cold dilute alkali with the development of a pale green colour and the disagreeable smell of *iso*cyanide (Found: N, 21·98. $C_8H_7ON_3S$ requires N, 21·76 per cent.).

The hydrazide was also heated with acetic anhydride in presence of a small quantity of fused sodium acetate on a water-bath instead of over a free flame, with greatly increased yield. Only a small fraction of the hydrazide was acted on during a period of two hours. Only the monoacetyl compound was obtained in this way.

Hydrazomonothio-ortho-*tolyldicarbonamide* (IV).

Semicarbazide hydrochloride (5 g.) dissolved in the least quantity of water was treated with anhydrous sodium carbonate (2·4 g.) and heated under reflux with *o*-tolyl mustard oil (6·6 g.) for twenty minutes while the hydrazide separated as a white solid. It was crystallised from alcohol; m.p. 201° with decomposition (Found: N, 25·12. $C_9HO_{12}N_4S$ requires N, 25·00 per cent.).

2-o-Tolylimino-3-acetyl-5-keto-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole.

The above hydrazide was covered with acetic anhydride in presence of a little powdered fused sodium acetate and carefully heated

with a small flame until the reaction commenced, yielding a clear solution which gave an oily product on being poured into water. After 24 hours' standing the solidified oil was washed well with alcohol and ether and crystallised from rectified spirit; m.p. 183° (Found: N, 17·10. $C_{11}H_{11}O_2N_3S$ requires N, 16·87 per cent.).

2-o-*Tolylimino*-5-*ketotetrahydro*-1 : 3 : 4-*thiodiazole.*

The above acetyl compound was boiled under reflux with fuming hydrochloric acid but was not dissolved. The solid product was washed with water, dried and crystallised from a large quantity of dilute alcohol; m.p. 210° (Found: N, 20·44. $C_9H_9ON_3S$ requires N, 20·29 per cent.).

Hydrazomonothio-p-*tolyldicarbonamide* (V).

Semicarbazide hydrochloride (5 g.) dissolved in the least quantity of water was treated with anhydrous sodium carbonate (2·4 g.) and boiled under reflux with *p*-tolyl mustard oil (6·6 g.). After 15 minutes, crystals of the hydrazide began to separate and the reaction came to an end after about half an hour. It was crystallised from alcohol; m.p. 192° (Found: N, 25·32. $C_9H_{12}ON_4S$ requires N, 25·00 per cent.).

Hydrazomonothio-p-*tolyldicarbonamide and acetic anhydride. Formation of* 2-p-*Tolylimino*-5-*keto*-2:3:4:5-*tetrahydro*-1:3:4-*thiodiazole and* p-*Tolyl*-2-*imino*-5-*thiol*-3-*acetyl*-2:3-*dihydro*-1:3:4-*triazole.*

The clear solution obtained within a few minutes' heating was poured into cold water and allowed to stand overnight. Next morning the oil was found to have partially solidified with a layer of crystals deposited over it. The white solid that came from the aqueous solution was carefully collected and crystallised from rectified spirit; m.p. 247°. It was 2-*o*-tolylimino-5-keto-2:3:4:5-tetrahydro-1:3:4-thiodiazole, insoluble in alkali and remaining unchanged on being boiled with fuming hydrochloric acid pointing to the fact that there was no acetyl group present (Found: N, 20·61. $C_9H_9ON_3S$ requires N, 20·29 per cent.). The solidified oil was washed carefully with ether and crystallised twice from rectified spirit; m.p. 154°. It readily dissolves in alkali from which acid precipitates it. It is acted on by ferric chloride, hydrogen peroxide and iodine solution. It is 2-*o*-tolylimino-3-acetyl-5-thiol-2:3-dihydro-1:3:4-triazole (Found: N, 21·97; S, 12·83. $C_{11}H_{11}ON_4S$ requires N, 22·58; S, 12·90 per cent.). As the quantity was very small it could not be deacetylated with hydrochloric acid.

Hydrazomonothio-xylyldicarbonamide (VI).

Semicarbazide hydrochloride (5 g.) dissolved in a small quantity of water was treated with anhydrous sodium carbonate (2·4 g.) and boiled under reflux with xylyl mustard oil (7·2 g.) in about 200 c.c. alcohol. Within half an hour the reaction was complete and the separated solid was crystallised from alcohol, m. p. 200° with decomposition (Found: N, 23·81. $C_{10}H_{14}ON_4S$ requires N, 23·53 per cent.).

2-Xylylimino-3-acetyl-5-keto-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole.—The hydrazide was treated as usual with fused sodium acetate and acetic anhydride and within two minutes a clear solution was obtained which was poured into water. An oil separated smelling strongly of mustard oil and solidified after 24 hours. It was washed with ether and crystallised from rectified spirit, m. p. 218° (Found: N, 16·00. $C_{12}H_{13}O_2N_3S$ requires N, 15·97 per cent.).

Hydrolysis.—The above acetyl compound was boiled for half an hour under reflux with fuming hydrochloric acid, and the product crystallised from rectified spirit; m.p. 232°. The substance slowly dissolved in cold dilute alkali with a pinkish colour which disappears on boiling but reappears on cooling (Found: N, 18·68. $C_{10}H_{11}ON_3S$ requires N, 19·00 per cent.).

Hydrazo-monothio-β-naphthyldicarbonamide (VII).

β-Naphthyl mustard oil (5 g.) was dissolved in alcohol by warming and to this was added an aqueous solution of semicarbazide hydrochloride (3 g.) treated previously with anhydrous sodium carbonate (1·4 g.). The mixture was then gently boiled under reflux for about 10 minutes and the separated hydrazide after washing with alcohol was crystallised from a large volume of the same solvent; m.p. 210° (decomp.) (Found: N, 21·10. $C_{14}H_{12}ON_4S$ requires N, 21·54 per cent.).

The hydrazide on being heated with acetic anhydride (though extremely carefully) decomposed completely. Among the decomposition products almost the calculated quantity of β-naphthyl mustard oil was isolated and identified.

Hydrazomonothio-phenyldicarbonamide (VIII) *and acetic anhydride. Formation of* 2-*Imino*-3-*acetyl*-5-*keto*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole and* 2-*Imino*-3 : 4-*diacetyl*-5-*keto*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole.*

Hydrazomonothiophenyldicarbonamide, $NHPh{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NH_2$, prepared from phenyl *iso*cyanate and

thiosemicarbazide according to Freund and Schander (*Ber.*, 1896, **29**, 2510) was treated with acetic anhydride in the usual way. The solid obtained from the oil after 24 hours was crystallised from rectified spirit, m.p. 275° (Found : N, 26·52, 26·72 ; S, 19·90. The monoacetyl compound, $C_4H_5O_2N_3S$ requires N, 26·42 ; S, 20·13 per cent.).

The solution after the separation of the solidified oil was concentrated to small bulk, and steam passed through it until the solution was almost free from acetic acid. The volume was again considerably reduced by evaporating on a water-bath and crystals came out on cooling ; these were recrystallised from a mixture of water and alcohol, m.p. 160° (Found : N, 21·04. The diacetyl compound, $C_9H_7O_3N_3S$ requires N, 20·90 per cent.). The free thiodiazole derivatives could not be prepared by deacetylation with hydrochloric acid for want of sufficient quantity of the acetyl derivatives.

In another experiment the hydrazide was boiled with excess of acetic anhydride for about 10 minutes and the clear solution found to smell of phenyl *iso*cyanate. The reaction mixture on being poured into water gave an oil which solidified on standing, and from which diphenylurea and acetanilide were isolated. The aqueous solution was evaporated to a syrup and kept in a desiccator containing potassium hydroxide under vacuum for two to three days when it was found not to solidify. It was then dissolved in water, steamed until free from acetic acid and evaporated almost to dryness. On cooling a solid separated which was found to be partially soluble in sodium hydroxide solution. This alkaline solution after acidification was evaporated to dryness, extracted with absolute alcohol and the alcoholic extract gave on concentration and cooling a crystalline mass, m.p. 92–93° (Found: N, 24·7 ; S. 18·67 per cent.).

The alkali insoluble solid on repeated fractional crystallisation from spirit yielded two compounds melting respectively at 115° and 296°. The former on analysis gave C, 42·61 ; H, 5·01, and the latter gave S, 19·2 ; N, 26·72 ($C_4H_5O_2N_3S$ requires S, 20·13 ; N, 26·42) and is evidently identical with acetyl iminothiobiazolone of Guha (*J. Amer. Chem. Soc.*, 1923, **55**, 1042).

Hydrazomonothio-sym-*diphenyldicarbonamide* (IX) *and acetic anhydride. Formation of* 1-*Phenyl*-2-*phenylimino*-5-*thiol*-2 : 3-*dihydro*-1 : 3 : 4-*triazole.*

Hydrazomonothio-*sym*-diphenyldicarbonamide, was prepared from 4-phenylthiosemicarbazide and phenyl *iso*cyanate. The solidified oil

obtained after the usual treatment was washed with ether and crystallised twice from alcohol. It melted at 208°. The substance was soluble in alkali and unchanged by boiling with strong hydrochloric acid, showing that no acetyl group was present (Found : N, 21·06. $C_{14}H_{12}N_4S$ requires N, 20·90 per cent.). On heating with excess of acetic anhydride for about ten minutes the main product was diphenylurea, m.p. 236°, mixed with a small quantity of the alkali soluble substance, m.p. 208°.

Hydrazomonothio-α-naphthyldicarbonamide (X).

Thiosemicarbazide (4 g.) dissolved in the least quantity of boiling water was treated with a few drops of acetic acid ; to this was gradually added α-naphthyl *iso*cyanate (7·4 g.) in about 200 c.c. of absolute alcohol. A vigorous reaction took place instantaneously, the hydrazide came out as a white solid and was crystallised from rectified spirit ; m.p. 213° (Found : N, 21·68. $C_{12}H_{12}ON_4S$ requires N, 21·54 per cent.).

Hydrazomonothio-α-naphthyldicarbonamide and acetic anhydride.

The hydrazide was covered with acetic anhydride in presence of a little powdered fused sodium acetate and gently heated to boiling for about five minutes ; the turbid solution was poured into water through a filter. The separated oil was stirred vigorously for ten minutes with hot water and within an hour or so the oil solidified, being freed from tar by washing successively with acetone, ether and benzene. It was then crystallised twice from boiling pyridine ; m.p. 293°. The compound contains no sulphur, is insoluble in acid and alkali and in all solvents excepting boiling pyridine (Found : N, 9·18 per cent.). It is therefore *sym*-α : α′-dinaphthyl urea (Cal. N, 8·97 per cent.).

Hydrazodicarbonamide (XI) *and acetic anhydride : Formation of* sym-*Diacetylhydrazine.*

Hydrazodicarbonamide (10 g.) prepared according to the method of Thiele (*Annalen*, 1892, **271**, 127) was heated with 30–40 c.c. of pure acetic anhydride in a sealed tube at 200° in an oil-bath for two hours when all dissolved. On opening the tube carbon dioxide escaped under great pressure. The solution was filtered from a small quantity of hydrazodicarbonamide and steam passed for four hours to remove acetic acid. The solution was then evaporated to a brown syrup on the water-bath, dissolved in acetone and boiled under reflux for thirty minutes with animal charcoal. After filtration and concentration,

excess of ether was added to the cold syrup under vigorous stirring when a beautiful crystalline mass separated. It was purified by precipitating again from an acetone solution and finally crystallised from benzene; m.p. 139° (yield, 4 gms.). It was proved to be *sym*-diacetylhydrazine (m.p. 138°) and on being heated with strong hydrochloric acid gave hydrazine dihydrochloride, m.p. 200°.

Our thanks are due to Mr. Sreekumaran Unni Nair for some preliminary work in connection with this paper.

The University, Dacca.
Department of Organic Chemistry,
Indian Institute of Science,
Bangalore.

[Accepted, 30-5-29.]

PRINTED AND PUBLISHED BY GEORGE KENNETH AT THE DIOCESAN PRESS, POST BOX 455, MADRAS—1929. C 8501.

Part VI.—The Fermentation of Toddy and an Account of the Micro-Organisms producing It. By M. Damodaran. Price, As. 12.

Part VII.—I. Estimation of Iodine in Soils. By Roland V. Norris and D. A. Rama Rao. II. Carbohydrate Changes during the Ripening of Plantains. By S. Ranganathan (Junior). Price, As. 12.

Part VIII.—I. The Oxidation of Sulphur in Suspensions of Activated Sludge and its Influence on the Solubilisation of Mineral Phosphates. By C. V. Ramaswami Ayyar, T. S. S. Perumal and Roland V. Norris. II. Studies in the Proteins of Indian Foodstuffs. Part I. The Proteins of Ragi (*Eleusine coracana*): Eleusinin, the Alcohol-Soluble Protein. By Nuggehalli Narayana and Roland V. Norris. Price, Re. 1.

Part IX.—I. Contributions to the Study of Spike Disease of Sandal (*Santalum album*, Linn.). Part II. Analysis of Leaves from Healthy and Spiked Trees. By A. V. Varadaraja Iyengar. II. Contributions to the Study of Spike Disease of Sandal (*Santalum album*, Linn.). Part III. Physico-Chemical Study of the Leaf-Sap. By A. V. Varadaraja Iyengar. Price, Re. 1.

Part X.—I. Studies on Soil Protozoa. Part I. Protozoan Fauna of Some Mysore Soils. By H. S. Madhava Rao. II. Studies on Soil Protozoa. Part II. The Function of Mitochondria in Some Soil Protozoa. By H. S. Madhava Rao. Price, Re. 1.

Part XI.—I. Studies in Enzyme Action. Part I. Amylase from Cholam (*Sorghum vulgare*). By V. N. Patwardhan and Roland V. Norris. II. Studies in Enzyme Action. Part II. The Nature of Amylase. By D. Narayanamurti and Roland V. Norris. Price, Rs. 1-8.

Part XII.—A Bio-Chemical Study of some Soil Fungi with special reference to Ammonia Production. By A. K. Thakur and Roland V. Norris. Price, Re. 1.

Part XIII.—The Atomic Weight of Antimony from Different Sources. By K. R. Krishnaswami. Price, Re. 1.

Part XIV.—Oil from the Seeds of *Adenanthera Pavonina*: A Source of Lignoceric Acid. By S. M. Mudbidri, P. Ramaswami Ayyar and H. E. Watson. Price, As. 8.

Part XV.—I. Constituents of some Indian Essential Oils. Part XXII. The Essential Oil from the Flower Heads of *Cymbopogon Coloratus*, Stapf. By P. P. Pillay, B. Sanjiva Rao and J. L. Simonsen. Part XXIII. The Essential Oil from the Fruits of *Piper Cubeba*, Linn. By B. Sanjiva Rao, V. P. Shintre and J. L. Simonsen. Part XXIV. The Essential Oil from the Rhizomes of *Curcuma Zedoaria*, Roscoe. By B. Sanjiva Rao, V. P. Shintre and J. L. Simonsen. II. The Constituents of Indian Turpentine from *Pinus Longifolia*, Roxb. Part IV. By P. Parameswaran Pillay and J. L. Simonsen. Price, Rs. 1-4.

Part XVI.—I. *a-iso*Propylglutaconic Acid. By K. V. Hariharan, K. N. Menon and J. L. Simonsen. II. Derivatives of Methyl 2: 2-Dimethyl*cyclo*-Pentan-3-one-1-Carboxylate. By C. S. Gibson, K. V. Hariharan and J. L. Simonsen. Price, As. 12.

Part XVII.—I. Thiophthalic Acids. Part I. By Gopal Chandra Chakravarti. II. Organic Cyclic Polysulphides: Condensation of Ethylene Mercaptan with Di- and Trichloracetic Acids. By Gopal Chandra Chakravarti and Jogendra Mohan Saha. Price, As. 8.

Part XVIII.—Bis-Semidine Inversion in Aromatic Dihydrazo-Compounds. By Praphulla Chandra Guha and Hirendra Kumar Banerjee. Price, As. 8.

Part XIX.—I. Contributions to the Study of Spike-Disease of Sandal (*Santalum Album*, Linn.). Part IV. Chemical Composition of Healthy and Spiked Sandal Stems. By D. A. Rama Rao and M. Sreenivasaya. II. Contributions to the Study of Spike Disease of Sandal (*Santalum Album*, Linn.). Part V. Transmission of Spike by Budding. By M. Sreenivasaya and G. Gopalaswami Naidu. Price, Re. 1.

VOLUME XII (A)—1929.

Part I.—Phototropic Compounds of Mercury. By Bh. S. V. Raghava Rao and H. E. Watson. Price, Re. 1.

Part II.—Photoelectric Emission from Phototropic Mercury Compounds. By Bh. S. V. Raghava Rao and H. E. Watson. Price, As. 12.

Part III.—Attempts to Synthesise *Ortho*-Thiolphenylhydrazine. By Praphulla Chandra Guha and Tejendra Nath Ghosh. Price, As. 6.

Part IV.—I. Characterisation of very small quantities of Proteins by Van Slyke's Method. By Nuggihalli Narayana and Mothnahalli Sreenivasaya. II. The Determination of Pyruvic Acid. By Basettihalli Hanumantha Rao Krishna and Mothnahalli Sreenivasaya. Price, As. 12.

Part V.—I. Studies on Soil *Actinomyces*. Part I. Introduction. By V. Subrahmanyan and Roland V. Norris. II. Studies on Soil *Actinomyces*. Part II. Their Mode of Occurrence in the Soil. By V. Subrahmanyan. Price, Re. 1.

Part VI.—I. A Study of the Symbiotic Fungus from the Mysore Lac Insect. By M. Sreenivasaya and S. Mahdihassan. II. The Golgi Apparatus of Free-Living Protozoa. By H. S. Madhava Rao. Price, As. 12.

Part VII.—I. Formation of Heterocyclic Compounds from Diethylxanthic Formic Ester. By Praphulla Chandra Guha and Devendra Nath Datta. II. Ring Closure of Hydrazo-Monothiodicarbonamides with Acetic Anhydride: Formation of Iminothiobiazolones and Iminothioltriazoles. By Praphulla Chandra Guha and Tarani Kanta Chakraborty. Price, Rs. 1-4.