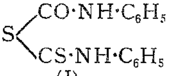
I.—FORMATION OF HETEROCYCLIC COMPOUNDS FROM DIETHYLXANTHIC FORMIC ESTER.[1]

By Praphulla Chandra Guha and Devendra Nath Datta.

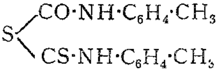
Diethylxanthic formic ester, $\mathrm{CO_2Et{\cdot}S{\cdot}CS{\cdot}OEt}$, was prepared by Holmberg (*J. pr. Chem.*, 1905, **71**, 264) by the action of chlorocarbonic ester upon potassium ethyl xanthate. Similar compounds, *viz.*, diethylxanthic acetic ester and ethylxanthic propionic acid and their 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 :



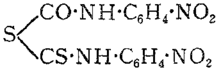
$$\mathrm{S}\begin{cases}\mathrm{CO{\cdot}NH{\cdot}C_6H_5}\\ \mathrm{CS{\cdot}NH{\cdot}C_6H_5}\end{cases}$$

(I)



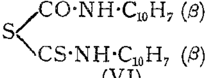
$$\mathrm{S}\begin{cases}\mathrm{CO{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3}\\ \mathrm{CS{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3}\end{cases}$$

(II & III)
(*ortho* and *para*)



$$\mathrm{S}\begin{cases}\mathrm{CO{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2}\\ \mathrm{CS{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2}\end{cases}$$

(IV & V)
(*meta* and *para*)



$$\mathrm{S}\begin{cases}\mathrm{CO{\cdot}NH{\cdot}C_{10}H_7}\ (\beta)\\ \mathrm{CS{\cdot}NH{\cdot}C_{10}H_7}\ (\beta)\end{cases}$$

(VI)

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

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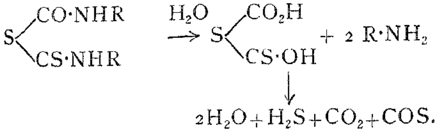
[1] Reprinted from the *Journal of the Indian Chemical Society*, 1929, 6, 65.

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

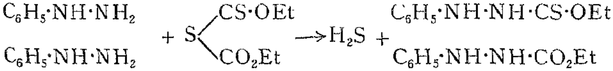


$$\mathrm{S}\begin{matrix}\diagup \mathrm{CO{\cdot}NHR} \\ \diagdown \mathrm{CS{\cdot}NHR}\end{matrix} \xrightarrow{H_2O} \mathrm{S}\begin{matrix}\diagup \mathrm{CO_2H} \\ \diagdown \mathrm{CS{\cdot}OH}\end{matrix} + 2\,\mathrm{R{\cdot}NH_2}$$

$$\downarrow$$

$$2H_2O + H_2S + CO_2 + COS.$$

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 :—

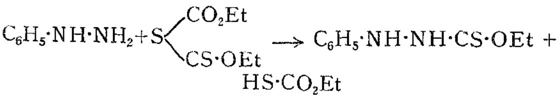


$$\begin{matrix}\mathrm{C_6H_5{\cdot}NH{\cdot}NH_2} \\ \mathrm{C_6H_5{\cdot}NH{\cdot}NH_2}\end{matrix} + \mathrm{S}\begin{matrix}\diagup \mathrm{CS{\cdot}OEt} \\ \diagdown \mathrm{CO_2Et}\end{matrix} \longrightarrow H_2S + \begin{matrix}\mathrm{C_6H_5{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}OEt} \\ \mathrm{C_6H_5{\cdot}NH{\cdot}NH{\cdot}CO_2Et}\end{matrix} \quad (A)$$

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 :

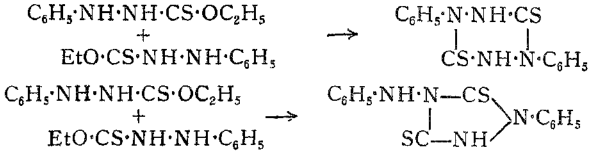


$$\mathrm{C_6H_5{\cdot}NH{\cdot}NH_2} + \mathrm{S}\begin{matrix}\diagup \mathrm{CO_2Et} \\ \diagdown \mathrm{CS{\cdot}OEt}\end{matrix} \longrightarrow \mathrm{C_6H_5{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}OEt} + \mathrm{HS{\cdot}CO_2Et}$$

(VII)

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-*p*-urazine or *N*-phenyl-*N*-anilinodithiourazole, thus :

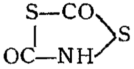


N-phenyl-*N*-anilinodithiourazole.

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.

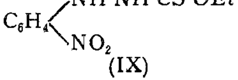
The action of strong hydrochloric acid upon the ester, $C_6H_5 \cdot NH \cdot NH \cdot CS \cdot OEt$, however, led to a heterocyclic five-membered compound (VIII) containing two sulphur atoms in the ring,



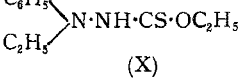
(VIII)

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 also tried ; they yielded the corresponding monothiocarbazinic esters (IX) and (X) as in the case of phenylhydrazine.



(IX)



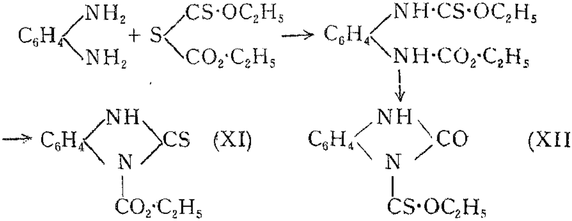
(X)

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

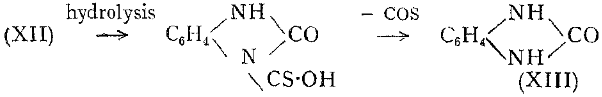
Action of Diamines.

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

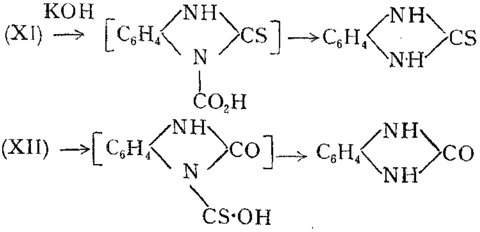
Firstly *o*-phenylene monothiodiurethane[1] is formed which under the conditions of the experiment suffers internal condensation in two different ways yielding *N*-carbethoxyphenylene thiourea (XI) and *N*-thiocarbethoxyphenylene urea (XII) thus :


(XI) (XII)

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.


(XIII)

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 :



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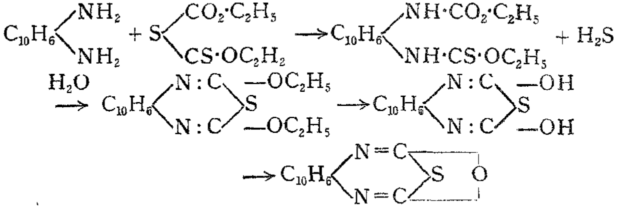
[1] A compound of the type of (XVI) has actually been isolated with ethylenediamine.

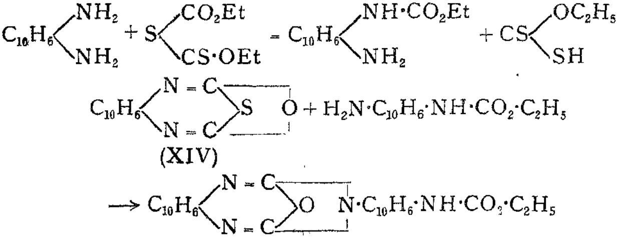
The action of 1 : 2-naphthylenediamine has also been studied but its behaviour with the di-ester appears to be a little peculiar[1] in so far as the two products finally isolated are quite different from compounds (XI, XII and XIII). Two compounds, 4 : 5-naphthylene-2 : 7-endoxy-1 : 3 : 6-thioheptadiazine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



(XIV)

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).



(XIV)

(XV)

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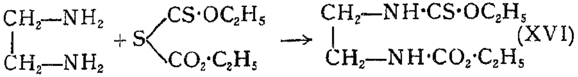
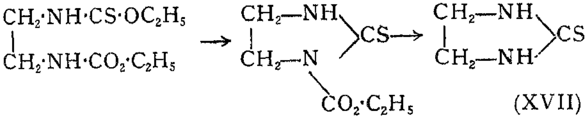
[1] It will be seen that the experiments with phenylene- and naphthylenediamines have not been conducted under identical conditions (*vide Experimental*).

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:



$$\begin{array}{l}CH_2-NH_2\\ |\\ CH_2-NH_2\end{array} + S\left<\begin{array}{l}CS\cdot OC_2H_5\\ CO_2\cdot C_2H_5\end{array}\right. \longrightarrow \begin{array}{l}CH_2-NH\cdot CS\cdot OC_2H_5\\ |\\ CH_2-NH\cdot CO_2\cdot C_2H_5\end{array} \quad (XVI)$$



$$\begin{array}{l}CH_2\cdot NH\cdot CS\cdot OC_2H_5\\ |\\ CH_2\cdot NH\cdot CO_2\cdot C_2H_5\end{array} \longrightarrow \begin{array}{l}CH_2-NH\\ |\\ CH_2-N\\ \quad\backslash\\ \quad CO_2\cdot C_2H_5\end{array}\!\!\left.\right>CS \longrightarrow \begin{array}{l}CH_2-NH\\ |\\ CH_2-NH\end{array}\!\!\left.\right>CS \quad (XVII)$$

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*, 1883, **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.

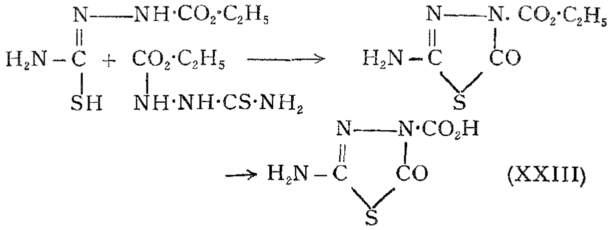
Semicarbazide reacts with the di-ester to yield semicarbazide monothiocarboxylic ethyl ester, $NH_2-CO-NH-NH-CS\cdot OC_2H_5$ (XVIII). It is interesting to note that the behaviour of thiosemicarbazide and 4-arylthiosemicarbazides towards the di-ester is different from that of semicarbazide. Semicarbazide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

$$NH_2\cdot CO\cdot NH\cdot NH_2 \longrightarrow NH_2\cdot CO\cdot NH\cdot NH\cdot CS\cdot OC_2H_5 \quad (XVIII)$$
$$NH_2\cdot CS\cdot NH\cdot NH_2 \longrightarrow NH_2\cdot CS\cdot NH\cdot NH\cdot CO_2\cdot C_2H_5 \quad (XIX)$$
$$C_6H_5\cdot NH\cdot CS\cdot NH\cdot NH_2 \longrightarrow C_6H_5\cdot NH\cdot CS\cdot NH\cdot NH\cdot CO_2\cdot C_2H_5 \quad (XX)$$
$$p\text{-}C_7H_7\cdot NH\cdot CS\cdot NH\cdot NH_2 \longrightarrow p\text{-}C_7H_7\cdot NH\cdot CS\cdot NH\cdot NH\cdot CO_2Et \quad (XXI)$$
$$C_{10}H_7\cdot NH\cdot CS\cdot NH\cdot NH_2 \longrightarrow C_{10}H_7\cdot NH\cdot CS\cdot NH\cdot NH\cdot CO_2\cdot C_2H_5 \quad (XXII)$$

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 ($NH_2 \cdot CS$) group of thiosemicarbazide, facilitates the formation of $NH_2 \cdot CO \cdot NH \cdot NH \cdot CS \cdot OEt$; whereas the $NH_2 \cdot CS$ group of thiosemicarbazide being less negative, facilitates the formation of $NH_2 \cdot CS \cdot NH \cdot NH \cdot CO_2 \cdot C_2H_5$.

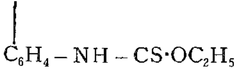
The action of strong hydrochloric acid upon the semicarbazide and thiosemicarbazide compounds (XVIII and XIX) is also quite interesting; the former is decomposed into alcohol, carbon oxysulphide and semicarbazide; whereas the latter yields 2-amino-4-carboxylic-5 keto-4 : 5-dihydro-1 : 3 : 4-thiodiazole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

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


(XXIII)

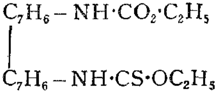
It liberates carbon dioxide from sodium bicarbonate and is readily soluble in sodium carbonate showing the presence of a carboxylic group; it does not form mercaptides with mercuric chloride and lead acetate, does not form disulphide with iodine, nor can it be desulphurised by treatment with mercuric 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).



$$\begin{array}{l} C_6H_4 - NH - CO_2 \cdot C_2H_5 \\ | \\ C_6H_4 - NH - CS \cdot OC_2H_5 \end{array}$$

(XXIV)



$$\begin{array}{l} C_7H_6 - NH \cdot CO_2 \cdot C_2H_5 \\ | \\ C_7H_6 - NH \cdot CS \cdot OC_2H_5 \end{array}$$

(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. $C_{10}H_{10}O_2N_2S$ 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 was filtered, 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 $C_{12}H_6ON_2S$ 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, $C_{25}H_{18}O_3N_4$ 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).

Action of Hydrochloric Acid upon Ethylene monothio-diurethane.

Ethylene monothio-diurethane was heated under reflux with concentrated hydrochloric acid for half an hour when a solution was obtained remaining clear on cooling. A small portion after neutralisation with alkali was found to yield no solid product, so the whole was diluted with water and evaporated to dryness on the water-bath when a crystalline residue was left, very soluble in water, alcohol and acetone; it was therefore washed with ether (in which it is almost insoluble) to remove any tarry matter. In order to isolate the free base it was dissolved in the least amount of water and then sodium acetate added when a solid was obtained.[1] This on being crystallised from dilute alcohol melted at 193°, identical with compound (XVII).

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[1] The free base can also be isolated by boiling with alcohol.

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. 1551–56°. 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.).

Benzidine monothiodicarboxylic ester (XXIV).—An alcoholic solution of the ester (2 g.) was added to benzidine (2 g.) under ice cooling. The reaction took place with rise of temperature and liberation of hydrogen sulphide. The reaction mixture was allowed to stand at the ordinary temperature for two to three hours and then heated under reflux for half an hour, the solid product obtained on cooling being filtered and crystallised from acetic acid. The filtrate on evaporation gave a second crop, m.p. 211–212°. It is soluble in dilute alkali but insoluble in dilute acid (Found: N, 8·41. $C_{18}H_{20}O_3N_2S$ requires N, 8·13 per cent.).

Tolidine monothiodicarboxylic ester (XXV) was obtained and purified as in the previous case; m.p. 125–26°. The substance is soluble in alkali but insoluble in acid (Found: N, 7·61. $C_{20}H_{24}O_3N_2S$ requires N, 7·52 per cent.).

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