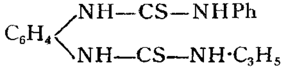
LENGTHENED *ORTHO*-DI-DERIVATIVES OF BENZENE AND THEIR RING-CLOSURE: FORMATION OF POLYMEMBERED HETEROCYCLIC COMPOUNDS FROM SUBSTITUTED PHENYLENE-DICARBAMIDES.[1]

By Tejendra Nath Ghosh and Praphulla Chandra Guha.

The ring-closing action of hydrochloric acid, sodium hydroxide and acetic anhydride upon hydrazodicarbamides, mono- and dithioamides has been studied in some detail and a large number of thiodiazole and triazole derivatives have been obtained (Freund, *Ber.*, 1895, **28**, 946; 1896, **29**, 2506; Arndt and co-workers, *Ber.*, 1921, **54**, 2089; 1922, **55**, 341; Fromm, *Annalen*, 1923, **433**, 1; *Monatsh.*, 1924, **44**, 298; *Ber.*, 1923, **56**, 1370; Guha, *J. Amer. Chem. Soc.*, 1922, **44**, 1502; 1923, **45**, 1036; 1925 **47**, 387). It was thought worth while to extend the field of such dicarbamides so as to comprise the corresponding —CO-NHR and —CS-NHR derivatives of aromatic and aliphatic 1:2-diamines. Phenylene- and ethylenediamines, it is well known, form dithiocarbamides with ammonium sulphocyanide which readily form phenylene- or ethylenethioureas. The following mixed and simple disubstituted dicarbamides as also the mono- and dithiocarbamides[2] have now been prepared from *o*-phenylene- or *o*-tolylenediamine.

$C_6H_4(NH{\cdot}CS{\cdot}NHPh)_2$ (I)
$C_6H_4(NH{\cdot}CS{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3)_2$ (*o*- and *p*-) (II, III)
$C_6H_4(NH{\cdot}CS{\cdot}NH{\cdot}C_6H_3(CH_3)_2)_2$ (IV)
$CH_3{\cdot}C_6H_3(NH{\cdot}CS{\cdot}NHPh)_2$ (V)
$C_6H_4(NH{\cdot}CS{\cdot}NH{\cdot}CH_3)_2$ (VI)
$C_6H_4(NH{\cdot}CS{\cdot}NH{\cdot}C_3H_5)_2$ (VII)



$$C_6H_4\left\langle\begin{matrix} NH{-}CS{-}NHPh \\ NH{-}CS{-}NH{\cdot}C_3H_5 \end{matrix}\right.$$ (VIII)

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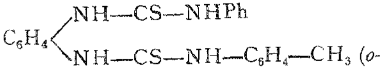
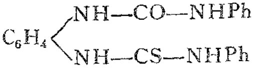
[1] Reprinted from the *Journal of the Indian Chemical Society*, 1929, **6**, 181.

[2] Compounds I, VII, XV are known (*Annalen*, 1885, 228, 200, *Ber.*, 1883, 16, 592) but no unsymmetrically substituted mono- or dithiodicarbamide is known.



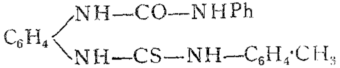
$$C_6H_4\left\langle\begin{array}{l}NH-CS-NHPh\\NH-CS-NH-C_6H_4-CH_3\end{array}\right.$$

(*o*- and *p*-) (IX, X)



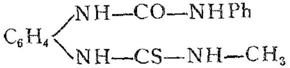
$$C_6H_4\left\langle\begin{array}{l}NH-CO-NHPh\\NH-CS-NHPh\end{array}\right.$$

(XI)



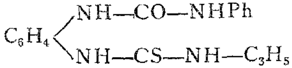
$$C_6H_4\left\langle\begin{array}{l}NH-CO-NHPh\\NH-CS-NH-C_6H_4\cdot CH_3\end{array}\right.$$

(XII)



$$C_6H_4\left\langle\begin{array}{l}NH-CO-NHPh\\NH-CS-NH-CH_3\end{array}\right.$$

(XIII)



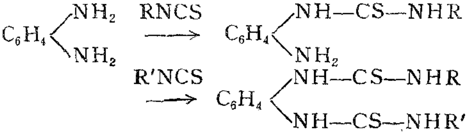
$$C_6H_4\left\langle\begin{array}{l}NH-CO-NHPh\\NH-CS-NH-C_3H_5\end{array}\right.$$

(XIV)

$C_6H_4(NH-CO-NH_2)_2$ (XV)

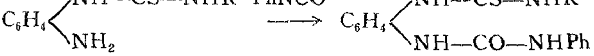
$C_6H_4(NH-CO-NHPh)_2$ (XVI)

The unsymmetrically substituted dithiocarbamides VIII, IX and X have now been obtained by the action of one molecule of mustard oil upon compounds of the diamine with one molecule of a mustard oil, thus :



$$C_6H_4\left\langle\begin{array}{l}NH_2\\NH_2\end{array}\right. \xrightarrow{RNCS} C_6H_4\left\langle\begin{array}{l}NH-CS-NHR\\NH_2\end{array}\right. \xrightarrow{R'NCS} C_6H_4\left\langle\begin{array}{l}NH-CS-NHR\\NH-CS-NHR'\end{array}\right.$$

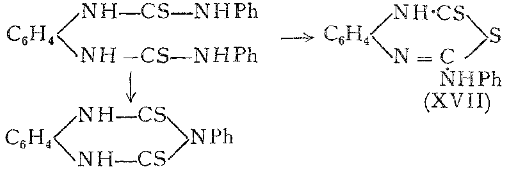
whereas the monothiodicarbamides, XI, XII, XIII and XIV have been prepared by the action of phenyl *iso*cyanate upon compounds of the diamine with one molecule of a mustard oil, thus :



$$C_6H_4\left\langle\begin{array}{l}NH-CS-NHR\\NH_2\end{array}\right. \xrightarrow{PhNCO} C_6H_4\left\langle\begin{array}{l}NH-CS-NHR\\NH-CO-NHPh\end{array}\right.$$

o-Phenylenediphenyldithiocarbamide (I) loses a molecule of aniline on being heated with strong hydrochloric acid or 20 per cent. potassium hydroxide solution. The elimination of aniline might take place in either of the following two different ways forming 2-anilino-4 : 5-benzo-7-thioketo-1 : 3 : 6-heptathiodiazine (XVII) or

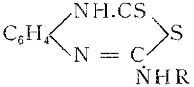
1-*N*-phenyl-2 : 7-dithioketo-4 : 5-benzo-1 : 3 : 6-heptatriazine (XVII*a*), thus :



(XVII)

(XVII*a*)

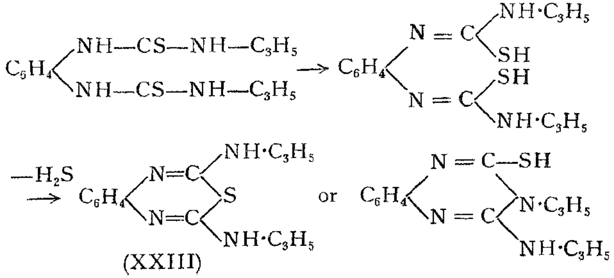
The compound actually isolated behaves like a mono-mercaptan as it has been found that for disulphide formation two molecules of the substance require only two atomic proportions of iodine (compare Guha, *J. Amer. Chem. Soc.*, 1922, **44**, 1502). So, the dimercaptanic formula has been rejected. The other disubstituted dithiocarbamides (II-VI and VIII-X) resemble the diphenyl compound in behaviour, yielding substituted aminoheptathiodiazines XVII—XXII, XXIV—XXVI respectively.



R=Ph, XVII ; *o*-tolyl, XVIII ; *p*-tolyl, XIX ; xylyl, XX ; Me XXII ; C_3H_5, XXIV ; XXV=XVIII ; XXVI=XIX.

It is significant that although in compounds VIII, IX, and X the two thiocarbamide groupings are substituted by two different groups (*viz.*, C_6H_5 : C_3H_5, C_6H_5 : *o*-$C_6H_4{\cdot}CH_3$, C_6H_5 : *p*-$C_6H_4{\cdot}CH_3$) aniline is invariably eliminated in each case.

The behaviour of *o*-phenylenediallyldithiocarbamide (VII) is peculiar and instead of allylamine one molecule of sulphuretted hydrogen is eliminated with the formation of 2 : 7-diallylamino-4 : 5-benzo-1 : 3 : 6-thioheptadiazine, XXIII, thus :

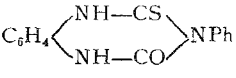


(XXIII)

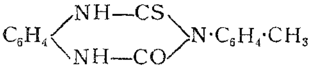
The alternative formula has been rejected on the ground of its showing no mercaptanic properties and also because it forms a diacetyl derivative from which no acetyl group can easily be removed by hydrolysis as would have been the case with an acetylthiol compound (*vide* Guha, *ibid*). Acetic anhydride brings about the same type of ring-closure yielding the diacetyl derivative of XXIII which can be deacetylated only by boiling with strong hydrochloric acid. This peculiar behaviour of the allyl compounds, *viz.*, favouring the formation of sulphur-containing rings will also be noticed in the case of mono-allylthiocarbamide, XXXVI.

The action of strong hydrochloric acid on the four phenylene mono-thiodicarbamides XI, XII, XIII and XIV has been studied with the result that they have been found to yield types of compounds quite different from those obtained from the compounds containing dithiocarbamide groupings.

Compounds XI and XII, which are substituted by aryl groups, give 1-*N*-phenyl-2-keto-4 : 5-benzo-7-thioketo-1 : 3 : 6-heptatriazine (XXVII) and 1-*N*-tolyl-2-keto-4 : 5-benzo-7-thioketo-1 : 3 : 6-heptatriazine (XXVIII) respectively.

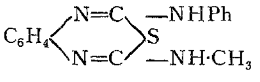


(XXVII)

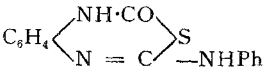


(XXVIII)

The mono-thiodicarbamide (XIII) yields with the loss of one molecule of water 2-methylamino-4 : 5-benzo-7-phenylamino-1 : 3 : 6-thioheptadiazine (XXIX), whereas from (XIV) there is obtained 2-phenylamino-4 : 5-benzo-7-keto-1 : 3 : 6-thioheptadiazine (XXX).

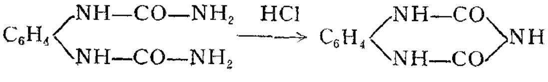


(XXIX)



(XXX)

Phenylenediurea (XV) yields phenylenebiuret (XXXI), whereas the corresponding diphenyl substituted compound (XVI) remains unaffected by the action of hydrochloric acid.



(XXXI)

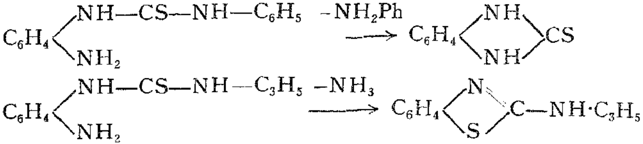
The first four of the following five mustard oil compounds of *o*-phenylenediamine, *viz.*,

$NH_2{\cdot}C_6H_4{\cdot}NH{\cdot}CS{\cdot}NHPh$ (XXXII),

$NH_2{\cdot}C_6H_4{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3$ (*ortho* and *para*) (XXXIII and XXXIV),

$NH_2{\cdot}C_6H_4{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}CH_3$ (XXXV),

and $NH_2{\cdot}C_6H_4{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_3H_5$ (XXXVI)
react with strong hydrochloric acid to yield *o*-phenylenethiourea, evidently with the elimination of the respective amines, whereas, the last one behaves in a quite different manner to yield 5-allylamino-2 : 3-benzo-1 : 4-thiazole (XXXVII), thus :

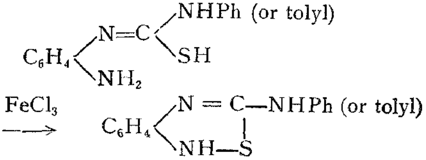


$$C_6H_4\left\langle\begin{matrix}NH{-}CS{-}NH{-}C_6H_5\\NH_2\end{matrix}\right. \xrightarrow{-NH_2Ph} C_6H_4\left\langle\begin{matrix}NH\\NH\end{matrix}\right\rangle CS$$

$$C_6H_4\left\langle\begin{matrix}NH{-}CS{-}NH{-}C_3H_5\\NH_2\end{matrix}\right. \xrightarrow{-NH_3} C_6H_4\left\langle\begin{matrix}N\\S\end{matrix}\right\rangle C{-}NH{\cdot}C_3H_5$$

(XXXVII)

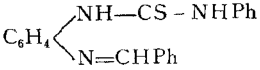
A suitable reagent for building up arylaminobenzothiodiazine compounds has been found in ferric chloride, which acting upon (XXXII) and (XXXIV) gives rise to 3 : 4-benzo-6-anilino-1 : 2 : 5-thiodiazine (XXXVIII) and 3 : 4-benzo-6-*p*-tolylamino-1 : 2 : 5-thiodiazine (XXXIX) respectively thus :



$$C_6H_4\left\langle\begin{matrix}N{=}C\left\langle\begin{matrix}NHPh\text{ (or tolyl)}\\SH\end{matrix}\right.\\NH_2\end{matrix}\right. \xrightarrow{FeCl_3} C_6H_4\left\langle\begin{matrix}N = C{-}NHPh\text{ (or tolyl)}\\ \quad\;\; |\\NH{-}S\end{matrix}\right.$$

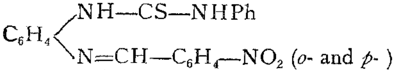
(XXXVIII, XXXIX)

The free amino-groups of the mustard oil compounds of phenylenediamine react readily with aldehydes to yield



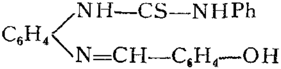
$$C_6H_4\left\langle\begin{matrix}NH{-}CS{-}NHPh\\N{=}CHPh\end{matrix}\right.$$

(XLIII)



$$C_6H_4\left\langle\begin{matrix}NH{-}CS{-}NHPh\\N{=}CH{-}C_6H_4{-}NO_2\end{matrix}\right. \text{ (}o\text{- and }p\text{-)}$$

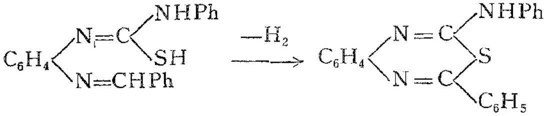
(XL and XLI)



$$C_6H_4\left\langle\begin{matrix}NH{-}CS{-}NHPh\\N{=}CH{-}C_6H_4{-}OH\end{matrix}\right.$$

(XLII)

of which the first one has been oxidised by ferric chloride to 2-phenyl-4 : 5-benzo-7-anilino-1 : 3 : 6-heptathiodiazine (XLIV), thus :



(XLIV)

EXPERIMENTAL.

2-Phenylamino-4 : 5-phenylene-7-thioketo-1 : 3 : 6-thioheptadiazine (XVII).—*o*-Phenylenediphenyldithiocarbamide (2 g., prepared according to the method given in *Annalen*, 1885, **228**, 200) was heated under reflux with hydrochloric acid (65 c.c., *d* 1·19) for about half an hour when a green solution mixed with some tarry matter was obtained. On further heating for 15 minutes, the tarry mass solidified. The reaction mixture was allowed to cool and the green precipitate filtered, washed with water and finally crystallised from water acidulated with a few drops of hydrochloric acid, separating in beautiful white rectangular plates, m.p. 290-291°. It can be precipitated by acid from a caustic soda solution. Yield 1·1 g. (Found : S, 22·61. $C_{14}H_{11}N_3S_2$ requires S, 22·45 per cent.). The presence of aniline in the acid filtrate was proved.

The acetyl derivative.—The above compound (0·5 g.) was heated with about 5 c.c. of acetic anhydride under reflux for about 15 minutes, when a perfectly clear solution was obtained, which, on being poured into cold water, yielded a white crystalline mass. It was further crystallised from acetic acid, m.p. 160°.

The disulphide.—Iodine dissolved in potassium iodide was added drop by drop to an alcoholic solution of the above thio-compound (XVII) and gently warmed. On dilution with water it gave a yellowish amorphous mass which was washed free from excess of iodine with potassium iodide solution, water and finally with alcohol; m.p. 210° (0·067 g. of the substance required 0·0312 g. of iodine for oxidation. $C_{14}H_{11}N_3S_2$ with one thiol group requires 0·03 g. of iodine ; with two thiol groups it requires 0·06 g. of iodine).

Action of caustic potash solution on o-*phenylenediphenyldithiocarbamide : Formation of Compound* (XVII).—*o*-Phenylenediphenyldithiocarbamide (2 g.) was heated under reflux with excess of potassium hydroxide solution (20 per cent.) for about 2 hours when a clear solution was obtained. The solution after cooling was acidified with hydrochloric acid when a white solid came down with slight evolution of sulphuretted hydrogen. The white precipitate after filtration was crystallised from hot water acidulated with a few drops of hydrochloric acid; m. p. 290-291°. It is soluble in cold dilute alkali and is precipitated by acids. It gives an insoluble mercaptide with mercuric chloride and a disulphide (m.p. 210°) with iodine (Found: S, 22·59. $C_{14}H_{11}N_3S_2$ requires S, 22·45 per cent.). The identity of this compound with (XVII), obtained on treatment with hydrochloric acid, was confirmed by the mixed melting point.

o-*Phenylenedi*-o-*tolyldithiocarbamide* (II).—An alcoholic solution of *o*-phenylenediamine (2·1 g.) was heated under reflux on the water-bath with *o*-tolyl mustard oil (3 g.) for about half an hour when a white crystalline precipitate was obtained and recrystallised from alcohol; m.p. 161°. Yield is almost quantitative (Found: S, 15·62. $C_{22}H_{22}N_4S_2$ requires S, 15·76 per cent.).

2-o-*Tolylamino*-4 : 5-*phenylene*-7-*thioketo*-1 : 3 : 6-*thioheptadiazine* (XVIII).—Two gms. of the above compound (II) were heated under reflux with hydrochloric acid (60 c.c., *d* 1·19) for about 30 minutes when a green solution with tarry matter was obtained. On further heating, the tarry mass solidified and was crystallised from alcohol; m.p. 300° (Found: S, 21·31. $C_{15}H_{13}N_3S_2$ requires S, 21·40 per cent.). The *acetyl* derivative was crystallised from acetic acid; m.p. 200°.

o-*Phenylenedi*-p-*tolyldithiocarbamide* (III).—The method of preparation was the same as in the case of the preceding compound (II). The yield was almost quantitative. It crystallised from alcohol in shining white plates, m.p. 178° (Found: S, 15·82. $C_{22}H_{22}N_4S_2$ requires S, 15·76 per cent.).

2-p-*Tolylamino*-4 : 5-*phenylene*-7-*thioketo*-1 : 3 : 6-*thioheptadiazine* (XIX).—The method of preparation was the same as in the case of the preceding compounds (XVII and XVIII). It was crystallised from alcohol; m.p. 300.° It is soluble in cold dilute alkali from which it is precipitated by acids (Found: S, 21·26. $C_{15}H_{13}N_3S_2$ requires S, 21·40 per cent.). The *disulphide* was prepared as in the case of the corresponding phenyl compound; m.p. 190° (0·206 g. of the substance required 0·088 g. of iodine for oxidation. $C_{15}H_{13}N_3S_2$ containing one thiol group requires 0·087 g. of iodine). The *acetyl* derivative was obtained in the usual way and was crystallised from acetic acid; m.p. 200.°

o-*Phenylenedi*-(1 : 3 : 4)-*xylyldithiourea* (IV).—The method of preparation was the same as in the case of the corresponding phenyl and tolyl compounds. It was crystallised from alcohol; m.p. 145° (Found: S, 14·39. $C_{24}H_{26}N_4S_2$ requires S, 14·74 per cent.).

Action of strong hydrochloric acid upon (IV): *Formation of* 2-(1 : 3 : 4)-*xylylamino*-4 : 5-*phenylene*-7-*thioketo*-1 : 3 : 6-*thioheptadiazine*

(XX).—This was prepared similarly to the compounds (XVII, XVIII, XIX) and was crystallised from alcohol; m.p. 295°. It is soluble in cold dilute alkali from which it can be precipitated by acids. It gave an amorphous *disulphide* (m.p. 172°) with iodine solution (Found: S, 20·13. $C_{16}H_{15}N_3S_2$ requires S, 20·44 per cent.). The *acetyl* derivative was crystallised from acetic acid; m.p. 296°.

o-*Toluylenediphenyldithiocarbamide* (V).—An alcoholic solution of *o*-toluylenediamine (1·2 g.) was heated under reflux on the water-bath with phenyl mustard oil (2·7 g.) for about 30 minutes when a white crystalline precipitate was obtained which was crystallised from alcohol; m.p. 142°. Yield is almost quantitative (Found: S, 16·48. $C_{21}H_{20}N_4S_2$ requires S, 16·32 per cent.).

Action of strong hydrochloric acid upon (V): *Formation of* 2-*Phenylamino*-4: 5-*methylbenzo*-7-*thioketo*-1 : 3: 6-*thioheptadiazine* (XXI).—The above compound (V, 2 g.) was heated under reflux with concentrated hydrochloric acid (60 c.c.) for about half an hour when a green solution was obtained, and on cooling deposited a solid which was crystallised from alcohol, m.p. 265°. It is soluble in cold dilute alkali from which it is precipitated by acids (Found: N, 14·21. $C_{15}H_{13}N_3S_2$ requires N, 14·04 per cent.). The presence of aniline in the acid filtrate was proved. The *disulphide* was prepared in the usual way; m.p. 137°. The *acetyl* derivative was crystallised from acetic acid, m.p. 185°.

o-*Phenylenedimethyldithiocarbamide* (VI).—Phenylenediamine (3 g.) was dissolved in alcohol to which methyl mustard oil (4 g.) was added and the solution boiled for some time. The clear solution, on cooling, gave colourless crystals which were recrystallised from alcohol, m. p. 175° (Found: S, 24·85. $C_{10}H_{14}N_4S_2$ requires S, 25·19 per cent.).

2-*Methylamino*-4 : 5-*benzo*-7-*thioketo*-1 : 3 : 6-*thioheptadiazine* (XXII)—Two grams of the compound (VI) were boiled with strong hydrochloric acid (65 c. c.) for about 2 hours. The solution, when cold, gave a white crystalline mass which was further crystallised from alcohol; m. p. 168°. It is soluble in cold alkali from which it is precipitated by acids (Found: N, 19·15. $C_9H_9N_3S_2$ requires N, 18·83 per cent.). The *disulphide* was prepared in the usual way; m.p. 194°.

2 : 7-*Diallylamino*-4 : 5-*benzo*-1 : 3 : 6-*thioheptadiazine* (XXIII).—Three g. of *o*-phenylenediallylthiourea (VII) (prepared according to the method given in *Annalen*, 1885, **228**, 201) were heated with strong hydrochloric acid (70 c. c.) under reflux for about 30 minutes when a greenish coloured clear solution was obtained. The cold solution, on dilution with water, gave no precipitate, but on making alkaline with ammonia a white solid mixed with tarry matter was obtained, and was

purified by dissolving in diltue hydrochloric acid and precipitating with ammonia. It was finally crystallised from acetone, m. p. above 300° (Found: N, 20·37. $C_{14}H_{16}N_4S$ requires N, 20·58 per cent.)

Action of acetic anhydride upon o-*Phenylenediallyldithiocarbamide*: *Formation of diacetyl compound of* (XXIII).—*o*-Phenylenediallyldithiourea (2 g.) was heated with 10 c. c. of acetic anhydride under reflux for about 45 minutes when a clear solution was obtained and on cooling gave a crystalline mass. It was further crystallised from acetic acid in slender white needles, m. p. 185° (Found: N, 16·11. $C_{18}H_{20}N_4S$ requires N, 15·73 per cent.). Deacetylation was effected by boiling with strong hydrochloric acid for about half an hour when a clear solution was obtained, and on being made alkaline gave a white precipitate which crystallised from acetone, m. p. above 300° (Found: N, 20·39 $C_{14}H_{16}N_4S$ requires N, 20·58 per cent.).

o-*Phenylene*-sym-*phenylallyldithiourea* (VIII).—An alcoholic solution of 1-*o*-aminophenyl-3-phenylthiocarbamide (2·5 g.) and allyl mustard oil (1 g.) was heated on the water-bath under reflux for about 2 hours. The reaction product was allowed to cool when a crystalline mass separated and was further crystallised from alcohol, m. p. 245° (Found: S, 18·48. $C_{17}H_{18}N_4S_2$ requires S, 18·71 per cent.)

2-*Allylamino*-4:5 *benzo*-7-*thioketo*-1 : 3 : 6-*thioheptadiazine*(XXIV).—Two g. of the compound (VIII) were heated with strong hydrochloric acid (50 c. c.) under reflux for about an hour. The solution became red with the separation of a solid which crystallised from alcohol, m.p. 293°. It is soluble in cold dilute alkali from which it can be precipitated by acids. The presence of aniline in the acid filtrate was proved (Found: N, 16·58. $C_{11}H_{11}N_3S_2$ requires N, 16·86 per cent.). The *disulphide* was prepared as usual; m. p. above 300°.

o-*Phenylene*-sym-*phenyl*-o-*tolyldithiourea* (IX).—An alcoholic solution of 1-*o*-aminophenyl-3-phenylthiocarbamide (2·4 g.) and *o*-tolyl mustard oil (1·5 g.) was heated on the water-bath under reflux for about 2 hours. The product on cooling gave a solid which crystallised from alcohol; m. p. 136° (Found: S, 16·59. $C_{21}H_{20}N_4S_2$ requires S, 16·32 per cent.).

2-o-*Tolylamino*-4 : 5-*phenylene*-7-*thioketo*-1 : 3: 6-*thioheptadiazine* (XXV).—Two g. of the compound (IX) were heated with strong hydrochloric acid (50 c. c.) under reflux for about an hour when a clear solution was obtained. This, on being further heated, gave a solid mass which was crystallised from alcohol; m. p. 300°. It is soluble in cold alkali from which it is precipitated by acids. The presence of aniline in the acid filtrate was proved (Found: N, 14·31. $C_{15}H_{13}N_3S_2$

requires N, 14·04 per cent.). Identity of this compound with the compound (XVIII) was further confirmed by the mixed melting point.

o-*Phenylene*-sym-*phenyl.*-p-*tolyldithiourea* (X).—The method of preparation was the same as in the case of the compound (IX). The substance was crystallised from alcohol; m. p. 165° (Found: S, 16·48. $C_{21}H_{20}N_4S_2$ requires S, 16·32 per cent.).

2-p-*Tolyamino*-4: 5-*phenylene*-7-*thioketo*-1: 3: 6-*thioheptadiazine* (XXVI).—The method of preparation was the same as in the case of the compound (XXV). The substance was crystallised from alcohol; m. p. 300° (Found: N, 14·28. $C_{15}H_{13}N_3S_2$ requires N, 14·04 per cent.). The identity of this compound with (XIX) was further confirmed by taking a mixed melting point.

1-*Phenylcarbamido*-2-*phenylthiocarbamidobenzene* (XI.)—An alcoholic solution of 1-*o*-aminophenyl-3-phenylthiocarbamide (2·4 g.) and phenyl *iso*cyanate (1·2 g.) was heated for about 30 minutes when a white solid separated and was crystallised from alcohol; m. p. 200° (after shrinking at 140°). (Found: N, 15·27. $C_{20}H_{18}ON_4S$ requires N, 15·46 per cent.).

1-*Phenyl*-2-*keto*-4: 5-*benzo*-7-*thioketo*-1: 3-6-*heptatriazine* (XXVII).—Two grams of the compound (XI) were heated under reflux with concentrated hydrochloric acid (60 c.c.) for about 2 hours when a solid mass with a greenish coloured mother-liquor was obtained. The solid was filtered, washed with water and crystallised from hot alcohol: m.p. 185°. It is soluble in cold ditute alkali from which it is precipitated by acids (Found: N, 15·30. $C_{14}H_{11}ON_3S$ requires N, 15·61 per cent.). The presence of aniline in the mother-liquor was proved.

The *disulphide* was obtained in the usual manner; m.p. 128-130°.

1-*Phenylcarbamido*-2-p-*tolyl-thiocarbamidobenzene* (XII).—An alcoholic solution of 1-*o*-aminophenyl-3-*p*-tolylthiocarbamide (5 g.) and phenyl *iso*cyanate (2·7g.)was heated for about 30 minutes when a white solid separated and was crystallised from alcohol; m. p. 165° (Found: N, 14·69. $C_{21}H_{20}ON_4S$ requires N, 14·97 per cent.).

1-p-*Tolyl*-2-*keto*-4: 5-*benzo*-7-*thioketo*-1: 3: 6-*heptatriazine* (XXVIII).—The method of preparation was the same as in the case of the compound (XXVII). The product was crystallised from hot alcohol; m. p. 175-176°. It is soluble in cold alkali from which it is precipitated by acids (Found: N, 14·67. $C_{15}H_{13}ON_3S$ requires N, 14·79 per cent).

The *disulphide* was obtained in the usual manner; m. p. 164°.

1-*Phenylcarbamido-2-methylthiocarbamidobenzene* (XIII).—An alcoholic solution of 1-*o*-aminophenyl-3-methylthiocarbamide (3 g.) and phenyl *iso*cyanate (2·4 g.) was heated for about half an hour when a white solid separated and was crystallised from alcohol; m. p. 98° (Found: N, 18·38. $C_{15}H_{16}ON_4S$ requires N, 18·67 per cent).

1-*Phenylamino*-3 : 4-*benzo*-6-*methylamino*-2 : 5 : 7-*thioheptadiazine* (XXIX).—Two grams of the compound (XIII) were heated under reflux with strong hydrochloric acid (60 c.c.) for about 2 hours. The clear solution, on cooling, gave a colourless crystalline mass which was recrystallised from alcohol; m. p. 195°. It is soluble in hydrochloric acid but insoluble in alkali (Found: N, 18·78. $C_{15}H_{14}N_4S$ requires N, 19·14 per cent.).

1-*Phenylcarbamido-2-allylthiocarbamidobenzene* (XIV).—The method of preparation was the same as in the case of the compound (XIII). The product was crystallised from alcohol; m. p. 160° (Found: N, 17·41. $C_{17}H_{18}ON_4S$ requires N, 17·17. per cent.).

1-*Phenylamino*-3 : 4-*benzo*-6-*keto*-2 : 5 : 7-*thioheptadiazine* (XXX). —Two grams of the compound (XIV) were heated with strong hydrochloric acid under reflux for about 2 hours. The clear solution on cooling, gave a crystalline mass which was recrystallised from hot water acidulated with a few drops of hydrochloric acid. It is soluble in hydrochloric acid but insoluble in alkali (Found: N, 12·46; S, 9·05. $C_{14}H_{11}ON_3S$, $3H_2O$ requires N, 12·39; S, 9·4 per cent.).

2 :7-*Diketo*-4: 5-*benzo*-1: 3: 6-*heptatriazine* (XXXI).—*o*-Phenylenediurea (XV) prepared according to the method given in *Ber.*, 1883, **16** 592; 2 g.) was heated under reflux with strong hydrochloric acid for about 40 minutes when a greenish black solution was obtained. The solution, on cooling, deposited crystals which were recrystallised from hot water acidulated with a few drops of hydrochloric acid It sublimed slowly without fusion above 300° into shining mica-like plates, and is soluble in cold alkali from which it is precipitated by acids (Found: N, 19·90. $C_8H_7N_3O_2$, $2H_2O$ requires N, 19·71 per cent.)

The *acetyl* derivative was crystallised from acetic acid; m.p. 190°.

o-Phenylene-sym-*diphenylcarbamide* (XVI).—Phenyl *iso*cyanate (2·3 g.) was added to an alcoholic solution of *o*-phenylenediamine (1 g.) and the solution boiled for sometime when a colourless crystalline mass came out which crystallised from alcohol: m. p. 220° (Found: N, 15·99. $C_{20}H_{18}O_2N_4$ requires N, 16·18 per cent.). Action of strong hydrochloric acid produced no change.

Action of strong hydrochloric acid upon (XXXII).—*Formation of o-Phenylenethiourea.*—1-*o*-Aminophenyl-3-phenylthiocarbamide, prepared according to the method of Lellmann (*Annalen*, 1885, **228**, 212) was heated with strong hydrochloric acid under reflux for about 10 minutes when a clear solution was obtained. The solution was further boiled for about 40 minutes when greenish white crystals came out, which crystallised from hot water acidulated with a few drops of hydrochloric acid; m.p. 301–302°. Lellmann (*Annalen*, 1884, **221**, 14) gave 290° as the m.p. of this compound (Found: N, 18·42. $C_7H_6N_2S$ requires N, 18·66 per cent.). The presence of aniline in the acid filtrate was proved.

The *disulphide* prepared in the usual manner melted at 230°.

The *acetyl* derivative melted at 200°.

1-o-*Aminophenyl*-3-o-*tolylthiocarbamide* (XXXIII).—It was prepared in the same manner as the phenyl compound. It was crystallised from benzene; m.p. 160° (Found: N, 16·18. $C_{14}H_{15}N_3S$ requires N, 16·34 per cent.). Like the corresponding phenyl compound (XXXII), it gave *o*-phenylenethiourea by the action of strong hydrochloric acid.

1-*o*-*Aminophenyl*-3-p-*tolylthiocarbamide* (XXXIV).—It was also prepared in the same manner as the corresponding phenyl compound (XXXII) and crystallised from benzene in shining white crystals, m.p. 146–147° (Found: N, 16·14. $C_{14}H_{15}N_3S$ requires N, 16·34 per cent.). It also gave *o*-phenylenethiourea with strong hydrochloric acid.

1-o-*Aminophenyl*-3-*methylthiocarbamide* (XXXV).—It was prepared in the same manner as the phenyl and tolyl compounds and was crystallised from benzene; m.p. 117° (Found: N, 23·07. $C_8H_{11}N_3S$ requires N, 23·20 per cent.). It also gave *o*-phenylenethiourea (m.p. 301–302°) with strong hydrochloric acid.

1-o-*Aminophenyl*-3-*allylthiocarbamide* (XXXVI).—It was also prepared similarly to the phenyl and tolyl compounds and was crystallised from benzene; m.p. 115° (Found: N, 20·04. $C_{10}H_{13}N_3S$ requires N, 20·28 per cent.).

Action of strong hydrochloric acid upon (XXXVI): *Formation of* 5-*Allylamino*-2 : 3-*benzo*-1 : 4-*thiazole* (XXXVII).—The compound (XXXVI; 1·5 g.) was heated under reflux with strong hydrochloric acid (55 c.c.) for about an hour giving a clear solution which, on cooling, and dilution with water, gave no precipitate; it was neutralised with dilute caustic soda under cooling when a white shining crystalline mass came out which was further crystallised from alcohol; m.p. 180° (Found: S, 16·52. $C_{10}H_{10}N_2S$ requires S, 16·84 per cent.).

The *acetyl* derivative melted at 198°.

Action of ferric chloride upon (XXXII): *Formation of* 6-*Phenylamino*-3 : 4-*benzo*-1 : 2 : 5-*thiodiazine* (XXXVIII).—Excess of ferric chloride solution was added to 1-*o*-aminophenyl-3-phenylthiocarbamide (3 g.) and the mixture heated under reflux for about an hour; when cooled, a yellow solid mass mixed with some black tarry matter separated. After the removal of the tarry matter with steam the residual solid crystallised from alcohol in yellow slender needles; m.p. 155–156°. It is insoluble in alkali but soluble in hot hydrochloric acid (Found: S, 13·13. $C_{13}H_{11}N_3S$ requires S, 13·27 per cent.).

6-p-*Tolylamino*-3 : 4-*benzo*-1 : 2 : 5-*thiodiazine* (XXXIX).—The method of preparation was the same as in the case of the previous compound (XXXVIII). It was crystallised from alcohol; m.p. 93° (Found: S, 12·13. $C_{14}H_{13}N_3S$ requires S, 12·54 per cent.).

1-o-*Nitrobenzalanilino*-3-*phenylthiocarbamide* (XL).—An alcoholic solution of 1-*o*-aminophenyl-3-phenylthiocarbamide (2·5 g.) and *o*-nitrobenzaldehyde (1·5 g.) was heated on a water-bath under reflux for half an hour. On cooling, orange-coloured crystals gradually separated and were recrystallised from alcohol, m.p. 215° (Found: N, 15·17. $C_{20}H_{16}O_2N_4S$ requires N, 14·89 per cent.).

1-m-*Nitrobenzalanilino*-3-*phenylthiocarbamide* (XLI).—To a hot alcoholic solution of 1-*o*-aminophenyl-3-phenylthiocarbamide (2·5 g.) an alcoholic solution of *m*-nitrobenzaldehyde (1·5 g.) was added when at once a yellowish white crystalline mass came out which crystallised from alcohol, m.p. 153-154° (Found: N, 15·21. $C_{20}H_{16}O_2N_4S$ requires N, 14·89 per cent.).

1-o-*Hydroxybenzalanilino*-3-*phenylthiocarbamide* (XLII).—It was prepared similarly to the foregoing compound and was crystallised from alcohol; m.p. 180° (Found: N, 12·05. $C_{20}H_{17}ON_3S$ requires N, 12·10 per cent.).

1-*Benzalamino*-3-*phenylthiocarbamide* (XLIII.)—It was prepared similarly to the compound (XLI); m.p. 265-267° (Found: N, 12·92. $C_{20}H_{17}N_3S$ requires N, 12·68 per cent.).

Action of ferric chloride upon (XLIII): *Formation of* 2-*Phenyl*-4 : 5-*benzo*-7-*phenylamino*-1 : 3 : 6-*thioheptadiazine* (XLIV).—1-Benzalanilino-3-phenylthiocarbamide (1·5 g.) was heated under reflux with an excess of ferric chloride solution for an hour when a yellow solid mixed with some tarry matter was obtained. After removing the tarry matter with steam, the solid was crystallised from alcohol; m.p. 105°. It is insoluble in alkali but soluble in hot acids (Found: N, 12·58. $C_{20}H_{15}N_3S$ requires N, 12·76 per cent.).

Phenylthiocarbamidophenylurethane, $CO_2Et\cdot NH\cdot C_6H_4\cdot NH\cdot CS\cdot NHPh$.—To a hot benzene solution of 1-*o*-aminophenyl-3-phenylthiocarbamide (2·4 g.) chlorcarbonic ester (1·1 g.) was added. The reaction took place at once and the separated white solid crystallised from alcohol; m.p. 288-290° (Found: N, 13·13. $C_{16}H_{17}O_2N_3S$ requires N, 13·33 per cent.). Strong hydrochloric acid was without action.

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