276. *The Reactions of Thiocarbonyl Chloride. Part V. With Compounds containing the* –NH·NH$_2$ *Group.*

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The interaction of thiocarbonyl chloride with alkyl- and aryl-hydrazines leads to the formation of compounds of the carbazide type (NHR·NH)$_2$CS; but in hydrochloric acid solution a new type of compound CS[N(NCS)R]$_2$ is obtained; in the case of certain arylhydrazines this may break down to form an aryl trithiocarbimide. The acyl hydrazides such as semicarbazide, thiosemicarbazide, and semioxamazide all form compounds of the type CS[N(NCS)·CO·NHR]$_2$, which break down on treatment with amines, forming substituted diureas. Some of the latter, notably *s*-dicarbamidothiourea and *s*-diphenyldiureidothiourea, give coloured compounds with metal ions (especially those of cobalt, copper, and mercury) and may have application as micro-analytical reagents.

The use of diphenylcarbazide (Cazeneuve, *Compt. rend.*, 1900, **131**, 346), dithio-oxamide (Rây, *Z. anal. Chem.*, 1929, **79**, 94), and diphenylthiocarbazone as reagents for detection and estimation of small quantities of certain metallic ions suggested an investigation of compounds containing the NH·NH·CS·NH·NH, NH·NH·CS·N=N, and similar groups. Such compounds or their precursors can be obtained by the regulated action of thiocarbonyl chloride on compounds containing the NH·NH$_2$ group.

Heller (*Annalen*, 1891, **263**, 269) obtained *s*-diphenylthiocarbazide from thiocarbonyl chloride and phenylhydrazine in ethereal solution. It is now found that phenylhydrazine hydrochloride reacts in aqueous solution with thiocarbonyl chloride to give phenylthiocarbimide and 1 : 2 : 4-*trithiocarbimidobenzene*. It is suggested that the formation of these compounds is due to the decomposition of the initial compound CS(NPh·NCS)$_2$ (I):

$$2\mathrm{Ph{\cdot}NH{\cdot}NH_2} + 3\mathrm{CSCl_2} \longrightarrow \mathrm{(I)} + 6\mathrm{HCl}$$
$$\mathrm{(I)} \longrightarrow \mathrm{Ph{\cdot}NCS} + \mathrm{Ph{\cdot}N(NCS)_2} \longrightarrow \mathrm{C_6H_3(NCS)_2{\cdot}NH_2}$$
$$\mathrm{C_6H_3(NCS)_2{\cdot}NH_2} + \mathrm{CSCl_2} \longrightarrow \mathrm{C_6H_3(NCS)_3} + 2\mathrm{HCl}$$

Substituted derivatives of (I) are sufficiently stable to be isolated.

Trithiocarbimidobenzene, a member of a hitherto uninvestigated series of compounds, was identified by analysis, by conversion into thioureas of the type C$_6$H$_3$(NH·CS·NHAr)$_3$ with arylamines, and by formation of a *monothiourethane* C$_6$H$_3$(NCS)$_2$(NH·CS·OEt) with alcohol. Comparison with 1 : 3 : 5-*trithiocarbimidobenzene* showed its orientation to be unsymmetrical.

With an acid substituent in the para-position (*e.g.*, R = NO$_2$ or Br), the initial compound, *e.g.*, CS[N(NCS)·C$_6$H$_4$R]$_2$, is more stable and was isolated, but the reaction proceeds wholly in this direction only when the concentration of hydrogen chloride approaches 10%. In neutral solution, *p*-bromo-, *p*-nitro-, and 2 : 4-dinitro-phenylhydrazine hydrochlorides yield the corresponding symmetrical thiocarbazides.

Thiocarbonyl chloride reacts with *as*-diphenylhydrazine giving N-*thiocarbimidodiphenylamine*, which, although giving normal analytical data and molecular weight, could not be induced to yield 1 : 1 : 4-triphenylthiosemicarbazide with aniline as might have been expected: $NPh_2\cdot NCS + NH_2Ph \longrightarrow NPh_2\cdot NH\cdot CS\cdot NHPh$.

Thiocarbonyl chloride with considerable excess of semicarbazide gives s-*dicarbamidothiourea*, $CS(NH\cdot NH\cdot CO\cdot NH_2)_2$, but semicarbazide hydrochloride and an excess of thiocarbonyl chloride react to give 3 : 5-*dithiocarbimidothiocarbonyldiurea* (II), the

$$2NH_2\cdot CO\cdot NH\cdot NH_2 + 3CSCl_2 = CS[N(NCS)\cdot CO\cdot NH_2]_2 + 6HCl$$

(II.)

structure of which was established by comparison with the analogous *compound* $CS[N(NCS)\cdot CO\cdot NPh_2]_2$ from 4 : 4-diphenylsemicarbazide, where there is no structural ambiguity.

The compounds from semicarbazide and 4 : 4-diphenylsemicarbazide reacted with arylamines as follows, all the resulting compounds being identified.

(*a*) $CS[N(NCS)\cdot CO\cdot NH_2]_2 + 4R\cdot NH_2 = 2NH_2\cdot CO\cdot NH\cdot NH\cdot CS\cdot NHR + CS(NHR)_2$

(*b*) $CS[N(NCS)\cdot CO\cdot NPh_2]_2 + 2R\cdot NH_2 = CS[N(CO\cdot NPh_2)\cdot NH\cdot CS\cdot NHR]_2$

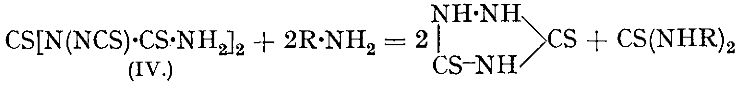
(III.)

Further characterisation of (II) was obtained through its reaction with alcohol to give the *bisthiourethane* $CS[N(CO\cdot NH_2)\cdot NH\cdot CS\cdot OEt]_2$, which reacted with arylamines thus:

(*c*) $CS[N(CO\cdot NH_2)\cdot NH\cdot CS\cdot OEt]_2 + 4R\cdot NH_2 = 2Et\cdot OH + 2NH_2\cdot CO\cdot NH\cdot NH\cdot CS\cdot NHR + CS(NHR)_2$

the product being identical with that of reaction (*a*).

Thiosemicarbazide reacts similarly with thiocarbonyl chloride to give 3 : 5-*dithiocarbimidothiocarbonyldithiourea* (IV), characterised by conversion into the thiourethane $CS[N(CS\cdot NH_2)\cdot NH\cdot CS\cdot OEt]_2$. With arylamines, it gives dithiourazole and thiocarbanilide.



$$CS[N(NCS)\cdot CS\cdot NH_2]_2 + 2R\cdot NH_2 = 2\left|\begin{array}{l} NH\cdot NH \\ CS{-}NH \end{array}\right\rangle CS + CS(NHR)_2$$

(IV.)

The reaction of semioxamazide with thiocarbonyl chloride runs parallel with that of semicarbazide, giving NN′-*dithiocarbimido*-NN′-*dioxamylthiourea*, $CS[N(NCS)\cdot CO\cdot CO\cdot NH_2]_2$, the reactions of which are similar to those of (II).

Methylhydrazine and thiocarbonyl chloride interact, giving NN′-*dithiocarbimidodimethylthiourea* (V). With aromatic amines, this reacts thus:

$$CS(NMe\cdot NCS)_2 + 4R\cdot NH_2 = 2NHMe\cdot NH\cdot CS\cdot NHR + CS(NHR)_2$$

(V.)

Stolle and Bowles, by interaction of thiocarbonyl chloride and hydrazine hydrate, obtained thiocarbohydrazide, $CS(NH\cdot NH_2)_2$. When the hydrate is replaced by a salt, such as the hydrochloride or sulphate, a new substance is produced, *viz.*, s-*dithiocarbimidothiourea*, $CS(NH\cdot NCS)_2$.

Of the compounds so far examined, *s*-dicarbamidothiourea gave interesting colour reactions with certain metallic ions. With copper in neutral solution a greenish-grey precipitate is obtained, and in ammoniacal solution small quantities of cupric ion produced a violet-red colour. The smallest quantity of copper capable of systematic identification is $0{\cdot}25\gamma$ in 50 ml. of water. The test should be capable of use as a colorimetric method for estimating small traces of copper, *e.g.*, in water supplies. The substance also gave a deep indigo precipitate with cobalt salts, quantities as small as 1γ being thus recognisable. At this dilution, nickel does not interfere.

The thiocarbazone from *s*-di-(*p*-bromophenyl)thiocarbazide gave reactions with lead similar to those obtainable from diphenylthiocarbazone.

The most interesting compound was s-*diphenyldiureidothiourea*, which gave a deep crimson precipitate on boiling with solutions containing mercuric ion. This precipitate is formed at dilutions of 1 in 10^6 of mercuric ion, at which point neither lead nor silver in concentrations below 1 in 10^3 interferes. The possible application of these reagents to micro-quantitative analysis is being investigated.

EXPERIMENTAL.

1 : 2 : 4-*Trithiocarbimidobenzene*, $C_6H_3(NCS)_3$.—Phenylhydrazine (10 g.) in hydrochloric acid (10%; 700 ml.) was shaken with thiocarbonyl chloride (15 g.). On standing for 18 hours, an oily solid separated. The supernatant liquid gave only phenylhydrazine hydrochloride on evaporation. The oily solid was extracted with acetone (20 ml.), and the residue crystallised from benzene, yielding 1 : 2 : 4-*trithiocarbimidobenzene*, m. p. 156° (Found: C, 43·4; H, 1·5; S, 38·4. $C_9H_3N_3S_3$ requires C, 43·4; H, 1·6; S, 38·4%). The acetone extract was evaporated and distilled with steam; phenylthiocarbimide was isolated and characterised by conversion into *s*-diphenylthiocarbamide, m. p. 153°.

1 : 2 : 4-*Tris(phenylthiocarbamido)benzene*, $C_6H_3(NH\cdot CS\cdot NHPh)_3$.—1 : 2 : 4-Trithiocarbimidobenzene (4 g.), aniline (4·5 g.), and benzene (100 ml.) were boiled together for 3 hours. On cooling, 1 : 2 : 4-*tris(phenylthiocarbamido)benzene* separated; it formed white micro-crystals from benzene, m. p. 120° (Found: S, 18·6. $C_{27}H_{24}N_6S_3$ requires S, 18·2%).

1 : 2 : 4-*Tris-(4-bromophenylthiocarbamido)benzene* was prepared in an analogous manner from *p*-bromoaniline; white crystals, m. p. 183° (Found: S, 12·8. $C_{27}H_{21}N_6Br_3S_3$ requires S, 12·6%).

3 : 4-*Dithiocarbamidophenylthiourethane*, $C_6H_3(NCS)_2\cdot NH\cdot CS\cdot OEt$.—Trithiocarbimidobenzene (2 g.) was boiled with absolute alcohol (50 ml.) for 10 hours. On cooling, the *compound* separated; white needles from alcohol, m. p. 74° (Found: S, 32·1. $C_{11}H_9ON_3S_3$ requires S, 32·5%).

1 : 3 : 5-*Trithiocarbimidobenzene*, $C_6H_3(NCS)_3$.—*s*-Triaminobenzene hydrochloride (15 g.) in dilute hydrochloric acid (700 ml.; 7%) was shaken with thiocarbonyl chloride (15 g.) for 24 hours. The solid which separated was a complex mixture from which ethyl acetate extracted 1 : 3 : 5-*trithiocarbimidobenzene*; small white prisms, m. p. 143° (Found: S, 38·2. $C_9H_3N_3S_3$ requires S, 38·4%).

1 : 2 : 4-*Trithiocarbamidobenzene*, $C_6H_3(NH\cdot CS\cdot NH_2)_3$, was precipitated on passing dry ammonia through 1 : 2 : 4-trithiocarbimidobenzene (5 g.) in benzene (50 ml.) until the solution was colourless; it formed white micro-crystals, m. p. 170° (Found: S, 31·8. $C_9H_{12}N_6S_3$ requires S, 32·0%).

2-*Amino*-1 : 4-*dithiocarbamidobenzene*, $C_6H_3(NH\cdot CS\cdot NH_2)_2NH_2$.—1 : 2 : 4-Trithiocarbamidobenzene (5 g.) and hydrochloric acid (20% HCl; 10 ml.) were boiled for 30 hours, hydrogen sulphide being evolved. On cooling, the *compound* separated; white needles, m. p. 149·5° (Found: S, 26·6. $C_8H_{11}N_5S_2$ requires S, 26·6%).

s-*Dicarbamidothiourea*.—Thiocarbonyl chloride (5 g.) in ether (20 ml.) was added to a stirred solution of semicarbazide (14 g.) in water (200 ml.). After 2 hours, the liquid was filtered, and, after a further 18 hours, the *compound* separated; white needles from water, m. p. 215° (decomp.) (Found: C, 19·1; H, 4·3; S, 16·3. $C_3H_8O_2N_6S$ requires C, 18·8; H, 4·2; S, 16·6%).

Compounds of s-*Dicarbamidothiourea with Metals*.—A solution of the reagent (0·2 g.) in aqueous alcohol (50%; 100 ml.) was used. Insoluble compounds were formed with many metals, but only those from copper and cobalt persisted at high dilutions. The results are summarised below, the colour being that obtained with the reagent and ammonia.

Metal ion.	Colour.	Metal ion.	Colour.
Pb	Pale yellow.	Ni	Brown-grey ppt. at high concn.
Ag	Deep blue ppt.	Co	Deep indigo ppt.
Au	Yellow ppt.	Cu	Red-violet.*
Mn	—	Fe	—
Zn	—	Hg	—

* Greenish-grey without ammonia.

The indigo-coloured precipitate from 1γ of cobalt ion in 50 ml. of water was easily visible in the Lovibond Nessleriser. At a concentration of 4γ in 50 ml. the precipitate was marked. The colour produced with 2·5γ of copper ion in water (50 ml.) is considerably deeper than that produced by rubeanic acid under similar conditions.

3 : 5-*Dithiocarbimidothiocarbonyldiurea* (II).—Semicarbazide hydrochloride (12 g.) in water (500 ml.) was shaken with thiocarbonyl chloride (15 g.) for 2 hours. The product was washed with water (500 ml.), ether (200 ml.), and carbon disulphide (200 ml.); yield, 10 g. of pale yellow micro-crystals, m. p. 186—194° (decomp.) (Found: C, 21·9; H, 1·6; S, 34·7. $C_5H_4O_2N_6S_3$ requires C, 21·6; H, 1·5; S, 34·8%). The *compound* was readily reduced by zinc dust and dilute hydrochloric acid to trithioformaldehyde, and was decomposed by dilute alkali to hydrogen sulphide, hydrazine, carbon dioxide, and ammonia.

s-*Diphenyldiureidothiourea*, $CS(NH{\cdot}NH{\cdot}CO{\cdot}NHPh)_2$.—Thiocarbonyl chloride (10 g.) in ether (200 ml.) was well shaken with phenylsemicarbazide (50 g.) in water (2 l.). The *compound* separated after an hour; slender needles, from water, m. p. 223° (Found : S, 9·5. $C_{15}H_{16}O_2N_6S$ requires S, 9·3%).

2-*Thion*-1-*phenyldiurea*, $NHPh{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$.—3 : 5-Dithiocarbimidothiocarbonyldiurea (6 g.), aniline (9 g.), and alcohol (150 ml.) were boiled for ½ hour. On cooling, 2-thion-1-phenyldiurea separated; small white needles, m. p. 198° (Found : S, 15·4. Calc. for $C_8H_{10}ON_4S$: S, 15·3%). On boiling phenylthiocarbimide (2 g.) with semicarbazide (3 g.) in alcohol (50 ml.), the same compound separated in needles, m. p. 198° (Found : S, 15·4%) (Arndt, Milde, and Tschenscher, *Ber.*, 1922, **55**, 341).

The p-*tolyl* analogue, prepared by the action of *p*-toluidine on 3 : 5-dithiocarbimidothiocarbonyldiurea and by heating *p*-tolylthiocarbimide and semicarbazide in alcohol, formed white needles, m. p. 208° (Found : S, 14·5. $C_9H_{12}ON_4S$ requires S, 14·3%); and the p-*bromophenyl* analogue, white plates, m. p. 202° from water (Found : S, 11·3. $C_8H_9ON_4BrS$ requires S, 11·1%).

3 : 5-*Dithiocarbimido*-1 : 1 : 7 : 7-*tetraphenylthiocarbonyldiurea*, $CS[N(NCS){\cdot}CO{\cdot}NPh_2]_2$.—4 : 4-Diphenylsemicarbazide (5 g.) in water (4 l.) containing hydrochloric acid (100 ml.) was stirred with thiocarbonyl chloride (4 g.) for 2 hours. The light yellow solid which separated was washed with ether, dried, and extracted with warm ligroin. On concentration, the solution deposited little yellow micro-crystals, m. p. 133° (Found : S, 16·5. $C_{29}H_{20}O_2N_6S_3$ requires S, 16·4%).

3 : 5-*Bis*(*phenylthiocarbamido*)-1 : 1 : 7 : 7-*tetraphenylthiocarbonyldiurea* (III; R = Ph).—The foregoing compound (6 g.) and aniline (2 g.) in ligroin (100 ml.) were boiled for ½ hour. The *compound* (III; R = Ph) separated on cooling; white needles from alcohol, m. p. 162·5° (Found : S, 12·4. $C_{41}H_{34}O_2N_8S_3$ requires S, 12·5%). It was readily decomposed by boiling 10% hydrochloric acid, giving carbon dioxide, hydrogen sulphide, phenylthiocarbimide, and *as*-diphenylsemicarbazide.

3 : 5-*Dithiourethanocarbonyldiurea*, $CS[N(CO{\cdot}NH_2){\cdot}NH{\cdot}CS{\cdot}OEt]_2$.—3 : 5-Dithiocarbimidothiocarbonyldiurea (6 g.) was boiled with absolute alcohol (50 ml.) until a clear solution was obtained (1 hour). The alcohol was removed by distillation, leaving a golden-yellow oil which solidified on cooling (7·5 g.); m. p. 30—32° (Found : S, 25·6. $C_9H_{16}O_4N_6S_3$ requires S, 26·1%). This *compound* (5 g.), aniline (5 g.), and alcohol (50 ml.) were boiled for ½ hour. On cooling, crystals of 2-thion-1-phenyldiurea were deposited. On concentration, the filtered alcoholic solution yielded thiocarbanilide, m. p. 153°. On dry distillation of the compound, alcohol was obtained, and identified by conversion into ethyl benzoate, b. p. 213°.

NN′-*Dithiocarbimido*-NN′-*dioxamylthiourea*.—Semioxamazide hydrochloride (9 g.) in water (400 ml.) was shaken with thiocarbonyl chloride (9 g.). After 2 hours, the *compound* separated, and was washed with water (200 ml.) and ether (100 ml.); light yellow micro-crystals, m. p. 223°, from nitrobenzene (Found : S, 29·25. $C_7H_4O_4N_6S_3$ requires S, 29·0%). Zinc dust and dilute acid reduced the compound to trithioformaldehyde, carbon dioxide, hydrogen sulphide, and ammonia.

1-*Oxamyl*-4-*phenylthiosemicarbazide*, $NHPh{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH_2$.—The foregoing compound (6 g.) and aniline (7·5 g.) in alcohol (100 ml.) were boiled for ½ hour. The *compound* separated on cooling; short white needles from water, m. p. 185·5° (Found : S, 13·6. $C_9H_{10}O_2N_4S$ requires S, 13·5%). It was also formed by boiling phenylthiocarbimide (3 g.), semioxamazide (2 g.), and alcohol (50 ml.); m. p. 185·5° (Found : S, 13·7%). It was hydrolysed by boiling water to phenylthiocarbimide and semioxamazide.

NN′-*Dithiocarbimidodimethylthiourea* (V).—Methylhydrazine sulphate (14 g.) in water (700 ml.) was shaken with thiocarbonyl chloride (15 g.) for 2 hours, during which the *compound* separated; orange micro-crystals, m. p. 139° (Found : S, 44·2. $C_5H_6N_4S_3$ requires S, 44·0%), from ligroin. On boiling with 20% sodium hydroxide solution, it was completely decomposed, forming methylhydrazine, carbon dioxide, and hydrogen sulphide.

4-*Phenyl*-1-*methylthiosemicarbazide*, $NHPh{\cdot}CS{\cdot}NH{\cdot}NHMe$.—The compound (V) (5 g.), aniline (10 g.), and alcohol (50 ml.) were boiled for ½ hour. The first crop of crystals to separate was thiocarbanilide, m. p. 153°, but the second consisted of a mixture of this with 4-phenyl-1-methylthiosemicarbazide. The final filtrate on dilution with water gave the latter compound; white needles, m. p. 143°. Synthesised by boiling methylhydrazine (3 g.) and phenylthiocarbimide (9 g.) in alcohol (100 ml.) for ½ hour, it formed white needles, m. p. 143° (*Ber.*, 1889, **22**, Ref. 670), not depressed by admixture with the previous preparation.

Dithiocarbimidothiourea.—(i) Hydrazine sulphate (12 g.) in water (700 ml.) was shaken with thiocarbonyl chloride (15 g.) for 2 hours. The solid product, washed with ether and water, was a light yellow solid, insoluble in all ordinary organic solvents. It decomposes at 196—200° (Found : S, 50·5. $C_3H_2N_4S_3$ requires S, 50·5%).

(ii) A solution of thiocarbohydrazide (5 g.) in hydrochloric acid (250 ml.; 10%) when shaken with thiocarbonyl chloride (6 g.) gave a light yellow powder (Found : S, 50·5%) which decomposed at 195—200°, not depressed by admixture with the compound prepared as in (i).

Dithio-p-*urazine*,

—Dithiocarbimidothiourea (5 g.), aniline (9 g.), and alcohol (50 ml.) were boiled for ½ hour. The filtered solution on concentration gave thiocarbanilide, m. p. 153°. Evaporation of the filtrate under reduced pressure gave, on addition of a few drops of concentrated hydrochloric acid, white crystals of dithio-*p*-urazine, m. p. 202—203°. This was also prepared from the product of method (ii), above.

When *p*-toluidine was used instead of aniline in the above experiment, ditolylthiourea, m. p. 177°, and dithio-*p*-urazine were obtained.

Dithio-*p*-urazine was obtained by heating potassium ethyl xanthate (3 g.), alcohol (20 ml.), and thiocarbohydrazide (2 g.) at 100° for 2 hours. The solution on precipitation with a few drops of concentrated hydrochloric acid gave dithio-*p*-urazine, m. p. 202—203° (Guha and De, J., 1924, **125**, 1215) (Found : S, 43·0. Calc. for $C_2H_4N_4S_2$: S, 43·2%).

N-*Thiocarbimidodiphenylamine*, $NPh_2{\cdot}NCS$.—*as*-Diphenylhydrazine hydrochloride (30 g.) in water (1½ l.) was shaken with thiocarbonyl chloride (15 g.). After 2 hours, the product was filtered off, dried, and extracted with boiling ligroin. On cooling, long white needles of N-*thiocarbimidodiphenylamine* separated, m. p. 63° (Found : S, 14·6; *M*, cryoscopic in benzene, 236. $C_{13}H_{10}N_2S$ requires S, 14·2%; *M*, 226). No reaction with alcohol could be induced, and with aniline no isolable product was obtained.

N-*Thiocarbimidophenylmethylamine*, $NPhMe{\cdot}NCS$.—Phenylmethylhydrazine in hydrochloric acid (5% HCl; 1 l.) was shaken with thiocarbonyl chloride (11 g.) for 2 hours. The oil was separated, extracted with ether, and the solution dried over anhydrous potassium carbonate. The filtered solution, on evaporation, gave N-*thiocarbimidophenylmethylamine* as a brown unstable oil (10 g.) (Found : S, 19·2. $C_8H_8N_2S$ requires S, 19·5%). On distillation in a vacuum, phenylthiocarbimide was produced. The oil (5 g.) when heated with aniline (5 g.) in alcohol (100 ml.) for ½ hour gave 1 : 4-diphenyl-1-methylthiosemicarbazide, m. p. 154°, together with thiocarbanilide and phenylthiocarbimide.

NN′-*Dithiocarbimidobis*-p-*nitrophenylthiourea*, $CS[N(C_6H_4{\cdot}NO_2){\cdot}NCS]_2$.—*p*-Nitrophenylhydrazine (7·6 g.) in hydrochloric acid (10%; 700 ml.) was shaken with thiocarbonyl chloride for 10 hours. The solid product, washed well with ether and water, crystallised from glacial acetic acid as light brown micro-crystals (Found : S, 22·3. $C_{15}H_8O_4N_6S_3$ requires S, 22·2%); it readily reacted with benzidine in alcohol, and readily dissolved in 2*N*-sodium hydroxide, forming a deep brown solution. With tin and hydrochloric acid, ammonium chloride, hydrogen sulphide, trithioformaldehyde, and *p*-phenylenediamine hydrochloride were formed.

NN′-*Diphenylthiocarbamidobis*-p-*nitrophenylthiourea*.—The above thiourea (3 g.) and aniline (3 g.) in alcohol (100 ml.) were boiled for 2 hours. After concentration, the filtrate, on addition of water, gave white plates of NN′-*diphenylthiocarbamidobis*-p-*nitrophenylthiourea*, m. p. 143° (Found : S, 15·0. $C_{27}H_{22}O_4N_8S_3$ requires S, 15·5%), which turned red on standing. Hydrolysis with 2*N*-hydrochloric acid gave phenylthiocarbimide, *p*-nitrophenylhydrazine hydrochloride, carbon dioxide, and hydrogen sulphide.

3 : 5-*Dithiocarbimidothiocarbonyldithiourea*, $CS[N(NCS){\cdot}CS{\cdot}NH_2]_2$.—Thiosemicarbazide (6·5 g.) in hydrochloric acid (1% HCl; 400 ml.) was shaken with thiocarbonyl chloride (11 g.). After 4 hours the orange precipitate was filtered off, washed with ether (100 ml.) and water (500 ml.), and dried; it formed orange micro-crystals, m. p. 240—250° (decomp.) (Found : S, 52·0. $C_5H_4N_6S_5$ requires S, 52·0%).

Dithiourazole.—The previous *compound* (4 g.) was heated with aniline (5 g.) and alcohol (30 ml.) on the water-bath for ½ hour, the mixture poured into water (400 ml.), and the thiocarbanilide which separated was filtered off and recrystallised; m. p. 153°. The aqueous-alcoholic filtrate on evaporation to 20 ml. gave, on cooling, broad prisms of dithiourazole, m. p. 245°, not depressed by admixture with authentic dithiourazole (Found : S, 48·0. Calc. for $C_2H_3N_3S_2$: S, 48·1%).

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