XXI.—*Some Derivatives of Thiocarbamide.*

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IN continuation of my work on the derivatives of methylsulphonic acid (*J. pr. Chem.* [2], **30**, 280), I studied at the suggestion of Herr O. Loew (in a private letter written after his having read the paper just mentioned) the action of thiocarbamide on trichloromethyl-

sulphonic chloride, $\text{CCl}_3 : \text{SO}_2\text{Cl}$, and from this I have been led on to investigate certain thiocarbamide compounds.

If the above-mentioned sulphonic chloride is added to an aqueous solution of thiocarbamide, no reaction takes place in the cold until after long standing, but, on warming, the chloride gradually dissolves, and sulphur is deposited. If, however, a cold or nearly cold solution of thiocarbamide in 80 to 90 per cent. alcohol is used, there is considerable development of heat on adding the chloride, and a mass of needles separates; the quantity of the latter being much increased by the subsequent addition of ether.

This compound was found to be identical with that obtained by Claus (*Annalen*, **179**, 139) by the action of chlorine on an alcoholic, or (with careful cooling) aqueous solution of thiocarbamide, viz., dithiocarbamide dichloride, $(\text{CSN}_2\text{H}_4)_2\text{Cl}_2$. In preparing it as above from trichloromethylsulphonic chloride, it is best to take quantities of the *pure* substances representing two molecular proportions of the sulphonic chloride and four of the thiocarbamide. The latter being dissolved in a small quantity of 90 per cent. alcohol, the chloride is gradually added, care being taken to avoid much rise of temperature. When the reaction is complete, an equal volume of ether is added, and, after the whole has stood for a short time, the dithiocarbamide dichloride may be collected and washed, first with a mixture of absolute alcohol and ether, and then with ether, and finally dried over sulphuric acid in a vacuum.

The compound thus prepared yielded the following results on analysis:—

- (a.) 0.1590 gram gave 33.3 c.c. N at 16° and 770 mm. mercury pressure = 24.75 per cent. N.
- (b.) 0.2841 gram ignited with copper oxide and lead chromate gave 0.1076 gram CO_2 and 0.0995 gram H_2O = 10.33 per cent. C and 3.89 per cent. H.
- (c.) 0.3280 gram gave 0.1238 gram CO_2 and 0.1166 gram H_2O = 10.29 per cent. C and 3.95 per cent. H.
- (d.) 0.1857 gram ignited with pure lime gave 0.2371 gram AgCl = 31.59 per cent. Cl.

	Calculated for $(\text{CSN}_2\text{H}_4)_2\text{Cl}_2$.	Found.	
H	3.59	3.89	3.95
C	10.96	10.33	10.29
N	25.10	24.75	—
Cl	31.83	31.59	—
S	28.70	—	—

A compound $\text{CSN}_2\text{H}_3\text{Cl}$ would require 2.72 per cent. H.

The filtrate from the above dithiocarbamide dichloride contains another product crystallising in stellate groups of the finest needles, and having probably the composition $(\text{CSN}_2\text{H}_4)_2(\text{CCl}_3\text{SO}_2)_2$. This will be referred to in a future paper.

Under similar conditions, methylsulphonic and dichloromethylsulphonic chlorides, $\text{CH}_3\cdot\text{SO}_2\text{Cl}$ and $\text{CHCl}_2\cdot\text{SO}_2\text{Cl}$, yield the same product, as does also phosphorus oxychloride, POCl_3 ;* but I failed to obtain it with acetyl chloride.

As already described by Claus, the above dithiocarbamide dichloride crystallises in rather small colourless needles, readily soluble in water, less so in alcohol, and insoluble in ether.

If a small portion is dissolved in 90 per cent. alcohol on a microscopic slide, the compound separates out again (after the slow evaporation of the alcohol) in highly characteristic plates (monoclinic?). It also crystallises in the same way from its cold aqueous solution, but in this case the plates are very much elongated and mixed with long needles.

In like manner, the dichloride, dissolved in water on a microscopic slide, gave—

- (a.) With dilute nitric acid, a crystalline precipitate, the crystals being like jagged daggers or long sword-like leaves (see below).
- (b.) With platinum tetrachloride, large thin rectangular crystals. I have not investigated this compound.

The very interesting reaction which this dichloride (or the corresponding dibromide) gives, on heating its aqueous or alcoholic solution, or on the addition of an alkali, has already been explained by Claus, according to the following equation:—

or a derivative of cyanamide, *e.g.*, dicyandiamidin. He was unable to obtain the cyanamide free from thiocarbamide for analysis; however, exactly the same reaction has quite recently been observed by Verneuil (*Compt. rend.*, **100**, 1296), for the corresponding selenium compound, $(\text{CSeN}_2\text{H}_4)_2\text{Cl}_2$, which sufficiently corroborates his view.

Dithiocarbamide dichloride cannot be recrystallised from water or alcohol, as the solutions invariably deposit sulphur. An aqueous solution strongly acidified with hydrochloric acid may, however, even be heated with impunity, and in the cold the dichloride separates out

* This phosphorus oxychloride was not quite pure.

in large thin plates (similar to those on the microscopic slide mentioned above); but I have never, even in this way, been able to obtain it quite free from deposited sulphur. Hence the necessity of preparing it pure in the first instance. It is stable at ordinary temperatures.

Action of Dilute Nitric Acid on Dithiocarbamide Dichloride.

If, as already indicated, dilute nitric acid is added to a moderately concentrated aqueous solution of the dichloride, most characteristic colourless crystals separate at once, while the liquid is found to contain free hydrochloric acid. These crystals are almost insoluble in dilute nitric acid, more soluble in water (but still only sparingly), practically insoluble in cold absolute alcohol, and insoluble in ether. The compound is thus easily obtained pure by washing successively with water, alcohol, and ether, and drying over sulphuric acid in a vacuum.

These crystals were also observed to be formed in the mother-liquor from the preparation of thiocarbamide nitrate: $\text{CSN}_2\text{H}_4\cdot\text{HNO}_3$ (formed by adding strong nitric acid to a concentrated aqueous solution of thiocarbamide), red fumes being at the same time evolved.

The pure compound gave the following results on analysis:—

- (a.) 0.3783 gram gave 0.1228 gram CO_2 and 0.1064 gram H_2O = 8.85 per cent. C and 3.12 per cent. H.
- (b.) 0.4097 gram gave 0.1232 gram CO_2 and 0.1138 gram H_2O = 8.20 per cent. C and 3.09 per cent. H.
- (c.) 0.1496 gram gave 37.6 c.c. N at 12° and 771 mm. = 30.27 per cent. N.
- (d.) 0.1510 gram gave 38.2 c.c. N at 11° and 766 mm. = 30.41 per cent. N.

	Calculated for $(\text{CSN}_2\text{H}_4)_2(\text{NO}_3)_2$.	Found.	
C	8.70	8.85	8.20
H	2.90	3.12	3.09
N	30.44	30.27	30.41

The nitrogen estimation (d) was made from a sample 10 days old. The two estimations of carbon and hydrogen were made from the same preparation.

Thiocarbamide nitrate, $\text{CSN}_2\text{H}_4\cdot\text{HNO}_3$, requires 3.61 p. c. H.

A compound, $\text{CSN}_2\text{H}_3\text{NO}_3$, would require 2.19 p. c. H.

„ $\text{CSN}_2\text{H}_3\text{NO}_2$, „ 2.48 „

This somewhat peculiar compound is therefore *dithiocarbamide dinitrate*, $(\text{CSN}_2\text{H}_4)_2(\text{NO}_3)_2$.

A further confirmation of its composition is given by the filtrate (from the dichloride and dilute nitric acid) being found to contain much free hydrochloric acid, but not a trace of chlorine, thus :—

That this filtrate contains extremely little dinitrate in solution is easily proved by the addition of a solution of silver nitrate. First silver chloride is thrown down, and then only a very small quantity of a silver thiocarbamide compound.

The above dinitrate is comparatively stable, and therefore differs in this respect from thiocarbamide nitrate, as described by Reynolds (*Annalen*, **150**, 231). Possibly the extreme instability of Reynolds' compound may have been due to the presence of a small quantity of free nitric acid.

Although a good many samples of the dinitrate were prepared, and kept for months in tubes over calcium chloride, only one exploded, and that one almost immediately after preparation (I noticed that in this case the crystals were very small, *i.e.*, the compound was very finely divided). It appears to withstand a temperature of 60° for some hours with little or no decomposition, but decomposes gradually on being heated more strongly. When kept in a dry tube, decomposition goes on very slowly, hydrocyanic acid being evidently evolved and sulphur deposited. It separates from the dilute mother-liquor of its preparation in beautiful long columnar prisms. Like the dichloride, it at once deposits sulphur when its solution is heated or on the addition of an alkali to it.

A solution of potassium nitrate likewise precipitates at once a cold aqueous solution of dithiocarbamide dichloride. The crystals in this case are somewhat different in form; they are long well-developed prisms (possibly monoclinic), among them being many well-crystallised individuals. From dilute nitric acid the crystals are more agglomerated.

Action of the Chlorides of Iodine on Thiocarbamide.

If iodine monochloride, ICl , or trichloride, ICl_3 , is added to a cold solution of thiocarbamide in alcohol, dithiocarbamide dichloride is formed, and iodine separates, even when the thiocarbamide is present in excess :—

With a concentrated solution, or with powdered thiocarbamide moistened with alcohol, the action is very violent.

In aqueous solution, the iodine seems to separate more slowly, indeed in an aqueous solution containing an excess of thiocarbamide, a certain amount of iodine compound seems to remain undecomposed until the solution is heated (comp. Verneuil on the seleniothiocarbamide compounds, *Compt. rend.*, **100**, 1296).

Action of Potassium Iodide on Dithiocarbamide Dichloride.—If equivalent quantities of these (finely powdered) be shaken up together in absolute alcohol, they react as shown in the equation:—

Here again the separation of iodine appears to go on more slowly if an aqueous solution is used.

Dithiocarbamide Di-iodide, $(\text{CSN}_2\text{H}_4)_2\text{I}_2$.

This can, however, be prepared by rubbing together in a mortar *pure* thiocarbamide and iodine in the proportions of their molecular weights, just sufficient alcohol being added to make a pasty mass. In this way the iodine is taken up, and a compound crystallising in long prisms formed. The reaction succeeds best with small quantities; for instance, 0.47 gram iodine and 0.28 gram thiocarbamide. The product is treated several times with cold benzene to remove traces of free iodine, and the nearly colourless residue is then dried between folds of filter-paper.

0.3528 gram gave 39.8 c.c. N at 12° and 768 mm. = 13.54 per cent. N.

$(\text{CSN}_2\text{H}_4)_2\text{I}_2$ requires 13.79 per cent.

When prepared, this di-iodide is quite stable and can be kept for any length of time in a dry tube. On being warmed it melts—at a comparatively low temperature—with liberation of iodine. It crystallises, as already mentioned, in long colourless prisms. There is some difficulty in getting good crystals for the microscope.

Benzene does not dissolve it, but water, alcohol, and ether do, with immediate separation of iodine, *which accounts for its not being formed in solution*. This decomposition of the di-iodide occurs even if it be dropped into absolute alcohol which has been cooled by a mixture of ice and salt, or on adding a drop of absolute alcohol to the di-iodide covered by a layer of benzene; chlorine and *concentrated* hydrochloric acid added to it likewise liberate iodine at once.

On heating the aqueous solution, or on addition of caustic alkali,

sulphur separates. *This separation of sulphur is therefore characteristic of the di- (chlor-, brom-, nitro-, &c.) derivatives of thiocarbamide.*

Dilute hydrochloric acid does not cause separation of iodine in the cold (indeed it seems insoluble in this and also in dilute nitric acid); on heating the mixture, however, iodine is liberated freely, but no precipitation of sulphur occurs. This shows that it is decomposed, under those conditions, more readily into iodine and thiocarbamide than into hydriodic acid, sulphur, thiocarbamide, and cyanamide (compare with the decomposition products of the dichloride or dibromide). Although the di-iodide appears to be insoluble in dilute nitric acid, still, if a drop of alcohol be added to a little of it on a microscopic slide, and then at once a drop of dilute nitric acid, the dinitrate is precipitated.

With regard to the action of cyanides on thiocarbamide and its dichloride, I need merely say at present that it appears to be impossible to prepare dithiocarbamide dicyanide, as this substance splits up immediately after formation. I hope, however, to go more fully into this point in a future paper.

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