

LXVII.—*Sulphinic Compounds of Carbamide and Thiocarbamide.*

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THE results of two previous papers communicated to the Society by the author (Trans., 1886, 191; 1887, 378), on various dihaloid and other derivatives of dithiocarbamide, led naturally to the inquiry whether similar compounds with organic acid radicles could be obtained. That they can be is proved by the preparation of the following compound.

Dithiocarbamide Di-trichloromethyl-sulphinate, $(\text{CSN}_2\text{H}_4)_2(\text{CCl}_3\text{SO}_2)_2$.

This, which is analogous to the dichloride $(\text{CSN}_2\text{H}_4)_2\text{Cl}_2$, the dinitrate $(\text{CSN}_2\text{H}_4)_2(\text{NO}_3)_2$, &c., can be prepared quite easily by the action of trichloromethyl-sulphinate of ammonium, $\text{CCl}_3\cdot\text{SOONH}_4$,* on dithiocarbamide dichloride. To a rather concentrated *cold* aqueous solution of the dichloride, a concentrated solution of the sulphinic salt is added. For instance, in one operation, 1.8 gram dichloride, dissolved in about 10 c.c. water and 4 grams sulphinate (containing some ammonium chloride), were used. Masses of very fine needles soon began to separate out.

After standing for some little time, until the quantity of crystals no longer appeared to increase, they were collected and washed with water till free from ammonium chloride (although they were not by any means insoluble in water), then pressed between paper, and finally dried over sulphuric acid in a vacuum.

0.2480 gram gave 22.3 c.c. N at 7° and 779 mm.

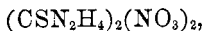
mercury pressure = 11.18 p.c. N.

Calculated for $(\text{CSN}_2\text{H}_4)_2(\text{CCl}_3\text{SO}_2)_2$ = 10.83 „

The reaction therefore is simply $(\text{CSN}_2\text{H}_4)_2\text{Cl}_2 + 2\text{CCl}_3\cdot\text{SOONH}_4 = (\text{CSN}_2\text{H}_4)_2(\text{CCl}_3\text{SO}_2)_2 + 2\text{NH}_4\text{Cl}$. It is not advisable to use an alcoholic instead of an aqueous solution, because then a much greater volume of solvent is required, and the evaporation which is necessary causes decomposition, with separation of sulphur.

* This salt is readily prepared by treating trichloromethyl sulphinic chloride, $\text{CCl}_3\cdot\text{SO}_2\text{Cl}$, with strong aqueous ammonia, and evaporating the solution until the salt begins to crystallise out (Loew, *Zeit. Chem.*, 1869, 82). If wanted pure, it can be freed from ammonium chloride by recrystallisation. As it decomposes rather quickly on keeping, it is best to prepare it fresh each time it is wanted. Much heat is absorbed during its solution.

That this is a *dithiocarbamide* compound is certain from the fact that its solution at once yields the characteristic dinitrate,



with dilute nitric acid, and immediately gives a precipitate of sulphur on the addition of caustic alkali, or on heating. The addition of hydrochloric acid greatly retards this deposition of sulphur, exactly as in the case of the dichloride, but does not prevent it. Bromine, of course, at once precipitates trichloromethylsulphonic bromide, $\text{CCl}_3\cdot\text{SO}_2\text{Br}$. This compound is much more soluble in alcohol than in water, and crystallises from the alcoholic solution on a microscopic slide in stellate groups of the finest needles, in shape not unlike that of a starfish. These are different in appearance from the more rounded groups—likewise of fine needles—of the compound to be mentioned further on, and whose composition is probably expressed by the formula $\text{CSN}_2\text{H}_3\cdot\text{CCl}_3\text{SO}_2$. It melts at $124\text{--}125^\circ$.

Thiocarbamide Trichloromethyl-sulphinic acid, $\text{CSN}_2\text{H}_4\cdot\text{CCl}_3\text{SOOH}$.

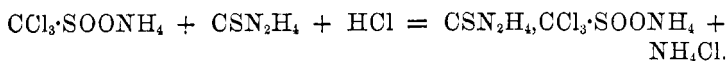
This is formed by dissolving thiocarbamide and trichloromethylsulphinic acid of ammonium in absolute alcohol in molecular proportions, and adding a distinct but not too large excess of concentrated hydrochloric acid; too much alcohol should not be used. Chloride of ammonium separates out, and the alcoholic filtrate on evaporation deposits crystals of the above compound, which may be freed from ammonium chloride by recrystallisation from a *small* quantity of water, and from sulphur by digestion with carbon bisulphide. It is much better to use alcohol than water in the first instance, as the evaporation—especially by heating—of solutions containing sulphinic acid compounds of thiocarbamide, always causes decomposition to a considerable extent, with separation of sulphur.

After being dried over sulphuric acid, the crystals were analysed.

- I. 0.3262 gram gave 30.1 c.c. N at 11° and 746 mm. mercury pressure = 10.80 per cent. N.
 II. 0.2333 gram, ignited with lime, gave 0.3854 gram AgCl = 40.87 per cent. Cl.

	N.	Cl.
Calculated for $\text{CSN}_2\text{H}_4\cdot\text{CCl}_3\cdot\text{SOOH}$...	10.79	41.04 p. c.
Found.....	10.80	40.87 „

The above reaction is therefore expressed by the equation—



This compound is readily soluble in water, even more so in abso-

lute alcohol, and also fairly soluble in ether,* its solution in any one of these being strongly acid to test-papers. It is not at all deliquescent. If slowly crystallised from water, it separates in beautiful well-developed flat prisms, laid on to each other in layers, and showing colours with polarised light. It melts at 139° , evidently with effervescence and deposition of sulphur. The aqueous solution appears to deposit sulphur slowly on heating. Addition of caustic alkali causes no precipitation of sulphur, at least no immediate precipitation, but an alliaceous odour is evolved. (Difference from *dithiocarbamide* compounds.) Bromine throws down, of course, the sulphonic bromide $\text{CCl}_3\cdot\text{SO}_2\text{Br}$.

Carbamide Trichloromethyl-sulphinate, $\text{CON}_2\text{H}_4\cdot\text{CCl}_3\cdot\text{SOOH}$.

This, the corresponding compound of carbamide, can be prepared in somewhat the same way as the thiocarbamide compound, only—on account of its instability—the use of water as solvent and of aqueous hydrochloric acid must be avoided. Carbamide and ammonium trichloromethyl-sulphinate (which need not be free from ammonium chloride) are dissolved in a little *absolute* alcohol, in approximately molecular proportions, and hydrochloric acid gas is passed through the solution, too large an excess of gas being avoided. For instance, 2.25 grams carbamide and 9 grams of the somewhat impure sulphinate were dissolved in 30 c.c. alcohol. The precipitated ammonium chloride is filtered off, and the filtrate evaporated to dryness, in the cold, in a vacuum. In this way, a syrupy mass of crystals is ultimately got, which is pressed dry between paper, to free it from hydrochloric and sulphinic acids, and recrystallised, first from absolute alcohol, and finally from absolute ether, carbamide and ammonium chloride being quite insoluble in the latter. (Much heat is absorbed by the solution of this compound, and indeed of trichloromethylsulphinic acid compounds generally.) A portion, thus crystallised from ether, was powdered, pressed between paper, and placed over sulphuric acid in a vacuum for analysis.

0.4021 gram gave 38.45 c.c. N at 12° and

772 mm. mercury pressure = 11.53 p. c. N.

Calculated for $\text{CON}_2\text{H}_4\cdot\text{CCl}_3\cdot\text{SOOH}$ = 11.50 „

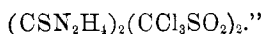
The above compound is extremely soluble in water and in cold

* From this last, it soon begins to separate in spongy masses of the finest needles, which, however, are not the pure compound, but apparently a mixture of it with thiocarbamide. Thus, two preparations were found to contain 11.71 and 14.07 per cent. nitrogen, and melted *with charring*, at 128 — 129.5° and 123.5° respectively. This point requires further investigation.

absolute alcohol, and also readily soluble in cold ether, but insoluble in benzene. It cannot be recrystallised from water, as the solution quickly begins to decompose, trichloromethyl-sulphinic acid and sulphur dioxide being set free. It is thus much less stable than the thiocarbamide compound. From ether and from alcohol, it separates in radiating groups of indistinct thin prisms, but I have been unable to get well-formed crystals, owing to the salt remaining in solution until the latter became syrupy, after which crystallisation spread rapidly through the whole mass. The melting point is not sharp. It appears to begin to melt at about 90° , but is not completely melted until the temperature rises to $96-100^{\circ}$; this is no doubt due to the dissociation of the salt and ultimate solution of the carbamide in the acid. Its fresh aqueous solution at once yields carbamide nitrate, $\text{CON}_2\text{H}_4\cdot\text{HNO}_3$, with nitric acid.

Trichloromethyl-sulphonyl Thiocarbamide, $\text{CSN}_2\text{H}_3\cdot\text{CCl}_3\text{SO}_2$ (?).

In one of the previous papers already referred to (Trans., 1886, 191), mention was made of a compound obtained along with dithiocarbamide dichloride, by the action of trichloromethyl-sulphonic chloride (2 mols.) on thiocarbamide (4 mols.) in alcoholic ethereal solution, and which was described as "crystallising in stellate groups of the finest needles, and having probably the composition



This surmise was, however, wrong, the last-mentioned compound having since been otherwise prepared (see p. 666), and the two are not identical.

This reaction has since then been further investigated. If the sulphonic chloride and thiocarbamide are allowed to act on each other, as described in the above paper, the dithiocarbamide dichloride (most of which separates) filtered off, and the alcoholic ethereal filtrate evaporated to dryness *in the cold* over sulphuric acid, a dry mass evolving a little hydrochloric acid is obtained. This mass contains some free sulphur, which, together with the hydrochloric acid, must arise, in part at least, from the decomposition of some dichloride which had not separated out (*loc. cit.*). The sulphur should be extracted by carbon bisulphide, and the residual mass may then be recrystallised from absolute alcohol, rejecting the first extraction, and with no more heating than is absolutely necessary, so as to avoid decomposition and separation of sulphur. Water may be used as solvent instead of alcohol, though it is less convenient. But from neither water nor alcohol is it easy to get a pure product, as there is a tendency to decomposition while in solution, even in the cold.

A number of different preparations were analysed with the following results:—

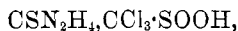
- I. 0.3786 gram gave 36.6 c.c. N at 17° and 769 mm. pressure = 11.49 per cent. N.
 II. 0.2902 gram gave 27.8 c.c. N at 7° and 75.2 mm. = 11.5 per cent. N.
 0.4271 gram., ignited with lead chromate and copper oxide, gave 0.1407 gram CO₂ = 8.98 per cent. C.*
 III. 0.3433 gram gave 0.0634 gram H₂O and 0.1233 gram CO₂ = 2.05 per cent. H and 9.80 per cent. C.
 IV. 0.2514 gram gave 0.0444 gram H₂O and 0.0870 gram CO₂ = 1.96 per cent. H and 9.44 per cent. C.
 V. 0.1157 gram, ignited with lime, gave 0.1973 gram AgCl = 42.2 per cent. Cl.

This compound might, therefore, so far as analysis goes, be one of the three following:—

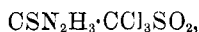
	No. 1. (CSN ₂ H ₄) ₂ (CCl ₃ SO ₂) ₂ .	No. 2. CSN ₂ H ₃ ·CCl ₃ SO ₂ .	No. 3. CSN ₂ H ₄ ·CCl ₃ SOOH.
C.....	9.28 p. c.	9.32 p.c.	9.25 p. c.
H.....	1.55 „	1.17 „	1.93 „
N.....	10.83 „	10.87 „	10.76 „
Cl.....	41.20 „	41.36 „	41.04 „

	Found.		
C.....	8.98	9.80	9.44
H.....	—	2.05	1.96
N.....	—	11.49	11.5
Cl	—	—	42.2

In these there is no appreciable difference in the percentage of any constituent present, excepting in that of the hydrogen, and even there the differences are very slight. And further, the compound was never got sufficiently pure to allow of deciding with accuracy between such slight differences. It is, however, not No. 1, (CSN₂H₄)₂(CCl₃SO₂)₂, which has already been described. Neither is it No. 3,

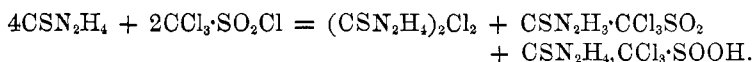


which, when pure, crystallises from water and from alcohol in a totally different form, and is, besides, much more soluble in both of these liquids than this compound. The inference therefore is that it is No. 2, viz., trichloromethyl-sulphonyl thiocarbamide,



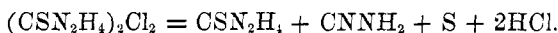
* The water of this combustion was unfortunately lost.

very probably mixed with more or less thiocarbamide and trichloromethyl-sulphinate, $\text{CSN}_2\text{H}_4\cdot\text{CCl}_3\cdot\text{SOOH}$,* its formation in that case being represented by the following reaction :—



That no volatile compound is formed here, is proved by the fact that if weighed quantities of the sulphonic chloride (2 mols.) and thiocarbamide (4 mols.) are allowed to act on each other, using the least possible quantity of alcohol as solvent, the solution transferred to a large watch-glass, and the alcohol then *rapidly* evaporated over sulphuric acid in a vacuum (so as to prevent decomposition of the $(\text{CSN}_2\text{H}_4)_2\text{Cl}_2$ formed), the total weight of the products obtained is the same as that of the original compounds taken, and does not alter substantially so long as the watch-glass remains in a dry atmosphere. If, on the other hand, a smaller proportion of thiocarbamide to sulphonic chloride is taken, a very distinct loss of weight ensues, owing to the formation and volatilisation of the free sulphinic acid, $\text{CCl}_3\cdot\text{SOOH}$. I have not so far been able to make out satisfactorily here the formation, in the first instance, of the third product in the above equation, viz., $\text{CSN}_2\text{H}_4\cdot\text{CCl}_3\cdot\text{SOOH}$, but the following consideration points to its presence.

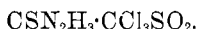
It will be remembered that when an aqueous solution of dithiocarbamide dichloride, $(\text{CSN}_2\text{H}_4)_2\text{Cl}_2$, is warmed, or has alkali added to it, it splits up according to the equation



It therefore occurred to me that further proof of the formation of the above compound, trichloromethyl-sulphonyl thiocarbamide, $\text{CSN}_2\text{H}_3\cdot\text{CCl}_3\text{SO}_2$, might be obtained by allowing weighed quantities of sulphonic chloride (2 mols.) and thiocarbamide (4 mols.) to react in a very small amount of alcohol, and then—after dilution with water—by titrating the liquid with alkali of known strength. If, in addition to the dithiocarbamide dichloride, $(\text{CSN}_2\text{H}_4)_2\text{Cl}_2$, the two compounds, $\text{CSN}_2\text{H}_3\cdot\text{CCl}_3\text{SO}_2$ and $\text{CSN}_2\text{H}_4\cdot\text{CCl}_3\cdot\text{SOOH}$, were really formed, it was probable that one of these two (the sulphinate) would be more readily decomposed by alkali than the other. As a matter of fact, on titrating *in the cold*, it is seen that the last fourth of alkali is used up much more slowly than the first three-fourths, and indeed, in one or two titrations, a sharp break seemed to occur after adding three-fourths of the total requisite alkali, the solution then remaining neutral for a short time in the cold. On warming, the neutralisation of the alkali is of course very rapid.

* See note on the effect of solution in ether on this compound.

There is, therefore, strong reason to suppose the foregoing compound to be trichloromethyl-sulphonyl thiocarbamide,



From alcohol, it crystallises in the finest silky needles, the whole mass looking exactly like cotton-wool. Sometimes the needles are so fine that they are only to be distinguished as such under the microscope at the edges of the round-shaped masses. From water, it also crystallises in the finest needles. It is very sparingly soluble in water, even more so than the dithiocarbamide compound, $(\text{CSN}_2\text{H}_4)_2(\text{CCl}_3\text{SO}_2)_2$, although, after once being dissolved, the crystals do not again separate out very quickly. It is moderately soluble in warm absolute alcohol, very sparingly in cold, and almost insoluble in ether. If a particle of it be placed on litmus-paper and then moistened with alcohol, the litmus is at once reddened. Its solution does *not* yield dinitrate with dilute nitric acid, nor does caustic alkali cause separation of sulphur; this proves that it is not a dithiocarbamide compound. Bromine, of course, at once precipitates the sulphonic bromide, $\text{CCl}_3\text{SO}_2\text{Br}$. It was never obtained sufficiently pure to allow of its melting point being determined with certainty.

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June, 1887.
