

CXXIX.—Interaction of Sulphur Monochloride and Organic Acid Amides.

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THE reaction of acid chlorides with amides, amines, and their derivatives appears to have been extensively studied. In particular, a number of investigations on the interaction of various amines and sulphur monochloride have been carried out (Claus and Krall, *Ber.*, 1871, **4**, 99; Edeleano, *Bull. Soc. chim.*, 1891, [iii], **5**, 173; Roorda Smit, *Ber.*, 1875, **8**, 1445; Schmidt, *Ber.*, 1878, **11**, 1168; Michaelis, *Ber.*, 1895, **28**, 165), but no systematic study of the interaction of sulphur monochloride and organic acid amides or their substituted derivatives appears to have been made.

The reaction of sulphur monochloride with dry ammonia gas is very vigorous. When sulphur monochloride is dropped into the gas, flashes of light are produced and heavy clouds of ammonium chloride are developed, with the simultaneous deposition of sulphur.

In view of this it is to be expected that—

(i) The amido-group in the organic amides will readily react with sulphur monochloride and give rise to sulphides :



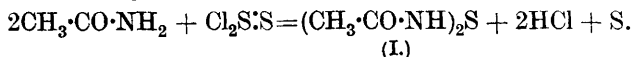
(ii) Amines will be more reactive than amides on account of their more strongly basic character.

(iii) Amides of the monocarboxylic acids, such as acetamide, may be expected to condense with sulphur monochloride more readily than the amides of the dicarboxylic acids, such as oxamide, because the two carbamyl groups in adjacent positions in the latter may be expected to increase the acidity, and thus render the NH_2 -group in such amides less reactive.

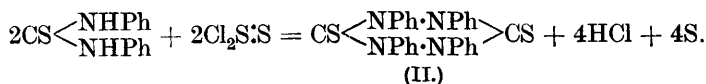
These expectations have been fulfilled by the results of the present work. Oxamide, succinamide, malonamide, phthalamide, and phthalimide do not react with sulphur monochloride. Oxanilide also proved unreactive, whilst malonanilide condensed in the manner characteristic of $\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot$ derivatives (this vol., p. 379).

As regards the other amides which have been investigated, namely, acetamide, butyramide, benzamide, benzanilide, carbamide, thiocarbamide, thiocarbanilide, and salicylamide, it may be noted in the first place that carbamide gave chiefly ammonium chloride and sulphur, along with hydrogen chloride. The reactions with acet-

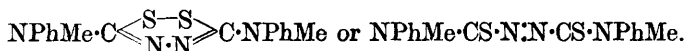
amide, butyramide, and benzamide followed a very simple course, two molecules of the amide condensing with one molecule of sulphur monochloride to give a diamido-sulphide. Thus :



The reaction with thiocarbanilide resulted in the condensation of two molecules of the anilide :



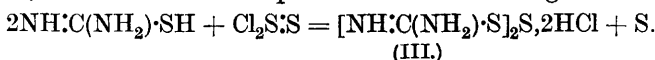
This reaction is similar in many respects to that observed by Hector (*J. pr. Chem.*, 1892, [ii], **44**, 492; compare also Dodt, *Ber.*, 1906, **39**, 1014), who found that two molecules of an unsymmetrical disubstituted thiocarbamide condense under the influence of sulphur monochloride, giving a product from which the four hydrogen atoms have been eliminated,



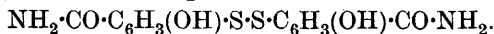
The reaction with thiocarbamide is specially interesting, as it can be explained on Werner's view of the constitution of thiocarbamide. Werner (T., 1919, **115**, 1168) suggested that in a neutral solution thiocarbamide is present in two forms in equilibrium, thus :



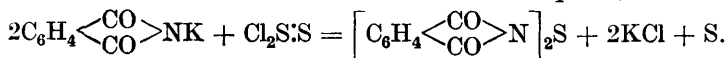
In the present case, the form (b) can be taken as the active modification, the reaction with sulphur monochloride being as follows :



Benzanilide reacts with sulphur monochloride to produce a trisulphide, $\text{S}(\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{COPh})_2$, similar to that resulting from acetanilide and sulphur monochloride (Schmidt, *loc. cit.*), whilst salicylamide produces a disulphide,



Although phthalimide has no action on sulphur monochloride, its potassium derivative reacts to form a di-imino-sulphide,



E X P E R I M E N T A L.

N-Sulphidobisacetamide (I).

Sulphur monochloride (25 grams), dissolved in a small quantity of benzene, was gradually added to a boiling solution of acetamide

(10 grams) in dry benzene (200 c.c.). The reaction began at once, with the slow evolution of hydrogen chloride. After six hours, the undissolved white mass was collected, washed with dry benzene to remove the undecomposed sulphur monochloride, and crystallised from alcohol, from which the product separated in slender needles, m. p. 192° .

The compound dissolved readily in hot water, and decomposed aqueous silver nitrate with the formation of silver sulphide. A solution in sodium carbonate, on boiling and then acidifying, evolved hydrogen sulphide (Found: S=21.48; N=19.27. $C_4H_8O_2N_2S$ requires S=21.62; N=18.92 per cent.).

N-Sulphidobisbenzamide, $(C_6H_5 \cdot CO \cdot NH)_2S$.

This substance was prepared from benzamide (10 grams) and sulphur monochloride (11 grams) in the same way as the preceding sulphide. The white, amorphous solid was sparingly soluble in benzene, from which it crystallised in fibrous needles melting at 188° . The product was insoluble in water and reacted neither with sodium carbonate solution nor with silver nitrate (Found: S=11.90; N=10.14. $C_{14}H_{12}O_2N_2S$ requires S=11.76; N=10.29 per cent.).

N-Sulphidobisbutyramide, $(C_3H_7 \cdot CO \cdot NH)_2S$.

This substance, prepared from butyramide (5 grams) and sulphur monochloride (5 grams), in presence of dry benzene (50 c.c.) in the same way as the sulphidobisacetamide, was deposited as a solid very sparingly soluble in benzene, from which it separated in minute white crystals melting sharply at 175° (Found: N=13.41; S=16.05. $C_8H_{16}O_2N_2S$ requires N=13.72; S=15.68 per cent.).

Sulphidodithiocarbamide Dihydrochloride (III).

Sulphur monochloride (7 grams) was slowly run into a boiling solution of thiocarbamide (9 grams) in absolute alcohol (100 grams) previously saturated with sulphur monochloride. When the vigorous reaction had abated, the mixture was boiled for three hours and the hard yellow mass collected and extracted with a large quantity of alcohol and carbon disulphide until no more sulphur was removed. The resulting, pale yellow substance was insoluble in chloroform, ethylene dichloride, benzene, light petroleum, acetic acid, carbon tetrachloride, or nitrobenzene, and melted with decomposition at $176-177^{\circ}$. On keeping under water it slowly deposited sulphur, hydrochloric acid being simultaneously formed. On treatment with sodium carbonate carbon dioxide was

evolved. Sodium hydroxide first precipitated sulphur, which then dissolved in excess of the boiling alkali, from which, on acidification, hydrogen sulphide was evolved. On treating the aqueous solution with silver nitrate, silver chloride was at once precipitated, but it immediately darkened on the addition of concentrated ammonia owing to the formation of silver sulphide (Found: S=37·12; Cl=28·30; N=22·00. $C_2H_6N_4S_3 \cdot 2HCl$ requires S=37·63; Cl=28·62; N=21·96 per cent.).

3 : 6-*Dithio*-1 : 2 : 4 : 5-tetraphenylhexahydro-1 : 2 : 4 : 5-tetrazine (II).

A mixture of thiocarbanilide (8 grams), sulphur monochloride (5 grams), and dry benzene (200 c.c.) was boiled for three hours, when the solid was collected and washed repeatedly with dry benzene to remove any excess of sulphur monochloride. The substance was then dissolved in benzene, the solution treated with reduced copper until the free sulphur had been eliminated, and evaporated until prismatic crystals, melting sharply at 160°, were deposited. The mixture with thiocarbanilide melted at 138°.

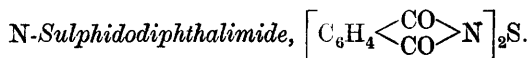
The tetrazine is stable and is not affected by water, in which it is insoluble (Found: C=68·39; H=4·50; N=12·90; S=14·67. $C_{26}H_{20}N_4S_2$ requires C=69·02; H=4·42; N=12·39; S=14·15 per cent.).

Trisulphidobisbenzanilide, $S(S \cdot C_6H_4 \cdot NH \cdot CPh)_2$.

Reaction quickly set in when benzanilide (14 grams) was heated with sulphur monochloride (10 grams). The dark brown solid formed was washed with dry petroleum and then precipitated from an alcoholic solution by means of water. The yellowish-white precipitate was purified in benzene solution by reduced copper as in the last experiment, and was obtained as a flocculent precipitate, m. p. 244° (Found: N=5·98; S=20·17. $C_{26}H_{20}O_2N_2S_3$ requires N=5·74; S=19·67 per cent.).

Disulphidobis-salicylamide, $S_2[C_6H_3(OH) \cdot CO \cdot NH_2]_2$.

A mixture of 5 grams of salicylamide, 50 c.c. of dry benzene, and 5 grams of sulphur monochloride was heated under reflux for three hours. The product was washed with dry benzene and caused to separate several times from methyl alcohol by spontaneous evaporation. It was thus obtained as a yellow, amorphous solid which melted and decomposed at 226° (Found: S=18·51. $C_{14}H_{12}O_4N_2S_2$ requires S=19·04 per cent.).



The dried potassium salt (compare Landsberg, *Annalen*, 1882, 215, 181) of phthalimide (two mols.) and sulphur monochloride (one mol.) were heated with dry light petroleum under reflux for one hour. The residue was repeatedly extracted with dry light petroleum and finally purified by treatment with reduced copper in benzene as in the previous cases. The compound was thus obtained as white crystals which melted at 190°, and decomposed on keeping (Found: N=8.41; S=9.64. $\text{C}_{16}\text{H}_8\text{O}_4\text{N}_2\text{S}$ requires N=8.64; S=9.87 per cent.).

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