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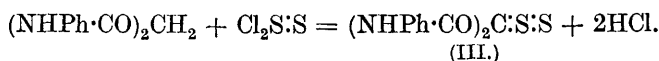
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(II). The question whether the compound (I) is stable under ordinary atmospheric conditions is a vital one, because the vapour tension of "mustard gas" is already so low as to place it on the line limiting the usefulness in war of toxic substances which rely for their effect on the amount of vapour introduced into the air under normal conditions of temperature and pressure. If the second sulphur atom remained in chemical combination, as in formula I, the vapour tension of the compound would be lower than that of "mustard gas," and its utility as a toxic agent would thereby be diminished, if not entirely destroyed.

The late Lieut.-Col. Harrison showed that the product containing the two sulphur atoms vaporised completely at the ordinary temperature, leaving only a residue of sulphur, and that the vapour evolved at different periods of the evaporation had the same order of toxicity as "mustard gas."

There is thus no doubt that the second sulphur atom in the product of the action of sulphur monochloride on ethylene behaves as if it were in solution in, and not in chemical combination with, the sulphide, and the objects of the present series of investigations are to show to what degree the instability of the dithio-grouping is affected by the molecular condition of the remainder of the molecule and to compare the relative stability exhibited by corresponding dithio-ketones of the general formula  $R_2C:S:S$ .

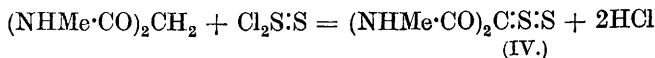
The first compound of the dithio-ketone series (III) was prepared by the action of sulphur monochloride on malonanilide in accordance with the equation :



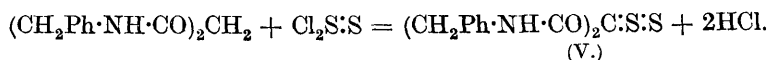
The formula given to it above is proved by the following considerations :

(1) It is a dithio-ketone, that is, it is formed from one molecule of the anilide and one molecule of sulphur monochloride with the elimination of two hydrogen atoms as hydrogen chloride.

(2) The two hydrogen atoms are not supplied by the phenyl groups, because a dithio-ketone (IV) is produced from malondimethylamide by a similar reaction :

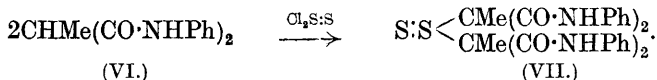


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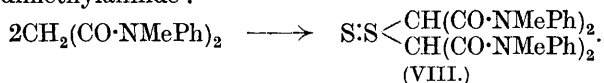


(3) The two hydrogen atoms eliminated are not those which were originally attached to the two nitrogen atoms, because when

sulphur monochloride reacts with methylmalonanilide (VI)—which, it will be noted, cannot form a dithio-ketone on the methine carbon atom, but can readily do so if the two hydrogen atoms attached to nitrogen are those affected—there is formed a disulphide (VII) in accordance with the equation :

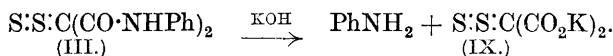


Similar disulphides are produced when tertiary alkylated amides are employed. Thus the disulphide (VIII) is produced from malondimethylanilide :

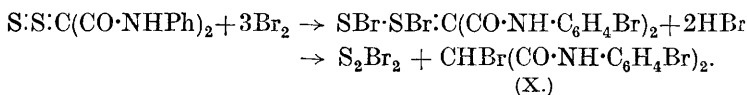


It should be added that these disulphides, unlike the dithio-derivative of "mustard gas" to which they are apparently related in composition, are stable substances. They are at present under investigation.

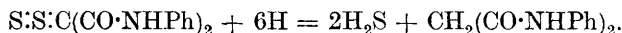
(4) The dithio-ketones behave on hydrolysis in a manner which is in accordance with that which might be expected from the proposed formula. Thus, dithiomesoxanilide (III), on hydrolysis with alkali hydroxides, yields aniline and the alkali salt of a dithio-acid which probably has the structure IX, because it yields hydrogen sulphide by treatment with mineral acids :



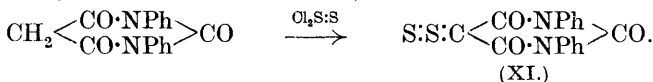
(5) When dithiomesoxanilide (III) is treated with bromine, sulphur bromide is produced, together with the compound (X), which is identical with that formed by the action of bromine on malonanilide (Backes, West, and Whiteley, this vol., p. 373). It is evident therefore that the reaction takes place thus :



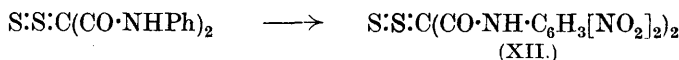
(6) On reduction with an alkaline solution of sodium hydro-sulphide dithiomesoxanilide is transformed into malonanilide and hydrogen sulphide :



(7) The action of sulphur monochloride on diphenylbarbituric acid also yields a dithio-ketone (XI) :



It is clear, therefore, that the formulæ assigned to the dithio-ketones are correct. It may be added that their stability is such that the action of fuming nitric acid on, for example, dithiomesoxanilide leads to the formation of a tetranitro-compound (XII) and leaves the dithio-group intact :



Already, therefore, compounds of both dithio-ketone and dithio-ether types have been isolated which exhibit a degree of stability altogether different from that of the hypothetical dithio-derivative formed in the "mustard gas" reaction. It is perhaps too soon to draw any definite conclusion, but the difference is so great that one is forced to consider whether in these reactions sulphur monochloride may not react in two forms, namely,  $\text{S}\cdot\text{Cl}\cdot\text{S}\cdot\text{Cl}$  and  $\text{Cl}_2\text{S:S}$ . This question has led to much controversy, and the general opinion at the present time is that the second formula is the correct one. Indeed, it would be difficult to explain the formation of "mustard gas" on any other assumption. Still, if it can be assumed that the reagent can react in either form according to the conditions of the experiment and that in the experiments described in the present paper it reacts in the form of  $\text{S}\cdot\text{Cl}\cdot\text{S}\cdot\text{Cl}$ , the dithio-ketones and the disulphides would have the formulæ  $\text{S}_2\text{C(CO}\cdot\text{NHPh)}_2$  and  $\text{S}\cdot\text{CH(CO}\cdot\text{NHPh)}_2$  respectively, and compounds of the latter type, for example, dithiosalicyclic acid (Friedländer), are known to have a high order of stability. These questions will form the subject of further investigation.

## EXPERIMENTAL.

### *Dithiomesoxanilide (III).*

Nine grams of malonanilide and 10 grams of sulphur monochloride ( $\text{S}_2\text{Cl}_2$ ) were heated under reflux with 50 c.c. of dry benzene. As soon as the benzene began to boil, hydrogen chloride gas was vigorously evolved. After three hours the evolution ceased and the product was filtered and washed thoroughly with dry benzene to free it from the excess of sulphur monochloride. The solid residue, which was almost pure and appeared to be free from any precipitated sulphur, was difficultly soluble in acetone, from which it crystallised in short, colourless needles, m. p. 214—215° (Found: N = 8.70;  $\text{S}_4$  = 20.10.  $\text{C}_{15}\text{H}_{12}\text{O}_2\text{N}_2\text{S}_2$  requires N = 8.86; S = 20.25 per cent.).

Two grams of this substance were boiled under reflux with a large quantity of absolute alcohol for two hours in order to determine whether either of the sulphur atoms was separable. The solid, after filtration, was repeatedly extracted with carbon disulphide (Found : N = 9.12; S = 20.33 per cent).

In order to see if the reaction took place in two stages, only half the quantity of sulphur chloride theoretically required was added to malonanilide and the condensation allowed to take place under the same conditions as before. The product was repeatedly boiled with alcohol to free it from any unchanged malonanilide. Almost one-half of the malonanilide was recovered and the other half was completely converted into a dithio-ketone. Thus the reaction appears to take place in one stage only, the substance  $[CH(CO \cdot NPh)_2]S_2$  not being formed.

*Nitration of Dithiomesoxanilide.*—A very vigorous reaction occurred when 5 grams of the anilide were treated with nitric acid (D 1.5), and the whole of the substance dissolved. The nitrated product slowly separated in fine crystals on further warming. It was collected, washed with concentrated nitric acid and with water, and dried, and then melted at  $232-233^\circ$  (Found : N = 16.72; S = 12.60.  $C_{15}H_8O_{10}N_6S_2$  requires N = 16.93; S = 12.90 per cent.).

*Hydrolysis of Dithiomesoxanilide.*—The anilide (15 grams) was hydrolysed by boiling for two hours under reflux with a solution of potassium hydroxide (10 grams) in water (16 grams). The aniline produced by the hydrolysis was extracted with ether and identified. From the aqueous solution a solid was isolated which reacted with hydrochloric acid to produce hydrogen sulphide, and was evidently potassium sulphide which had been formed during the hydrolysis.

*Bromination.*—Ten grams of dithiomesoxanilide (1 mol.) were treated with bromine (rather more than 3 mols.) in glacial acetic acid solution. The product, after spontaneous evaporation of the acetic acid, smelt of sulphur bromide. When the smell became faint the product was boiled with alcohol under reflux. The solution deposited on cooling light, white tufts, which melted sharply at  $239^\circ$  after repeated crystallisation. The substance was found to be identical with the tribromomalonanilide prepared by the direct bromination of malonanilide (Backes, West, and Whiteley, this vol., p. 373).

*Reduction of Dithiomesoxanilide.*—Malonanilide, m. p.  $224-225^\circ$ , was produced when dithiomesoxanilide (10 grams), dissolved in boiling alcohol (100 c.c.), was reduced by an alkaline solution of sodium sulphide by Brand's method (*Ber.*, 1909, **42**, 3464).

*Dithiomesoxodimethylamide (IV).*

This substance, prepared from malondimethylamide (1.5 grams) and sulphur monochloride (about 2 grams) in the same way as dithiomesoxanilide, was difficultly soluble in absolute alcohol. It separated from a concentrated solution in slender needles and ultimately as a crystalline powder which melted at 216–217° (Found : N = 14.24; S = 33.24.  $C_5H_8O_2N_2S_2$  requires N = 14.58; S = 33.33 per cent.).

*Dithiomesoxodibenzylamide (V).*

This substance was prepared from 4 grams of malondibenzylamide and 2 grams of sulphur chloride. The product was dissolved in absolute alcohol, from which it separated in fine, white crystals melting at 204° (Found : N = 8.57; S = 18.18.  $C_{17}H_{16}O_2N_2S_2$  requires N = 8.34; S = 18.61 per cent.).

*Malondimethylanilide Disulphide (VIII).*

A mixture of 5 grams of malondimethylanilide, 50 grams of dry benzene, and 2.7 grams of sulphur chloride was heated under reflux for three hours. The action was not so vigorous as in the case of malonanilide. The product was washed with dry benzene to remove the unchanged sulphur monochloride, dissolved in hot acetic acid, and precipitated from the solution by hot water. This treatment was repeated until the substance had a constant melting point, 218–219° (Found : S = 10.52.  $C_{34}H_{34}O_4N_4S_2$  requires S = 10.22 per cent.).

*Methylmalonanilide Disulphide (VII).*

Methylmalonanilide was prepared by heating a mixture of methyl methylmalonate (17 grams) and aniline (19 grams) for five hours at 140° and finally at 150–160° until the distillation of methyl alcohol ceased. After crystallisation from alcohol the product melted at 180°.

A mixture of 10 grams of methylmalonanilide, 100 c.c. of dry benzene, and 5 grams of sulphur monochloride was heated under reflux. Evolution of hydrogen chloride began to take place at once. After three hours, the solid was collected, washed with dry benzene, and crystallised from absolute alcohol, when it was obtained as a crystalline powder melting at 229–230° (Found : S = 11.01.  $C_{32}H_{30}O_4N_4S_2$  requires S = 10.70 per cent.).

*5-Disulphido-1 : 3-diphenylbarbituric acid (XI).*

Sulphur monochloride (2.7 grams) dissolved in a small quantity of benzene was gradually added to a boiling mixture of benzene (50 c.c.) and diphenylbarbituric acid (5.6 grams). The acid, which was not soluble in benzene, rapidly disappeared and hydrogen chloride was evolved. After two hours, the brown liquid was cooled and filtered, and the solvent allowed to evaporate. The residue was again dissolved in benzene and, after the solvent had evaporated, crystallised from a mixture of benzene and light petroleum, when it melted sharply at  $181^{\circ}$ . The molecular weight, determined by the cryoscopic method in benzene solution, was 355.5 (Found :  $S = 19.20$ .  $C_{16}H_{10}O_3N_2S_2$  requires  $S = 18.72$  per cent.;  $M = 342$ ).

In conclusion, I take this opportunity of expressing my sincere gratitude to Prof. J. F. Thorpe and Dr. M. A. Whiteley for the keen interest they have shown and the kind encouragement they have given me throughout this work. I also express my thanks to the Chemical Society for a grant from their Research Fund, which has partly defrayed the expenses incurred in this investigation.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,  
SOUTH KENSINGTON.

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