CIII.—Some Reactions of Benzyl Mercaptan. Benzyl Tri- and Tetra-sulphides.

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THE attempted synthesis of organic polysulphides by the condensation of mercaptans and sulphoxides, which led to the detailed examination of the action of hydrochloric acid on benzyl sulphoxide, and was described in a recent paper by one of us (Smythe, Trans., 1909, **95**, 349), has been continued. Some results of this study form the subject of the present communication. The tri- and tetrasulphides of benzyl have been isolated, benzyl disulphoxide has been shown to be capable of easy reduction by benzyl mercaptan and hydrogen sulphide, and further illustrations of the reducing properties of mercaptan have been furnished by its reactions with sulphur dioxide and benzyl disulphoxide.

EXPERIMENTAL.

Action of Sulphur Dioxide on Benzyl Mercaptan. Benzyl Trisulphide.

A convenient amount of benzyl mercaptan (b. p. 195°) is dissolved in about seven times its volume of glacial acetic acid, and the liquid saturated simultaneously with sulphur dioxide and hydrogen chloride, the gases being passed in at intervals for several days. No apparent reaction takes place at first, but after a lapse of time, varying from a few days to a week or two, the odour of mercaptan disappears, and, occasionally, a white, crystalline mass is precipitated. The product is then distilled in a current of steam, whereby impurities in the mercaptan are removed; the non-volatile residue, after solidification and drying, is fractionally crystallised from alcohol, to which enough ethyl acetate is added to prevent precipitation of oil. In this way it is resolved into two components, which prove to be benzyl disulphide and benzyl trisulphide.

Benzyl disulphide melts at 71°; on analysis:

0.1016 gave 0.2540 CO₂ and 0.0550 H_2O . C = 68.20; H = 6.02.

0.1258 , 0.2386 BaSO₄. S = 26.04.

M.W. (by cryoscopic method) = 233.

 $\begin{array}{ccc} C_{14}H_{14}S_2 & \text{requires} & C=68\cdot30 \ ; & H=5\cdot69 \ ; & S=26\cdot04 & \text{per cent.} \\ & M.W.=246. \end{array}$

Benzyl trisulphide melts at 49°, and crystallises well from alcohol and ethyl acetate in long, thin laths, apparently monoclinic, which sometimes attain a length of an inch or more. These have a strongly developed cleavage, and flatten under the spatula somewhat like fibrous ammonium chloride. The compound is excessively soluble in benzene. It may be noted that its melting point is the same as that of the monosulphide. Analysis yielded the following results:

0.1882 gave 0.4166 CO₂ and 0.0874 H₂O. C=60.35; H=5.16. 0.1983 , 0.4982 BaSO₄. S=34.46.

M.W. (by cryoscopic method) = 268.

 $C_{14}H_{14}S_3$ requires C = 60.40; H = 5.02; S = 34.58 per cent. M.W. = 278.

When solutions in alcohol of benzyl trisulphide and silver nitrate are mixed, a crystalline compound is precipitated. The reaction takes place even in very dilute (0.5 per cent.) solution. The compound crystallises from boiling absolute alcohol in pure white needles, which are unstable in contact with the mother liquor, but can be kept for a long time without darkening in a dry atmosphere. These crystals melt and decompose suddenly at 96°, the residue turning brownish-red. The substance appears to be an *additive compound* of silver nitrate and the trisulphide:

0.2396 gave 0.0578 Ag. Ag = 24.13. $C_{14}H_{14}S_{3}AgNO_{3}$ requires Ag = 24.08 per cent.

In respect to the formation and composition of this compound, the trisulphide thus resembles the disulphide of benzyl.

Attempts have been made to determine the relative quantities of di- and tri-sulphide, the only organic products formed by the action of sulphur dioxide on benzyl mercaptan, the method adopted for their separation being that of fractional crystallisation. In view of the great number of crystallisations necessary to effect a satisfactory separation, the results can only be regarded as approximate, although they are doubtless accurate enough for the purpose in hand. In one experiment, 30 grams of benzyl mercaptan yielded 24.3 grams of solid products, and these were resolved into 9.6 grams of disulphide and 9.8 grams of trisulphide, leaving an unresolved mixture of these weighing 1.5 grams (loss = 3.4 grams). In another case, 67.7 grams of solid products yielded 31.6 grams of disulphide, 30.4 grams of trisulphide, and 0.6 gram unresolved (loss = 5.1 gram).

It is clear, then, from these figures, that the di- and tri-sulphides are formed in, practically, the same amounts, and the following equation expressing the reaction may be regarded as quantitative:

 $4\mathbf{C}_{6}\mathbf{H}_{5} \cdot \mathbf{C}\mathbf{H}_{2} \cdot \mathbf{S}\mathbf{H} + \mathbf{S}\mathbf{O}_{2} = (\mathbf{C}_{6}\mathbf{H}_{5} \cdot \mathbf{C}\mathbf{H}_{2})_{2}\mathbf{S}_{2} + (\mathbf{C}_{6}\mathbf{H}_{5} \cdot \mathbf{C}\mathbf{H}_{2})_{2}\mathbf{S}_{3} + 2\mathbf{H}_{2}\mathbf{O}.$

It may be remarked, incidentally, that this reaction furnishes an interesting example of the oxidising properties of sulphur dioxide.

Holmberg, who has lately studied the action of thionyl chloride on ethyl mercaptan (Annalen, 1907, **359**, 81), gives evidence to show that, having regard to the organic compounds, the reaction is quantitative and expressible by an equation quite analogous to the one above, namely:

 $4C_{2}H_{5} \cdot SH + SOCl_{2} = (C_{2}H_{5})_{2}S_{2} + (C_{2}H_{5})_{2}S_{3} + H_{2}O + 2HCl.$

The action of thionyl chloride on phenyl mercaptan has been investigated more recently by Tasker and Jones (Trans., 1909, **95**, 1910), who, led by the observation that sulphur dioxide is given off during the reaction, have proposed various equations involving the formation of sulphur, sulphur suboxide, and phenyl tetrasulphide, although there is no direct evidence of the production of any of these compounds. These authors appear to have overlooked the obvious fact that the sulphur dioxide proceeds from the decomposition of thionyl chloride by the water formed during the reaction. Supposing that all the water were decomposed in this way, then Holmberg's general equation, expressing the reaction between thionyl chloride and mercaptans, namely:

 $4RSH + SOCl_2 = R_2S_2 + R_2S_3 + H_2O + 2HCl,$

would become

 $4\mathbf{RSH} + 2\mathbf{SOCl}_2 = \mathbf{R}_2\mathbf{S}_2 + \mathbf{R}_2\mathbf{S}_3 + 4\mathbf{HCl} + \mathbf{SO}_2.$

Leaving out of consideration the small amount of secondary reaction between sulphur dioxide and mercaptan which would be possible under the conditions of experiment, then all reactions between thionyl chloride and mercaptan should take place between the limits set by these two equations. The determinations by Tasker and Jones of the total titre (mercaptan, thionyl chloride, hydrochloric acid, and sulphur dioxide) with standard iodine and alkali for varying quantities of phenyl mercaptan and thionyl chloride confirm this statement, although they furnish no evidence, as these authors seem to think, for the formation of phenyl tetrasulphide (*loc. cit.*, p. 1914, equation A).

There is thus no reason to think that phenyl mercaptan behaves towards thionyl chloride differently from ethyl mercaptan, and it seems likely that sulphur dioxide and thionyl chloride react in a similar manner with all mercaptans.

Action of Sulphur Chloride on Benzyl Mercaptan.

Benzyl tetrasulphide has been prepared by Holmberg's method (Annalen, 1908, **359**, 81) as follows. Five grams of freshly distilled sulphur chloride (b. p. 135°), dissolved in 25 c.c. of carbon tetrachloride, were added slowly to a solution of 12 grams of benzyl mercaptan in 50 c.c. of carbon tetrachloride, the mixture being well cooled. A violent reaction set in, and much hydrogen chloride was evolved. On distilling in a current of steam, carbon tetrachloride and excess of mercaptan were removed, and an ambercoloured oil remained, which solidified on keeping. On crystallisation from alcohol, this product was obtained as a white, crystalline powder, melting at 49-50°. Analysis proved this to be benzyl tetrasulphide:

M.W. (by cryoscopic method) = 310.

 $C_{14}H_{14}S_4$ requires C=54.19; H=4.52; S=41.29 per cent. M.W.=310.

The yield in the above reaction is 10.4 grams, which is practically quantitative, on the assumption that the equation of reaction is as follows, and having regard to the amount of sulphur chloride taken:

 $2C_6H_5 \cdot CH_2 \cdot SH + S_2Cl_2 = (C_6H_5 \cdot CH_2)_2S_4 + 2HCl.$

It is essential, in preparing the tetrasulphide, that the mercaptan should be in considerable excess and the reagents well diluted, otherwise dark-coloured oils, difficult to handle, are produced.

When a solution of the tetrasulphide in acetic acid is treated with zinc dust, hydrogen sulphide is evolved, and on distilling the product in a current of steam, an oil passes over which is readily identified by its odour and its reaction with iodine, whereby benzyl disulphide, m. p. 71°, is produced, as benzyl mercaptan. It is evident that the reduction takes place according to the equation:

 $(\mathbf{C_6H_5} \cdot \mathbf{CH_2})_2\mathbf{S_4} + 3\mathbf{H_2} = 2\mathbf{C_6H_5} \cdot \mathbf{CH_2} \cdot \mathbf{SH} + 2\mathbf{H_2S}.$

Chlorine attacks the tetrasulphide in solution of carbon tetrachloride, sulphur chloride and benzyl chloride being produced. The solution in the tetrachloride was saturated in the cold with dry chlorine, and then heated for some hours under reflux to remove excess of chlorine. On distilling the product, at first under diminished and then under atmospheric pressure, two fractions were obtained, boiling at 130° and 179° respectively. The former was proved to be sulphur chloride by the reaction with water; the latter, on treatment with alcoholic solution of sodium sulphide, gave sodium chloride and benzyl sulphide (m. p. 49°), and was thus shown to be benzyl chloride. The reaction may thus be expressed by the equation:

 $(C_6H_5 \cdot CH_2)_2S_4 + 3Cl_2 = 2C_6H_5 \cdot CH_2Cl + 2S_2Cl_2.$

Benzyl tetrasulphide does not react with methyl iodide, whereby it differs from the monosulphide; and it does not form an additive compound with silver nitrate, being distinguished in this respect from the di- and tri-sulphides. It is not oxidised by nitric acid (D 1.3). Both the tri- and tetra-sulphides are oxidised by hydrogen peroxide. It is hoped that experiments on this subject at present in progress will throw some light on the constitution of these compounds. As the first four sulphides of benzyl have now been prepared, it is not without interest to note their melting points, which are given in order from the mono- to the tetra-sulphide, namely, 49° , 71° , 49° , $49-50^{\circ}$.

Action of Benzyl Mercaptan on Benzyl Disulphoxide.

3.9 Grams of benzyl disulphoxide and 8.8 grams of benzyl mercaptan were dissolved in glacial acetic acid, and the solution saturated with hydrogen chloride. After a few days, a sudden reaction set in with evolution of heat, and, on cooling, crystals were deposited from the solution. The acids and the excess of mercaptan were now removed by distillation in a current of steam. The residue weighed 9.8 grams, and was found to be a simple substance, melting at 71° after recrystallisation, and giving the characteristic reaction for benzyl disulphide with silver nitrate. A determination of sulphur further proves it to be the disulphide. (Found, S=26.39. Calc., S=26.10 per cent.) It seems clear that reaction has taken place in the manner expressed by the equation:

 $(C_6H_5 \cdot CH_2)_2S_2O_2 + 4C_6H_5 \cdot CH_2 \cdot SH = 3(C_6H_5 \cdot CH_2)_2S_2 + 2H_2O.$

This is confirmed by the yield of disulphide, which is 94 per cent. of that required by the equation.

Hydrogen sulphide reacts in a similar way to mercaptan, reducing

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benzyl disulphoxide to disulphide, and being itself oxidised to sulphur.

Eight grams of the disulphoxide were dissolved in glacial acetic acid and saturated simultaneously with hydrogen chloride and hydrogen sulphide. After keeping some days, the product was distilled in a current of steam, and the residue, after solidification, was extracted with alcohol. This dissolved out 7.1 grams of a compound melting at 71°, and giving the reactions characteristic of benzyl disulphide, and the insoluble portion was recognised as sulphur. The reaction may thus be expressed by the equation:

 $(\mathbf{C}_{6}\mathbf{H}_{5}\cdot\mathbf{C}\mathbf{H}_{2})_{2}\mathbf{S}_{2}\mathbf{O}_{2}+2\mathbf{S}\mathbf{H}_{2}=(\mathbf{C}_{6}\mathbf{H}_{5}\cdot\mathbf{C}\mathbf{H}_{2})_{2}\mathbf{S}_{2}+2\mathbf{H}_{2}\mathbf{O}+\mathbf{S}_{2},$

and in agreement with this, the yield is 92 per cent. of that required by the equation.

Similar reactions have been tried with benzyl sulphone and benzyl sulphoxide, but without success; the conditions, however, in the latter case are necessarily somewhat different, since hydrogen chloride has to be replaced by other condensing agents owing to its action on the sulphoxide (Trans., 1909, **95**, 349).

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