CCXXIV.—*Stereoisomerism of Disulphoxides and Related Substances. Part VIII. Isomeric Tetrabromides of a Disulphide.*

By G. MACDONALD BENNETT and F. SYDNEY STATHAM.

DIBROMIDES of organic sulphides have long been known (Cahours, *Annalen*, 1865, **135**, 355), but the usual formulation R_2S,Br_2 gives no information as to their structure. From the modern point of view the most probable structures are $R_2\overset{\oplus}{S} - Br\}\overset{\ominus}{Br}$ and $R_2\overset{|}{S}{<}^{Br}_{Br}$, in the latter of which the two bromine atoms would be identical in function and the sulphur atom would have ten electrons in the outer shell. If the former is correct, the dibromides are bromo-sulphonium bromides and should be stereochemically analogous to the sulphonium salts and sulphoxides.

The investigation of stereoisomerism with such substances is difficult owing to their instability, but the tetrabromide of *p*-dimethyldithiolbenzene (Zincke and Frohneberg, *Ber.*, 1909, **42**, 2721) has given positive results. These authors had described this tetrabromide as dimorphous, but we have now shown that the two forms are isomeric chemical individuals by observations of their separate and joint effects in depressing.the freezing point of benzene.

In addition to the usual method of preparation from bromine and the disulphide, the dibromides are formed when hydrogen bromide acts on the two stereoisomeric dioxides (Part III; J., 1928, 3189), and they are converted into these dioxides by the action of moist silver oxide. The β-dioxide yields the pure β-tetrabromide, and the α-dioxide a mixture of the α- and the β-tetrabromide, the conditions being inevitably such as are known to promote the conversion of the α- into the β-isomeride. In the opposite change of tetrabromides into dioxides, the α-tetrabromide furnished α-dioxide almost exclusively and the β-tetrabromide gave a mixture of about equal amounts of the two dioxides. These results afford further support of the idea that the two pairs of substances are stereochemically analogous.

Attempts to find other cases of such isomeric polybromides have so far been unsuccessful. The *tetrabromides* of diethyldithiolbenzene and of dibenzyldithiolethane were isolated, but appeared to be single substances. The tetrabromides of diphenyldithiolethane and 1 : 3-dimethyldithiolbenzene and the hexabromide of 1 : 3 : 5-trimethyltrithiolbenzene were too unstable for isolation, substitution with evolution of hydrogen bromide occurring very readily. The tetrabromide of dithian could not be recrystallised.

It would seem that there must be some special factor which renders the tetrabromide of *p*-dimethyldithiolbenzene relatively stable—possibly a mutual attraction between the outer fields of a bromine atom and the adjacent methyl group.

EXPERIMENTAL.

Reinvestigation of the Tetrabromides of p-*Dimethyldithiolbenzene.*—The β-tetrabromide, formed from the sulphide by direct combination with dry bromine in chloroform, crystallises from that solvent in garnet-red monoclinic needles which melt with dissociation at from 86° to 90° with different specimens. It is unstable in the air and the bromine content (Found : Br, 65·1. Calc. : Br, 65·3%) falls when the substance is kept in a desiccator for a few hours. Exposed to the atmosphere, it passes fairly rapidly, with evolution of hydrogen bromide, into the dioxide.

The β-isomeride, crystallised from pure dry chloroform, gives the almost black, stout prisms of the α-isomeride, melting at 105—110° with different specimens (Found : Br, 65·2%). The striking difference in colour is due to the massiveness of the crystals of the α-isomeride. The two substances are similar in colour when crushed

The depression of the freezing point of benzene by saturation with these two substances was observed :—

Depression produced by saturation with the α-tetrabromide	0·145°
Depression after addition of the β-tetrabromide also	0·200°
Depression produced by saturation with the β-tetrabromide	0·169°
Depression after addition of α-tetrabromide also	0·209°

These experiments were repeated with similar results, and there can be no doubt that the α- and the β-tetrabromide are distinct chemical individuals.

Action of Hydrogen Bromide on the Dioxides of p-*Dimethyldithiolbenzene.*—The α-dioxide gave with dry hydrogen bromide in dry chloroform first a yellowish precipitate of monoxide dibromide and then a dark mass of tetrabromide. Microscopic examination showed this to be a mixture of about equal parts of the α- and the β-tetrabromide. When this was kept in contact with the chloroform (now moist), it was soon converted into pure β-tetrabromide. The β-dioxide in similar circumstances furnished the red crystals of pure β-tetrabromide at once.

Hydrolysis of the Tetrabromides to the Dioxides.—The isomerides were separately mixed with water containing an excess of fresh silver oxide, the solution was filtered after a time, and the material recovered by evaporation in a vacuum at laboratory temperature. The product from the α-tetrabromide, once crystallised from alcohol, melted at 177—180° and was therefore nearly pure α-dioxide (m. p.

183°). The β-tetrabromide yielded a dioxide mixture of m. p. 145—167°, which indicates the presence of the two dioxides in about equal proportion, their mixtures showing no depression of m. p.

Tetrabromide from p-*Diethyldithiolbenzene.*—Bromine combines with the disulphide in benzene solution to give red needles of the *tetrabromide*, m. p. 73—78° (decomp.), having the appearance of chromic anhydride (Found : Br, 62·1. $C_{10}H_{14}Br_4S_2$ requires Br, 61·8%). This substance was recrystallised from chloroform, but no evidence was found of a second form. This tetrabromide is definitely less stable than those from dimethyldithiolbenzene.

Experiments on the action of hydrogen bromide on the two dioxides (preceding paper) gave products which were somewhat different in melting point but appeared to be identical under the microscope, so that no conclusive indication was obtained of isomerism.

Tetrabromide of Dibenzyldithiolethane.—The *tetrabromide*, prepared from benzene solution, was an orange-red crystalline solid, m. p. 80—85° (decomp.) (Found : Br, 54·7. $C_{16}H_{18}Br_4S_2$ requires Br, 53·9%). It decomposed rapidly and could not be recrystallised.

THE UNIVERSITY, SHEFFIELD. [*Received, May* 21*st*, 1931.]