

NOTE.

The Reaction of Bromine with isoPropyl Alcohol. By JOHN FREDERICK JAMES DIPPY, HERBERT BEN WATSON, and EDMUND DENYS YATES.

ACCORDING to Etard (*Compt. rend.*, 1892, **114**, 753), $\alpha\alpha\alpha$ -tribromoacetone is formed, together with *isopropyl* bromide, by treatment of *isopropyl* alcohol with bromine. Friedel (*Bull. Soc. chim.*, 1865, **3**, 250) states that both tri- and tetra-bromoacetones are produced, but he did not separate them. A study by Brochet (*Compt. rend.*, 1894, **119**, 1270; *Ann. Chim. Phys.*, 1897, **10**, 134) of the reaction of chlorine with the same alcohol led to the isolation of *as*-tetrachloroacetone only.

In our experiments, bromine was added slowly to 500 c.c. of *isopropyl* alcohol (b. p. 82°) contained in a flask under a reflux condenser. At first reaction proceeded vigorously, much heat being evolved, but ultimately warming on the water-bath became necessary and after addition of 300 c.c. of bromine (somewhat less than 1 mol.) there was no further change. Two layers separated. The top layer (175 g.) consisted of constant-boiling hydrobromic acid (b. p. 124° . %HBr, 46.6). Careful fractionation of the lower layer gave the following: *isopropyl* bromide, 570 g. (b. p. 61° . Br found, 64.8; calc., 65%), monobromoacetone, 40 g. (b. p. $38-40^\circ/14$ mm. Br found, 59.0; calc., 58.4%), *as*-dibromoacetone, 18 g. (b. p. $53-56^\circ/14$ mm. Br found, 73.7; calc., 74.1%), $\alpha\alpha\alpha$ -tribromoacetone, 35 g. (b. p. $128-129^\circ/14$ mm. Br found, 81.6; calc., 81.4%), and *as*-tetrabromoacetone, 240 g. [b. p. $139^\circ/14$ mm., 258° (decomp.)/ 760 mm., m. p. 36.8° (De Jong, *Rec. trav. chim.*, 1903, **22**, 286, gives $37-38^\circ$). Br found, 85.5; calc., 85.5%]. No acetone was detected. Both the tri- and the tetra-bromoacetone gave bromoform with caustic soda or ammonia, and carbylamine with aniline and alkali.

The main products of this reaction are therefore *isopropyl* bromide and *as*-tetrabromoacetone. It is obvious that acetone first produced by oxidation reacts with bromine, while the hydrogen bromide formed simultaneously attacks a further portion of the alcohol. The yield of products isolated was 88% of the theoretical.—
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