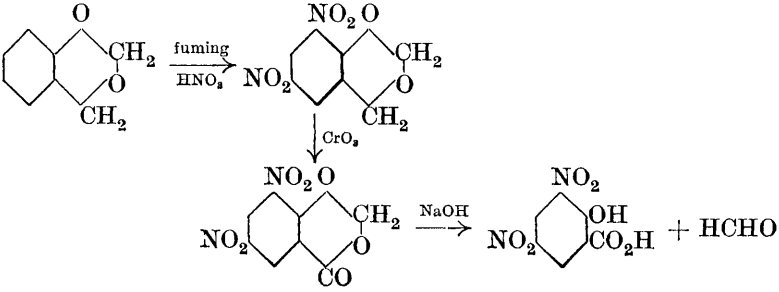
CCCXLI.—1 : 3-*Benzdioxin.*

By Frederick Daniel Chattaway and Harry Irving.

1 : 3-Benzdioxin has been obtained by eliminating the nitro-group from 6-nitro-1 : 3-benzdioxin (Chattaway and Calvet, *Anal. Soc. Fís. Quím.*, 1928, **26**, 420) and also by heating *o*-hydroxybenzyl alcohol with methylene sulphate (Baker, this vol., p. 1770).

Its properties and reactions have now been somewhat more fully studied. When nitrated by fuming nitric acid, it yields 6 : 8-*dinitro*-1 : 3-*benzdioxin.* This is readily oxidised by chromic acid to 6 : 8-*dinitro*-4-*keto*-1 : 3-*benzdioxin,* which when heated with aqueous alkali yields 3 : 5-dinitrosalicylic acid and formaldehyde :



EXPERIMENTAL.

6-*Acetamido*-1 : 3-*benzdioxin* was obtained when a solution of 9 g. of 6-nitro-1 : 3-benzdioxin in 50 c.c. of acetic anhydride at 100° was reduced by the addition of 10 g. of sodium in small portions. It was also formed when 6-amino-1 : 3-benzdioxin was heated with acetic anhydride containing a drop of concentrated sulphuric acid. It crystallised from boiling acetic acid, in which it was sparingly soluble, in small colourless rhombic plates, m. p. 224° with slight decomposition (Found : C, 62·0; H, 5·5; N, 7·2. $C_{10}H_{11}O_3N$ requires C, 62·2; H, 5·7; N, 7·25%).

Preparation of 1 : 3-*Benzdioxin*.—In the following preparation, the troublesome isolation of 6-aminobenzdioxin is avoided.

250 C.c. of concentrated hydrochloric acid were added in portions of 10 c.c. to 60 g. of finely powdered 6-nitro-1 : 3-benzdioxin (1 mol.) and 120 g. of granulated zinc (excess) in 750 c.c. of ethyl alcohol at 70°. Reduction proceeded vigorously with the evolution of much heat, and the addition of the acid was so regulated that no material loss of alcohol occurred through volatilisation. The nitrobenzdioxin slowly dissolved and the solution became very dark in colour. When reduction was complete (1 hour), the solution was filtered from any excess of zinc, cooled, and diazotised slowly (20 minutes) at 0° to − 5° (mechanical stirrer) with 30 g. of finely powdered sodium nitrite (1·3 mols.). The solution was then stirred for a further 10 minutes and warmed gradually on a water-bath. Nitrogen and acetaldehyde were freely evolved and when the evolution of nitrogen ceased the solution was distilled in a current of steam. Alcohol, which came over first, was collected separately (A) until a test portion gave a turbidity on large dilution with water. Distillation was continued until the distillate was no longer milky. Chloroform then extracted 9·3 g. of 1 : 3-benzdioxin from the aqueous distillate. Fractionation of the alcoholic distillate (A) under a long column gave nearly pure alcohol, and an aqueous residue from which chloroform extracted a further 1·6 g. of benzdioxin. The benzdioxin was purified by distillation in steam (twice), in which it is readily volatile; finally, after drying over sodium sulphate, it was twice fractionated under reduced pressure (20 mm.).

1 : 3-Benzdioxin is at the ordinary temperature a colourless liquid which has a pleasant smell recalling that of the catechol ethers. Cooled in a freezing mixture, it solidifies to a mass of colourless crystals, m. p. 12·5°. It is practically insoluble in water, but very readily soluble in all organic solvents. It boils without decomposition at 210—211°/754 mm., 161—162°/225 mm., 100·5—

101·5°/20 mm. It has $d_{4^\circ}^{20\cdot2^\circ}$ 1·174 and $n_{\mathrm{D}}^{20\cdot2^\circ}$ 1·5478, whence $[R_L]_{\mathrm{D}}$ = 36·78 (calc., 36·63).

Nitration of 1 : 3-*Benzdioxin* : *Formation of* 6 : 8-*Dinitro*-1 : 3-*benzdioxin*.—20 C.c. of fuming nitric acid (*d*, 1·5) to which a little urea nitrate had been added were cooled to − 5°, and 2 g. of 1 : 3-benzdioxin added drop by drop (5 minutes) with vigorous shaking. After 5 minutes, the pale brown liquid formed was poured over crushed ice; 6 : 8-*dinitro*-1 : 3-*benzdioxin* (2 g.) then separated as a viscous, pale yellow solid, which was repeatedly macerated with water and washed by decantation to free it from excess of nitric acid and any nitrosalicylic acids formed. It was collected, dried on a water-bath, and recrystallised from alcohol, in which it was rather sparingly soluble, and from which it separated in flattened prisms of a very pale yellow colour, m. p. 135—136° (Found : C, 42·8; H, 2·8; N, 12·5. $C_8H_8O_6N_2$ requires C, 42·5; H, 2·65; N, 12·4%).

[The remainder of the work described in this paper was carried out in association with Mr. Max Goepp of the Queen's College.]

Oxidation of 6 : 8-*Dinitro*-1 : 3-*benzdioxin* : *Formation of* 6 : 8-*Dinitro*-4-*keto*-1 : 3-*benzdioxin*.—2 G. of chromic acid (1 mol. + a slight excess) were added to 5·5 g. of 6 : 8-dinitro-1 : 3-benzdioxin dissolved in 50 c.c. of hot acetic acid. Oxidation proceeded smoothly with the evolution of heat and the reaction was completed by boiling for 4 minutes. On cooling, 6 : 8-*dinitro*-4-*keto*-1 : 3-*benzdioxin* (5·3 g.) separated as a crystalline solid. It was moderately easily soluble in boiling acetic acid, from which it separated in fine colourless slender prisms, m. p. 196·5—197·5° (Found : N, 11·65. $C_8H_4O_7N_2$ requires N, 11·6%).

Hydrolysis of 6 : 8-*Dinitro*-4-*keto*-1 : 3-*benzdioxin to* 3 : 5-*Dinitrosalicylic Acid and Formaldehyde*.—1 G. of the substance was boiled with 50 c.c. of 10% aqueous caustic soda. The solid slowly dissolved, formaldehyde was evolved, and a deep orange-coloured solution resulted, from which disodium 3 : 5-dinitrosalicylate separated on cooling. On acidification, the free acid separated as a crystalline solid. It crystallised from dilute hydrochloric acid in fine colourless needles containing water of crystallisation. After being dehydrated at 110°, it melted at 173° and did not depress the melting point of authentic specimens of anhydrous 3 : 5-dinitrosalicylic acid prepared by the nitration of both 3- and 5-nitrosalicylic acid with ice-cold fuming nitric acid (compare Hübner, *Annalen*, 1879, **195**, 46).

THE QUEEN'S COLLEGE, OXFORD.

[*Received*, *July* 20*th*, 1931.]