

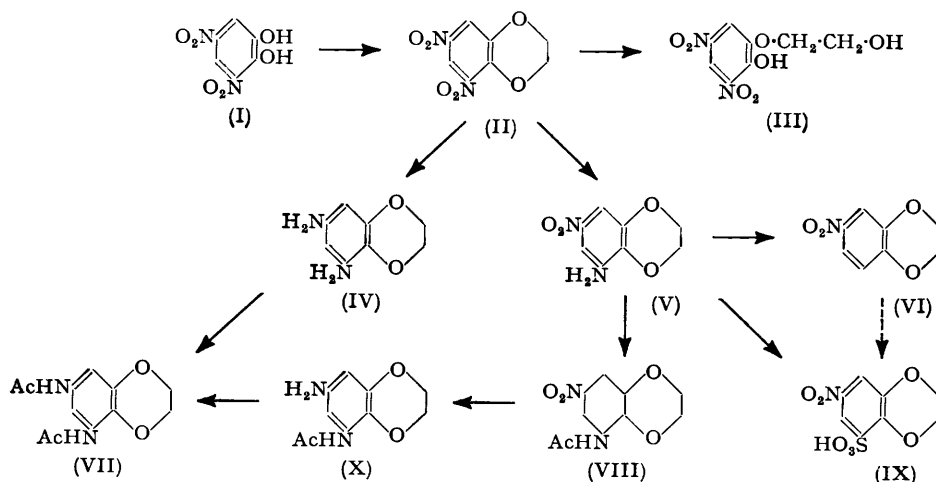
Derivatives of Benzo-1 : 4-dioxan. Part II. Some Compounds derived from 5 : 7-Dinitrobenzo-1 : 4-dioxan.*

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Preparation and orientation of 5 : 7-dinitro-, 5-amino-7-nitro-, and 5 : 7-diamino-benzo-1 : 4-dioxan, and 7-nitrobenzo-1 : 4-dioxan-5-sulphonic acid, and some intermediates and derivatives are described.

THE reactions described in this paper are shown in the annexed chart ; that marked with a broken arrow has already been recorded elsewhere. Most of the conversions were carried out in the usual way and they determine the orientation of all the compounds as those of 3 : 5-dinitropyrocatechol and 6-nitrobenzo-1 : 4-dioxan † are known. The following points merit mention.



The starting material, 5 : 7-dinitrobenzo-1 : 4-dioxan (II), had to be prepared indirectly *via* 3 : 5-dinitropyrocatechol (I), because no direct nitration method starting from benzo-1 : 4-dioxan has yet been found. Synthesis of 3 : 5-dinitropyrocatechol described very briefly by Nietzky and Moll (*Ber.*, 1893, **26**, 2182) and Kehrmann and Prunier (*Helv. Chim.*

* Part I, *J.*, 1954, 18.

† Ring Index names and numbering are used.

Acta, 1924, 7, 984) is detailed in the Experimental section and an improved hydrolysis of 3 : 5-dinitropyrocatechol monoacetate (cf. Baltzly and Buck, *J. Amer. Chem. Soc.*, 1941, 63, 2022) has been found to give higher yields.

3 : 5-Dinitropyrocatechol has been converted into 5 : 7-dinitrobenzo-1 : 4-dioxan by the action of 1 : 2-dibromoethane in an alkaline solution of glycol on the analogy of the preparation of benzo-1 : 4-dioxan (Heertjes, Dahmen, and Wierda, *Rec. Trav. chim.*, 1941, 60, 569). A by-product of this reaction had the composition $C_8H_8O_7N_2$, and was probably 2-2'-hydroxyethoxy-4 : 6-dinitrophenol (III), formed by hydrolysis of 5 : 7-dinitrobenzo-1 : 4-dioxan with water. This water results partly from the formation of the potassium salt of catechol, and partly from the decomposition of the dibromoethane with potassium carbonate, yielding vinyl bromide, water, and carbon dioxide.

5-Amino-7-nitrobenzo-1 : 4-dioxan (V) was diazotised and converted with sulphur dioxide and copper into the mononitro-monosulphinic acid, which was oxidised to 7-nitrobenzo-1 : 4-dioxan-5-sulphonic acid (IX), identical with that obtained by direct sulphonation of 6-nitrobenzo-1 : 4-dioxan (Heertjes and Revallier, *ibid.*, 1950, 69, 262), but not previously oriented.

EXPERIMENTAL

M. p.s. and those recorded in Part I, are corrected.

3 : 5-Dinitropyrocatechol (I).—Pyrocatechol diacetate (75 g.; m. p. 62—63°; cf. Green, *J.*, 1927, 502) was gradually added to nitric acid (*d* 1.52; 400 ml.) which was stirred and cooled below -5°. The mixture was poured on ice shavings (3 kg.), and, after melting of the ice, the yellow precipitate of dinitropyrocatechol monoacetate was collected, washed with ice-water until free from acid, and dried (78 g., 82%; m. p. 123.8—124.6°). To obtain the 3 : 5-dinitropyrocatechol, the monoacetyl derivative was dissolved in methanol (450 ml.) and concentrated hydrochloric acid (5 ml.) and kept at room temperature (24 hr.); after evaporation of all the liquid the solid yellow residue was washed with water and dried at 110° (21 g., 98%; m. p. 166.0—166.5°).

5 : 7-Dinitrobenzo-1 : 4-dioxan (II).—3 : 5-Dinitropyrocatechol (20 g.) and anhydrous potassium carbonate (7 g.) in glycol (200 ml.) were heated at 50° until the evolution of carbon dioxide ceased and the liquid obtained had a dark red colour. Nitrogen was passed over the mixture throughout this and the following operations. 1 : 2-Dibromoethane (100 g.) was added and the mixture was gently refluxed (135°) till the colour changed to brown. Anhydrous potassium carbonate (*ca.* 2 g.) was added till the liquid became dark red again. This was repeated every time the colour changed to brown and stopped when on addition no change to a red was obtained (4—6 hr.). The mixture was then poured into water (2 l.). The precipitated 5 : 7-dinitrobenzo-1 : 4-dioxan (18 g., 80%) crystallised from acetone as faintly yellow needles, m. p. 145.5—145.7° (Found : N, 12.3, 12.4. $C_8H_8O_6N_2$ requires N, 12.4%).

The precipitate of 5 : 7-dinitrobenzo-1 : 4-dioxan was sometimes accompanied by a red crystalline substance, insoluble in boiling acetone. After extraction of the main product with acetone, this red substance was treated with dilute hydrochloric acid, yielding yellow (?) 2-2'-hydroxyethoxy-4 : 6-dinitrophenol, which, crystallised from acetone and from water, had m. p. 155.7—156.0° (Found : C, 39.2; H, 3.3; N, 11.5. $C_8H_8O_7N_2$ requires C, 39.35; H, 3.3; N, 11.5%).

Boiling 5 : 7-dinitrobenzo-1 : 4-dioxan with aqueous potassium carbonate yielded also a red substance, which could be converted with dilute hydrochloric acid into the same yellow substance. For the preparation of 5 : 7-dinitrobenzo-1 : 4-dioxan this side reaction could be avoided by placing a water separator between the flask and the reflux condenser to keep the water content of the mixture as low as possible.

5-Amino-7-nitrobenzo-1 : 4-dioxan (V).—A fine suspension of 5 : 7-dinitrobenzo-1 : 4-dioxan (12 g.) in ethanol (100 ml.) was heated to 40°. Stannous chloride dihydrate (36 g.) in ethanol (36 ml.) and concentrated hydrochloric acid (36 ml.) was added dropwise at 40—60°. After a clear red-brown solution had been obtained, stirring was continued for another $\frac{1}{2}$ hr. The mixture was poured into water (150 ml.), unchanged dinitro-compound was filtered off, and the filtrate treated with alkali until most of the tin compounds had redissolved. The remaining solid substance was collected and extracted with acetone. After removal of the acetone the amine crystallised in orange needles (5.7 g., 55%), m. p. 147.2—147.8 (from aqueous acetone, 1 : 1) (Found : N, 14.3, 14.35. $C_8H_8O_4N_2$ requires N, 14.3%).

Diazotizing the amine and boiling it with ethanol yielded a mononitro-compound, m. p.

118.2—119.4°. The mixed m. p. with 6-nitrobenzo-1:4-dioxan (VI) (m. p. 121—122°; cf. Heertjes, Dahmen, and Wierda, *Rec. Trav. chim.*, 1941, **60**, 569) was 119.6—121.4°. When 5-amino-7-nitrobenzo-1:4-dioxan (1.6 g.) was heated with acetic anhydride (8 ml.) for 15 min. and then cooled and diluted with water (40 ml.) the *acetamide* (VIII) separated and crystallised from acetone in faint pink needles, m. p. 234.9—235.4° (Found: N, 11.8, 11.9. $C_{10}H_{10}O_5N_2$ requires N, 11.8%).

5:7-Diaminobenzo-1:4-dioxan (IV).—5:7-Dinitrobenzo-1:4-dioxan (10.5 g.), suspended in ethanol (100 ml.), was hydrogenated in the presence of Raney nickel at room temperature. After removal of the catalyst and washing with ethanol, the filtrate was concentrated at diminished pressure to a small volume. The *diamine* (4.6 g., 60%) separated in white prisms, m. p. 109.6—110.3° (Found: N, 17.0, 16.9. $C_8H_{10}O_2N_2$ requires N, 16.9%). To the filtrate some drops of concentrated hydrochloric acid were added and by evaporation a second portion (2.6 g., 26%) of the amine was obtained as hydrochloride.

The *diacetyl* derivative (VII) was prepared by dissolving the free diamine in the calculated amount of acetic anhydride (exothermal reaction). After cooling, a thick syrup was obtained, which solidified slowly. Repeated crystallisation from water gave white needles, m. p. 203.0—203.3° (Found: N, 11.15, 11.3. $C_{12}H_{14}O_4N_2$ requires N, 11.2%).

5-Acetamido-7-aminobenzo-1:4-dioxan (X).—A suspension of 5-acetamido-7-nitrobenzo-1:4-dioxan (2 g.) in ethanol (70 ml.) was hydrogenated in the presence of Raney nickel at room temperature. During the reaction the product separated. It was dissolved by heating the mixture to the b. p. and the catalyst was removed by filtration of the hot solution. 5-Acetamido-7-aminobenzo-1:4-dioxan (1 g., 59%) crystallised, on cooling, in white feathers, m. p. 198.7—199.7° (from ethanol) (Found: N, 13.65, 13.7, 13.8. $C_{10}H_{12}O_3N_2$ requires N, 13.5%). Probably a small part has been hydrolysed. By acetylation the diacetyl derivative (VII) was formed.

7-Nitrobenzo-1:4-dioxan-5-sulphinic Acid (cf. Gattermann, *Ber.*, 1899, **32**, 1136).—5-Amino-7-nitrobenzo-1:4-dioxan (2.5 g.) in concentrated hydrochloric acid (7.5 ml.) and water (37.5 ml.) was diazotized with sodium nitrite (2 g.) in water (10 ml.) at 0°. The solution was added dropwise to ice-cooled water (50 ml.) which was saturated with sulphur dioxide and contained copper powder (17.5 g.) while sulphur dioxide was bubbling through this mixture. The solution and the precipitate were both extracted with ether. The extract was dried and the ether was removed. The sulphinic acid (0.5 g., 15%) remaining, after crystallisation from ether, had m. p. 135° (decomp.).

7-Nitrobenzo-1:4-dioxan-5-sulphonic Acid (IX).—A solution of the 5-sulphinic acid (0.43 g.), potassium permanganate (0.5 g.), and potassium carbonate (0.5 g.) in water (10 ml.) was heated at 100° (15 min.). The excess of potassium permanganate was then decomposed with ethanol, and the manganese oxide filtered off. After cooling, the white crystalline potassium sulphonate (0.4 g., 74%) was collected and washed with acetone.

The sulphonyl chloride was prepared by heating the potassium salt (0.3 g.) with phosphorus pentachloride (0.6 g.) at 150°/(15 min.). After cooling, the phosphorus oxychloride was decomposed with water. The white residue (0.24 g., 85%), after crystallisation from dilute acetic acid, had m. p. 169.4—170.8°. The sulphonic acid prepared by direct sulphonation of 6-nitrobenzo-1:4-dioxan (*loc. cit.*) was converted into a sulphonyl chloride, m. p. 170.6—171.4°, not depressed on admixture with this product.

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