

*Derivatives of Benzo-1 : 4-dioxan. Part III.\**

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Preparation and orientation are given of 3 : 6-dinitropyrocatechol, 5 : 6-dinitro-7-amino-, 5 : 6-dinitro-, and 5 : 8-dinitro-benzo-1 : 4-dioxan, and some nitro-, amino-, and chloro-derivatives thereof.

IN the annexed chart the reactions described in this paper are shown. Most of the conversions were carried out by standard methods.

The following points merit mention. The dinitrobenzo-1 : 4-dioxan obtained by nitration, either directly or *via* the mononitro-derivative (II), of 6-acetamidobenzo-1 : 4-dioxan (I), followed by deacetylation and deamination, was the 5 : 6-dinitro-derivative (XI), since (i) it is known that in mononitration the first nitro-group enters the 7-position (Heertjes and Revallier, *Rec. Trav. chim.*, 1950, **69**, 262), (ii) the obtained product is not identical with 5 : 7-dinitrobenzo-1 : 4-dioxan described in Part II, and (iii) the diamino-compound (XV) obtained by reduction gave a condensation product with phenanthraquinone, which proves the *ortho*-position of the amino-groups.

Deamination of 7-amino-5 : 6-dinitrobenzo-1 : 4-dioxan (V) was effected in the normal way by diazotisation in sulphuric-acetic acid and boiling with alcohol and copper. Heating the amine with sodium nitrite, alcohol, and hydrochloric acid gave a monochloronitrobenzo-1 : 4-dioxan. This compound was not identical with 6-chloro-7-nitrobenzo-1 : 4-dioxan and proved to be the 6-chloro-5-nitro-derivative (VI), since it was converted *via* the chloro-amine (VII) into 6-chlorobenzo-1 : 4-dioxan (IX) described in Part I, and since the acetyl derivative (VIII) of the chloro-amine was not identical with 5-acetamido-7-chlorobenzo-1 : 4-dioxan prepared from 5-acetamido-7-aminobenzo-1 : 4-dioxan described in Part II.

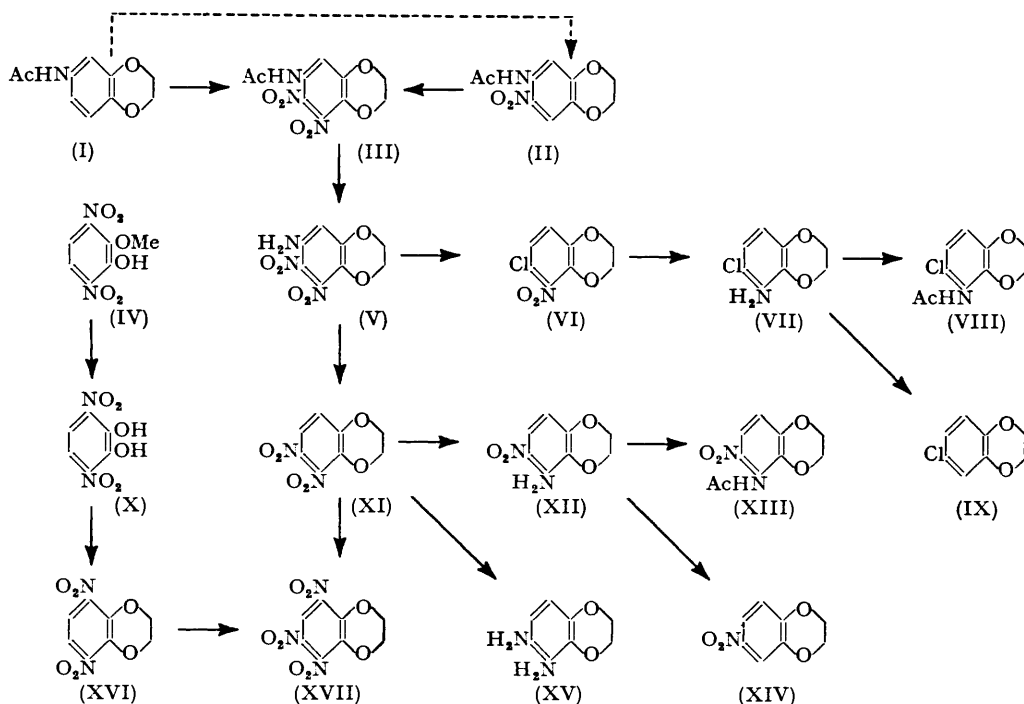
Conversion of 5 : 6-dinitrobenzo-1 : 4-dioxan (XI) into a monoamino-mononitro-derivative could not be realised by partial reduction by the conventional methods (sodium polysulphide, stannous chloride, sodium dithionite, catalytic reduction) : in all cases a mixture of the dinitro- and diamino-derivative was obtained. However, by heating the dinitro-compound with ethanol and concentrated aqueous ammonia at 130–150°, the dinitro-derivative was converted exclusively into 5-amino-6-nitrobenzo-1 : 4-dioxan (XII). The orientation of this compound followed from its conversion into 6-nitrobenzo-1 : 4-dioxan (XIV).

3 : 6-Dinitropyrocatechol (X), not described in the literature, was prepared by boiling 3 : 6-dinitroguaiacol (IV) (Oxford, *J.*, 1926, 2009) with 48% aqueous hydrogen bromide.

\* Parts I and II, *J.*, 1954, 18, 1868.

It is worth mention that this method is unsatisfactory for demethylation of the other known dinitro-guaiacols (3 : 4-, 4 : 5-, 5 : 6-).

3 : 6-Dinitroprocatechol was converted into 5 : 8-dinitrobenzo-1 : 4-dioxan (XVI) by reaction with 1 : 2-dibromoethane in an alkaline solution of glycol. The product was obtained impure, in a poor yield, and was difficult to purify by crystallisation; during the reaction the evolution of nitrogen oxides had been observed; moreover the nitrogen



content of the crystallised compound was far too low; the presence of a monohydroxy-mononitro-compound therefore seemed probable. The crystallised impure 5 : 8-dinitrobenzo-1 : 4-dioxan was therefore dissolved in benzene and washed with a cold 2*N*-potassium hydroxide solution. This manipulation raised the nitrogen content to nearly the theoretical amount. Owing to the small amounts available the impurity could not be isolated.

5 : 6-Dinitro- and the crude 5 : 8-dinitrobenzo-1 : 4-dioxan on nitration gave the same trinitro-derivative (XVII), which was not identical with 5 : 6 : 7-trinitrobenzo-1 : 4-dioxan (Heertjes, Dahmen, and Wierda, *Rec. Trav. chim.*, 1941, **60**, 569) and must therefore be 5 : 6 : 8-substituted.

#### EXPERIMENTAL

M. p.s are corrected.

**7-Amino-5 : 6-dinitrobenzo-1 : 4-dioxan (V).**—Finely powdered 6-acetamidobenzo-1 : 4-dioxan (46 g.; cf. Heertjes and Revallier, *ibid.*, 1950, **69**, 262) was added in portions to a stirred mixture of nitric acid (*d* 1.4; 400 ml.) and nitric acid (*d* 1.52; 100 ml.), kept at 10°. The mixture was diluted with water (500 ml.), and the precipitated 7-acetamido-5 : 6-dinitrobenzo-1 : 4-dioxan (51 g., 76%) crystallised several times from acetone, or acetone-methanol (1 : 1) or acetone-acetic acid (1 : 1), then having m. p. 230.8—231.0° (Found : N, 14.7, 14.8.  $C_{10}H_9O_7N_3$  requires N, 14.8%).

The acetamidonitro-derivative was also prepared from 7-acetamido-6-nitrobenzo-1 : 4-dioxan by nitration with the same nitric acid.

The free *amine* was obtained by boiling 7-acetamido-5 : 6-dinitrobenzo-1 : 4-dioxan (200 g.) with ethanol (750 ml.) and concentrated hydrochloric acid (75 ml.) for 4 hr. The product

separated from the solution on cooling and, when crystallised from ethanol, had m. p. 215.7—216.3° (Found : N, 17.5, 17.5.  $C_8H_7O_6N_3$  requires N, 17.4%).

5 : 6-Dinitrobenzo-1 : 4-dioxan (XI).—A suspension of 7-amino-5 : 6-dinitrobenzo-1 : 4-dioxan (20 g.) in acetic acid (500 ml.) was diazotised with sodium nitrite (17 g.) in concentrated sulphuric acid (200 ml.) at 15°, until the mixture no longer gave a precipitate of the amine on dilution with water (2 hr.). The mixture was poured into absolute ethanol (400 ml.), and copper powder (1 g.) was added. After 24 hr. at room temperature the diazonium compound was completely decomposed. The mixture was diluted with water, and the precipitated crude product (10 g.) collected. A second portion (5.5 g.) of the substance was obtained from the upper layer formed, containing ethyl acetate, by concentrating this to a small volume. The total yield was 82%. 5 : 6-Dinitrobenzo-1 : 4-dioxan crystallised in yellow needles, m. p. 185.6—186.1° (from ethanol) (Found : C, 42.3, 42.4; H, 2.8, 2.5; N, 12.4, 12.3.  $C_8H_6O_6N_2$  requires C, 42.5; H, 2.7; N, 12.4%).

5 : 6 : 8-Trinitrobenzo-1 : 4-dioxan (XVII).—5 : 6-Dinitrobenzo-1 : 4-dioxan (2 g.), dissolved in nitric acid (*d* 1.52; 25 ml.), was kept at 10° for ½ hr., then poured into water. The precipitated trinitro-derivative was crystallised several times from ethanol and from isobutanol, forming yellow needles, m. p. 180.4—181.0° (Found : N, 15.5, 15.3.  $C_8H_5O_8N_3$  requires N, 15.5%). The m. p. was depressed on admixture with 5 : 6 : 7-trinitrobenzo-1 : 4-dioxan.

5-Amino-6-nitrobenzo-1 : 4-dioxan (XII).—5 : 6-Dinitrobenzo-1 : 4-dioxan (5 g.) was heated with concentrated aqueous ammonia (5.5 ml.) and ethanol (20 ml.) for 3 hr. in a sealed tube at 130—150°. Cooling the mixture and filtering the crude product from the mother-liquor yielded the quantitative amount of 5-amino-6-nitrobenzo-1 : 4-dioxan, orange needles, m. p. 142.8—143.3° (from ethanol or dilute acetic acid) (Found : N, 14.2, 14.1.  $C_8H_8O_4N_2$  requires N, 14.3%).

The nitro-amine was diazotised and boiled with ethanol to decompose the diazonium compound. On dilution with water 6-nitrobenzo-1 : 4-dioxan was precipitated (cf. Heertjes, Dahmen, and Wierda, *ibid.*, 1941, 60, 569).

On treatment of a solution of 5-amino-6-nitrobenzo-1 : 4-dioxan (0.5 g.) in acetic acid (20 ml.) with acetic anhydride for ½ hr. at 75° and pouring the mixture into water the acetyl derivative was precipitated, which crystallised from water as pale yellow needles, m. p. 185.9—186.7° (Found : N, 11.75, 11.7.  $C_{10}H_{10}O_5N_2$  requires N, 11.8%).

5 : 6-Diaminobenzo-1 : 4-dioxan (XV).—5 : 6-Dinitrobenzo-1 : 4-dioxan (5 g.) was heated with concentrated hydrochloric acid (40 ml.), water (20 ml.), and granulated tin (10 g.) at 90° (2 hr.). The mixture was cooled, diluted with water to 150 ml., and treated with enough aqueous potassium hydroxide solution (20%) to redissolve the tin compounds, then extracted with benzene. On evaporation of the benzene from the extract the diamine remained as a white crystalline powder (m. p. 101.9—102.9°) which was readily oxidised on contact with air (Found : N, 16.9, 17.1.  $C_8H_{10}O_2N_2$  requires N, 16.9%).

Condensation of the base with phenanthraquinone gave a yellow solid, m. p. 292—294°.

6-Chloro-5-nitrobenzo-1 : 4-dioxan (VI).—To a mixture of 7-amino-5 : 6-dinitrobenzo-1 : 4-dioxan (20 g.), ethanol (200 ml.), and concentrated hydrochloric acid (20 ml.), heated to 40°, sodium nitrite (6 g.) was added in portions in 15 min. After ½ hour's boiling the clear solution obtained was cooled and poured into water. The precipitated 6-chloro-5-nitrobenzo-1 : 4-dioxan (14 g., 78%), after repeated crystallisation from aqueous methanol (1 : 1), had m. p. 75.6—76.3° (Found : C, 44.6; H, 2.9; N, 6.5, 6.6; Cl, 16.25, 16.3.  $C_8H_6O_4NCl$  requires C, 44.6; H, 2.8; N, 6.5; Cl, 16.45%).

5-Amino-6-chlorobenzo-1 : 4-dioxan (VII).—(a) A solution of 6-chloro-5-nitrobenzo-1 : 4-dioxan (14 g.) in benzene (200 ml.) was hydrogenated in presence of Raney nickel at room temperature. After filtration of the catalyst 5-amino-6-chlorobenzo-1 : 4-dioxan hydrochloride (14 g., 97%) was precipitated by passage of hydrogen chloride through the filtrate.

(b) A mixture of 6-chloro-5-nitrobenzo-1 : 4-dioxan (10 g.), concentrated hydrochloric acid (50 ml.), ethanol (50 ml.), and granulated tin (15 g.) was boiled till all the tin had dissolved and the solution gave no precipitate on dilution with water. The mixture was cooled, diluted with water (300 ml.), and basified with sodium hydroxide solution, then extracted with benzene, from which the amine was obtained on evaporation as a yellow oil. The amine slowly oxidises on contact with air.

Treatment of the amine with an excess of acetic anhydride at room temperature and dilution with water gave a precipitate of the acetyl derivative (VIII), white needles (from benzene), m. p. 155.9—156.7° (Found : N, 6.0, 6.1.  $C_{10}H_{10}O_3NCl$  requires N, 6.15%).

Diazotising the amine and boiling it with ethanol yielded 6-chlorobenzo-1 : 4-dioxan, a

yellow liquid, b. p. 98—102°/4 mm., which on nitration gave 6-chloro-7-nitrobenzo-1 : 4-dioxan, m. p. 161.7—162.2° (see Part I).

The acetyl derivative (VIII) described showed a very strong depression on admixture with 5-acetamido-7-chlorobenzo-1 : 4-dioxan (see below). Because the 6-position of chlorine has been proved above, and moreover the compounds under discussion are not substituted in the 7-position [see the m. p. of the nitro-compound (VI)], the structure as given is proved.

*5-Amino-7-chlorobenzo-1 : 4-dioxan.*—5-Acetamido-7-aminobenzo-1 : 4-dioxan (0.9 g.) in concentrated hydrochloric acid (3 ml.) and water (5 ml.) was diazotised with a solution of sodium nitrite (0.35 g.) in water (3 ml.) at 10°. The mixture was poured into a solution of cuprous chloride (0.6 g.) in concentrated hydrochloric acid (3 ml.). After 24 hr. at room temperature the diazonium compound was completely decomposed. The precipitated *5-acetamido-7-chlorobenzo-1 : 4-dioxan* was filtered off and crystallised several times from water; it had m. p. 135.6—136.2° (Found: N, 6.1, 6.1.  $C_{10}H_{10}O_3NCl$  requires N, 6.15%).

*3 : 6-Dinitropyrocatechol (X).*—*3 : 6-Dinitroguaiacol* (5.2 g.; cf. Oxford, *J.*, 1926, 2009) was refluxed with aqueous hydrogen bromide (48%, 52 ml.) for  $\frac{1}{2}$  hr. *3 : 6-Dinitropyrocatechol* separated from the liquid in yellow needles. After cooling and dilution with water the product was collected and washed with water (4.6 g., 95%; m. p. 164.5—165.5°). Repeated crystallisations from aqueous ethanol raised the m. p. to 169.4—169.7° (Found: N, 14.0, 14.05.  $C_8H_6O_3N_2$  requires N, 14.0%).

*5 : 8-Dinitrobenzo-1 : 4-dioxan (XVI).*—Condensation of *3 : 6-dinitropyrocatechol* with ethylene dibromide was effected as described for the preparation of *5 : 7-dinitrobenzo-1 : 4-dioxan* (see Part II). Contrary to analogous condensations, during this reaction the formation of nitrogen oxides was observed. Pouring the reaction mixture in water gave a dark brown precipitate, which was collected and extracted with benzene. The yellow benzene solution was washed with aqueous potassium hydroxide (2N), then with water. After removal of the benzene the remaining *5 : 8-dinitrobenzo-1 : 4-dioxan*, crystallised from ligroin (b. p. 60—80°) or aqueous ethanol (1 : 1), had m. p. 99.6—102.5° (yield 15%) (Found: C, 42.6; H, 2.7; N, 12.2, 12.35.  $C_8H_6O_3N_2$  requires C, 42.5; H, 2.6; N, 12.4%).

Nitration of this compound with nitric acid (*d* 1.52) in small excess gave *5 : 6 : 8-trinitrobenzo-1 : 4-dioxan* (90% yield), m. p. 180.0—180.6°, not depressed on admixture with the product obtained by nitration of the *5 : 6-dinitro-derivative* (Found: N, 15.5, 15.3. Calc. for  $C_8H_5O_3N_3$ : N, 15.5%).

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