408. *Derivatives of Benzo-1,4-dioxan. Part V.**

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The behaviour of some polynitrobenzo-1,4-dioxan compounds, especially their reactivity towards alcoholic ammonia, is reported.

IT is known that aromatic polynitro-compounds can be converted by ammonia into amino-nitro-compounds. Because this could be a convenient method for preparing amino-nitro-derivatives of benzo-1,4-dioxan, which are used in the preparation of azo-dyes, the ammonolysis of some polynitrobenzo-1,4-dioxan compounds was investigated. The reactions to be described are represented in the annexed chart.

6,7-Dinitrobenzo-1,4-dioxan [1] (I) is unchanged during 3 hr. by an excess of ammonia in ethanol at 130°; under milder conditions 5,6,7-trinitrobenzo-1,4-dioxan (III) is converted by ammonia into amino-nitro-compounds (see below). Crude 6,7-dinitrobenzo-1,4-dioxan is usually contaminated with 5,6,7-trinitrobenzo-1,4-dioxan (III), from which it is difficult to separate it by crystallisation, and treatment with alcoholic ammonia proved a convenient method for the purification of the former.

The preparation of 6-amino-7-nitrobenzo-1,4-dioxan has been described elsewhere.[2] Reduction of 6,7-dinitrobenzo-1,4-dioxan (I) to 6,7-diaminobenzo-1,4-dioxan (II) and preparation of the mono- and di-acetyl derivatives of the amine are given in this paper. The condensation product of 6,7-diaminobenzo-1,4-dioxan with 9,10-phenanthraquinone was obtained by Robinson and Robinson [3] who, however, did not describe the free diamine.

The reaction of 5,6,7-trinitrobenzo-1,4-dioxan [1] (III) with ammonia was also studied by Robinson and Robinson [3] who isolated and identified two of the three products obtained by us. It has been found that when 5,6,7-trinitrobenzo-1,4-dioxan (III) is treated with an amount of ammonia sufficient to replace only one nitro-group, mainly 6-amino-5,7-dinitrobenzo-1,4-dioxan (IV) is formed. The structure was established by deamination of this compound to 5,7-dinitrobenzo-1,4-dioxan.[4] The crude product also contains a small quantity of the known 5-amino-6,7-dinitrobenzo-1,4-dioxan [3] (VI).

6-Amino-5,7-dinitrobenzo-1,4-dioxan (IV) was converted by an excess of ammonia in

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* Parts I—IV, *J.*, 1954, 18, 1868; 1955, 1313; 1957, 3445.

[1] Heertjes, Dahmen, and Wierda, *Rec. Trav. chim.*, 1941, **60**, 569.

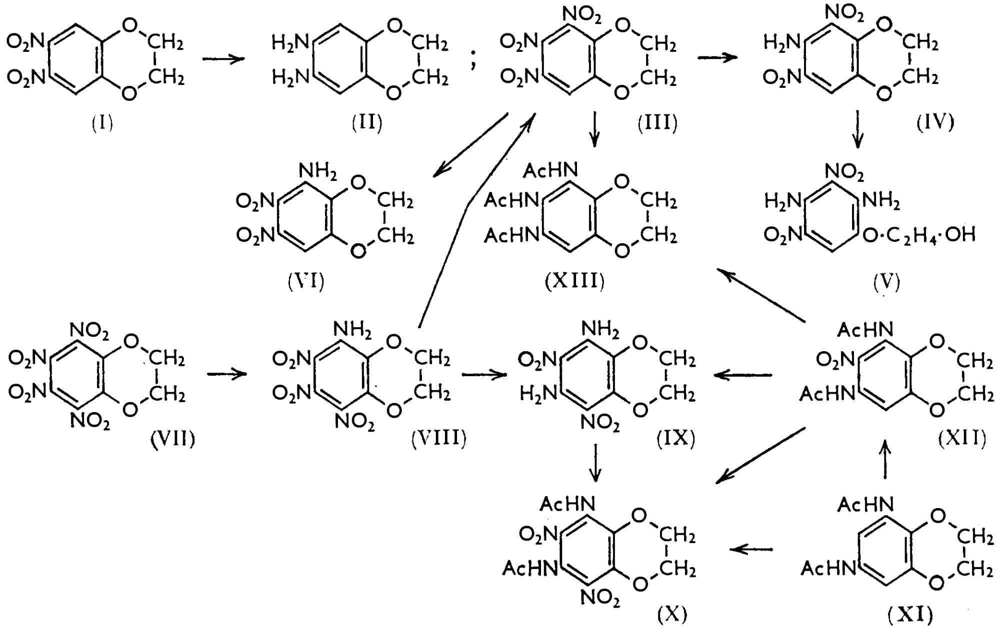
[2] Heertjes and Revallier, *Rec. Trav. chim.*, 1950, **69**, 262.

[3] G. M. Robinson and R. Robinson, *J.*, 1917, **111**, 929.

[4] Heertjes, Knape, and Talsma, *J.*, 1954, 1868.

ethanol into 2,4-diamino-3,5-dinitrophenyl 2-hydroxyethyl ether (V) which had previously [3] been obtained directly from the trinitro-compound.

5,6,7,8-Tetranitrobenzo-1,4-dioxan [1] (VII) was converted in ethanol into 5-amino-6,7,8-trinitrobenzo-1,4-dioxan (VIII) by an amount of ammonia sufficient to replace only one nitro-group. No other monoamino-trinitro-compound was isolated. The structure of the monoamino-compound was established by deamination to 5,6,7-trinitrobenzo-1,4-dioxan (III). With an amount of ammonia sufficient to replace two of the four nitro-groups 5,6,7,8-tetranitrobenzo-1,4-dioxan (VII) gave 5,7-diamino-6,8-dinitrobenzo-1,4-dioxan (IX). The structure of this compound followed from the identification of its diacetyl derivative with 5,7-diacetamido-6,8-dinitrobenzo-1,4-dioxan (X) obtained by nitration of 5,7-diacetamidobenzo-1,4-dioxan [4] (XI) with nitric acid (*d* 1·52). The 6-nitro-derivative of 5,7-diacetamidobenzo-1,4-dioxan (XII) is obtained if the nitration is carried out with nitric acid (*d* 1·4). The 6-position of the nitro-group follows from conversion of the 5,7-diacetamido-mononitrobenzo-1,4-dioxan into a triacetamidobenzo-1,4-dioxan which appeared to be identical with 5,6,7-triacetamidobenzo-1,4-dioxan (XIII) obtained by reduction of 5,6,7-trinitrobenzo-1,4-dioxan and acetylation of the resulting triamino-compound.



EXPERIMENTAL

M. p.s are corrected.

*6,7-Diaminobenzo-*1,4-*dioxan* (II).—Granulated tin (22·5 g.) was added to a suspension of 6,7-dinitrobenzo-1,4-dioxan (I) (11·5 g.) in hydrochloric acid (*d* 1·19; 40 ml.). The mixture was heated at 80° for 60 min. The clear solution obtained was made alkaline with sodium hydroxide (40 g.) in water (200 ml.). The resulting suspension was extracted with benzene. The extract was dried and the benzene was distilled off under reduced pressure with exclusion of oxygen. 6,7-*Diaminobenzo-*1,4-*dioxan* was obtained and, recrystallised from benzene, had m. p. 122—123° (3·5 g., 35·7%) (Found: N, 16·9. $C_8H_{10}N_2O_2$ requires N, 16·9%).

The mono- and di-acetyl derivatives were obtained by use of acetic anhydride in benzene.

To prepare the monoacetyl derivative a dilute solution of acetic anhydride in benzene was added slowly to a solution of the diamine in benzene at 60°. Crystallisation gave 6-acetamido-7-amino-, m. p. 130—131° (from benzene), and 6,7-diacetamido-benzo-1,4-dioxan, m. p. 241° (decomp.) (from acetic acid).

6-*Amino*-5,7-*dinitrobenzo*-1,4-*dioxan* (IV).—To a suspension of 5,6,7-trinitrobenzo-1,4-dioxan (III) (10 g.) in boiling ethanol (300 ml.), ammonia (5·8 ml.; *d* 0·905) in ethanol (30 ml.) was added in 3 hr. A red solution was formed. On cooling, orange needles of 6-*amino*-5,7-*dinitrobenzo*-1,4-*dioxan* separated. These were filtered off and crystallised from 1 : 1 acetone–water (yield, 4·5 g., 51%), then having m. p. 164—165° (Found: N, 17·4, 17·5. $C_8H_7N_3O_6$ requires N, 17·4%).

In the crude product a small amount of yellow crystals of 5-amino-6,7-dinitrobenzo-1,4-dioxan (VI), m. p. 202—203°, was present and was separated.

A suspension of the aminodinitrobenzo-1,4-dioxan (1·5 g.) in acetic acid (100 ml.) was added dropwise to a solution of sodium nitrite (2 g.) in sulphuric acid (45 ml., *d* 1·84) at 0°. The mixture was stirred for 1 hr. and then added to a solution of sodium hypophosphite (5 g.) in 10N-sulphuric acid (20 ml.). After being kept overnight the mixture was diluted with water (200 ml.) and extracted with ether (3 × 30 ml.). The extracts were evaporated and the residue was crystallised several times from dilute acetic acid. It had m. p. 141—143°, not depressed on admixture with 5,7-dinitrobenzo-1,4-dioxan.

2,4-*Diamino*-3,5-*dinitrophenyl* 2-*Hydroxyethyl Ether* (V).—6-Amino-5,7-dinitrobenzo-1,4-dioxan (IV) (0·5 g.) in ethanol (15 ml.) was refluxed with aqueous ammonia (0·5 ml.; *d* 0·905) for 1 hr. After cooling, the precipitate was filtered off, extracted several times with boiling acetone, and recrystallised from acetic acid. It had m. p. 240—241° alone or mixed with the product obtained by treating 5,6,7-trinitrobenzo-1,4-dioxan with ammonia in ethanol as described in ref. 3.

5-*Amino*-6,7,8-*trinitrobenzo*-1,4-*dioxan* (VIII).—To a suspension of 5,6,7,8-tetranitrobenzo-1,4-dioxan (VII) (10 g.) in boiling ethanol (300 ml.) 0·5N-ethanolic ammonia (126 ml.) was added during 1½ hr. The resulting solution was filtered hot and then cooled. The crude *monoamine* crystallised and was filtered off (3 g., 30%). Recrystallised from acetone–ethanol (1 : 1), it had m. p. 224·5° (Found: N, 19·3. $C_8H_6N_4O_8$ requires N, 19·6%).

The structure was established by diazotising the substance (1·1 g.) in acetic acid (30 ml.) with sodium nitrite (0·95 g.) in sulphuric acid (10 ml.; *d* 1·84) at 10—15°. The mixture was stirred for 2 hr., then added dropwise to boiling ethanol (40 ml.) in 10 min., refluxed for ½ hr., and poured on ice. The precipitated 5,6,7-trinitrobenzo-1,4-dioxan, when crystallised from acetone, had m. p. and mixed m. p. 154—155°.

5,7-*Diamino*-6,8-*dinitrobenzo*-1,4-*dioxan* (IX).—A stream of dry ammonia (100 ml./min.) was passed through a suspension of 5,6,7,8-tetranitrobenzo-1,4-dioxan (VII) (10 g.) in boiling ethanol (500 ml.) for 30 min. A red solution was first formed and then orange 5,7-*diamino*-6,8-*dinitrobenzo*-1,4-*dioxan* separated. After cooling, the precipitate was filtered off and crystallised from ethanol (yield 6 g., 72%; m. p. 262—263°) (Found: N, 21·9. $C_8H_8N_4O_6$ requires N, 21·9%).

With acetic anhydride and a drop of concentrated sulphuric acid, this amine gave its *diacetyl derivative* (XIII), m. p. 284·0—284·8° (from ethanol) (Found: C, 42·6; H, 4·0; N, 16·1. $C_{12}H_{12}N_4O_8$ requires C, 42·4; H, 3·6; N, 16·4%).

When 5,7-diacetamidobenzo-1,4-dioxan (XI) (2 g.) was added in portions to stirred nitric acid (30 ml.; *d* 1·52) at −10° and the mixture was stirred for a further 10 min. and then poured on ice, the precipitate (1·5 g., 43%), m. p. 282—284° (from ethanol), did not depress the m. p. of the last-mentioned diacetyl derivative.

5,7-*Diacetamido*-6-*nitrobenzo*-1,4-*dioxan* (XII).—5,7-Diacetamidobenzo-1,4-dioxan (2 g.) was nitrated as just described but with 30 ml. of nitric acid (*d* 1·40). The *mononitro-compound*, when crystallised from ethanol, had m. p. 261—262° (1·2 g., 50%) (Found: C, 49·0; H, 4·5; N, 14·4. $C_{12}H_{13}N_3O_6$ requires C, 48·8; H, 4·4; N, 14·2%).

5,6,7-*Triacetamidobenzo*-1,4-*dioxan* (XIII).—5,6,7-Trinitrobenzo-1,4-dioxan (8 g.) in ethanol (500 ml.) was hydrogenated in presence of Raney nickel with the theoretical amount of hydrogen. After filtration, the alcohol was distilled under reduced pressure in absence of oxygen. The residue was treated with an excess of acetic anhydride, and later diluted with water. The precipitated 5,6,7-*triacetamidobenzo*-1,4-*dioxan* recrystallised from ethanol–water (2 : 1), then having m. p. 280—282° (4 g., 44%) (Found: C, 54·9; H, 5·7; N, 13·8. $C_{14}H_{17}N_3O_5$ requires C, 54·7; H, 5·5; N, 13·7%).

Hydrogenation (Raney nickel) of the nitration product (HNO_3, *d* 1·40) of 5,7-diacetamidobenzo-1,4-dioxan (XI) and subsequent acetylation gave 5,6,7-triacetamidobenzo-1,4-dioxan, m. p. and mixed m. p. 280—282°.

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