177. *The Condensation of Formaldehyde with* p-*Nitrophenol.*

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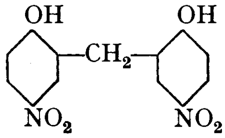
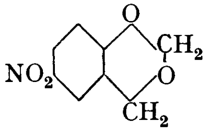
It has long been known that either 5 : 5′-dinitro-2 : 2′-dihydroxydiphenylmethane (I) or 6-nitrobenz-1 : 3-dioxin (II) may be formed from formaldehyde and *p*-nitrophenol according to the conditions of the condensation.

The condensation easily proceeds further if excess of formaldehyde is used, the final product being *di*-(6-*nitrobenzdioxinyl*-8)*methane* (III).


(I.)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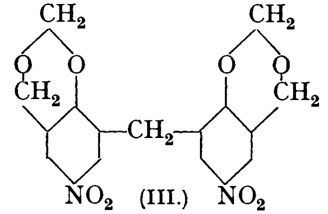
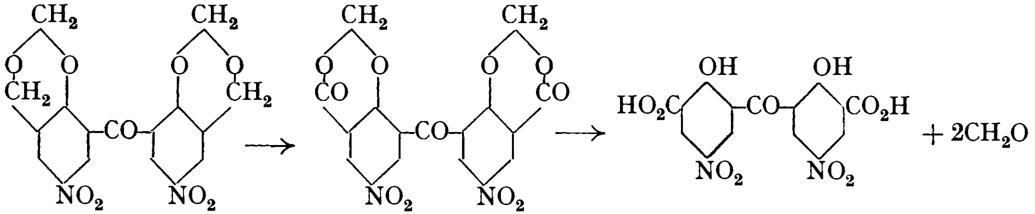

(III.)

This on oxidation by chromic acid in hot acetic acid forms *di*-8 : 8′-(6-*nitrobenzdioxinyl*) *ketone* (IV), which on account of its very slight solubility separates immediately and thus escapes further oxidation. This can, however, be effected by a solution of chromic acid in cold concentrated sulphuric acid; *di*-8 : 8′-(6-*nitro*-4-*ketobenzdioxinyl*) *ketone* (V) is then formed, which is easily hydrolysed by potassium hydroxide to formaldehyde and *di*-3 : 3′-(5-*nitrosalicylic acid*) *ketone* (VI), each of the two dioxin rings behaving in these reactions like the single dioxin ring in 6-nitrobenzdioxin.


(IV.) (V.) (VI.)

To obtain any one of the three products which may be formed by the interaction of formaldehyde and *p*-nitrophenol in anything approaching a pure condition it is necessary to use the exact quantity of formaldehyde and a proper concentration of acid, to regulate the temperature at which the reaction takes place, and to ensure that the formaldehyde and *p*-nitrophenol are in solution when the sulphuric acid is added.

Preparation of 5 : 5′-*Dinitro*-2 : 2′-*dihydroxydiphenylmethane* (I).—This compound, which is described as an amorphous yellow solid melting indistinctly at 230°, is stated (D.R.-P. 73946) to be formed when 15 parts of 40% CH_2O are added to 56 parts of *p*-nitrophenol dissolved in 200 parts of conc. H_2SO_4 at 0°, and the mixture gradually warmed to 60°. We have been unable to prepare it by this procedure.

When 10 c.c. of 40% CH_2O aq. (1 mol.) and 6 c.c. of H_2O were added to 24 c.c. of conc. H_2SO_4, the temp. rose to 75—80°. The hot mixture was added rapidly with vigorous shaking to a solution of 38 g. (2 mols.) of *p*-nitrophenol in 5 c.c. of H_2O at about 75°. The temp. rose to 120—130°, which was maintained until the product separated into a greenish semi-solid mass and a clear supernatant liquid. The solid was dissolved in warm 4% NaOH aq., filtered from 5-nitrobenzdioxin (if any was formed), and acidified with HCl aq.; 5 : 5′-dinitro-2 : 2′-dihydroxydiphenylmethane then separated (yield, 37 g.). It is unusually easily sol. in EtOH, and sparingly sol. in hot AcOH, from which it separates in soft, somewhat irregular, pale yellow crystals, m. p. 268° (Found : N, 9·5. Calc. for $C_{13}H_{10}O_6N_2$: N, 9·65%).

The *diacetyl* derivative, prepared by warming the substance with Ac_2O and a drop of H_2SO_4, crystallised from hot AcOH in well-formed, almost colourless, elongated prisms, m. p. 153° (Found : N, 7·2. $C_{17}H_{14}O_8N_2$ requires N, 7·5%). By hydrolysis with warm 5% NaOH aq. the parent substance was regenerated.

When dissolved in fuming HNO_3 at 0—5°, (I) yields 3 : 3′ : 5 : 5′-*tetranitro*-2 : 2′-*dihydroxydiphenylmethane*, small, pale yellow prisms from AcOH, m. p. 253° (Found : N, 14·6. $C_{13}H_8O_{10}N_4$ requires N, 14·7%).

Preparation of 6-*Nitrobenzdioxin* (II).—A mixture of 15 c.c. of H_2O and 45 c.c. of conc. H_2SO_4 at 15° was added rapidly in one portion with vigorous shaking to a solution of 20 g. (1 mol.) of *p*-nitrophenol in 25 c.c. (2 mols.) of 40% CH_2O aq. also at 15°. The mixture set in a few seconds to a pasty mass (the temp. rising to about 80°), which was shaken vigorously for about 15 min. and then poured into 500 c.c. of H_2O. 6-Nitrobenzdioxin, which separated as a pale yellow solid, was washed successively with hot H_2O, very dil. NH_3 aq. (until the filtrate was only very pale yellow), acidified H_2O, and hot H_2O. Crystn. from boiling EtOH gave 19 g. of pure 6-nitrobenzdioxin, m. p. 149—150°.

Chlorination in AcOH yielded 8-*chloro*-6-*nitrobenzdioxin*, colourless needles from EtOH, m. p. 152—153° (Found : Cl, 16·4. $C_8H_6O_4NCl$ requires Cl, 16·5%). Similarly bromination yielded 8-*bromo*-6-*nitrobenzdioxin*, colourless needles from EtOH, m. p. 165—166° (Found : Br, 30·3. $C_8H_6O_4NBr$ requires Br, 30·8%).

Oxidised by CrO_3, 8-chloro-6-nitrobenzdioxin yielded 8-*chloro*-6-*nitro*-4-*ketobenzdioxin*, colourless elongated prisms from EtOH, m. p. 125—126° (Found : Cl, 15·65. $C_8H_4O_5NCl$ requires Cl, 15·5%). Hydrolysed with 5% NaOH aq., it yielded 3-*chloro*-5-*nitrosalicylic acid*, hair-like needles from EtOH, m. p. 202—203° (Found : N, 6·5. $C_7H_4O_5NCl$ requires N, 6·4%).

8-Bromo-6-nitrobenzdioxin yielded similarly 8-*bromo*-6-*nitro*-4-*ketobenzdioxin*, colourless prisms from EtOH, m. p. 120—121° (Found : Br, 29·3. $C_8H_4O_5NBr$ requires Br, 29·3%) and 3-*bromo*-5-*nitrosalicylic acid*, colourless hair-like crystals from dil. HCl, m. p. 223—224° (Found : N, 5·25. $C_7H_4O_5NBr$ requires N, 5·3%).

When 6-nitrobenzdioxin is reduced, the 6-aminobenzdioxin diazotised, and Cu_2Cl_2 added, 6-*chlorobenzdioxin* is formed; small pearly leaflets from EtOH, m. p. 98—99° (Found : Cl, 20·3. $C_8H_7O_2Cl$ requires Cl, 20·8%). 6-*Iodobenzdioxin*, similarly prepared, crystallises from EtOH in colourless needles, m. p. 58° (Found : C, 36·4; H, 2·5. $C_8H_7O_2I$ requires C, 36·6; H, 2·7%).

Preparation of Di-(6-*nitrobenzdioxinyl*)*methane* (III).—A mixture of 50 c.c. of H_2O and 200 c.c. of conc. H_2SO_4 at 75—80° was added, with vigorous shaking, to a solution of 70 g. (1 mol.) of *p*-nitrophenol in 150 g. (3 mols. + slight excess) of 40% CH_2O aq., also at about 75°. The temp. rose to about 130° and *di*-(6-*nitrobenzdioxinyl*)*methane* slowly separated as a buff-coloured solid. After 1 hr.'s heating on a water-bath, this was separated, washed successively with excess of 4% NaOH aq., slightly acidified H_2O, and hot H_2O (a theor. yield, 94·5 g., was obtained), and crystallised from boiling AcOH, in which it was sparingly sol., forming clusters of very slender, colourless prisms, m. p. 225° (Found : C, 54·4; H, 3·8; N, 7·5. $C_{17}H_{14}O_8N_2$ requires C, 54·5; H, 3·7; N, 7·5%).

Oxidation. 10 G. of di-(6-nitrobenzdioxinyl)methane were dissolved in 500 c.c. of hot AcOH, a solution of 15 g. of CrO_3 in 100 c.c. of AcOH added, and the mixture heated to boiling for 5 min. and then cooled to 40°; minute well-formed crystals (9 g.) of *di*-(6-*nitrobenzdioxinyl*) *ketone* (IV) separated. This substance is very sparingly sol. in boiling AcOH (about 1 g. in 1 l.), and moderately easily sol. in hot nitrobenzene, from which it crystallises in small well-formed prisms with domed ends. It chars above 285° without previously melting (Found : C, 52·4; H, 3·1; N, 7·3. $C_{17}H_{12}O_9N_2$ requires C, 52·5; H, 3·1; N, 7·2%).

Oxidation of Di-(6-*nitrobenzdioxinyl*) *Ketone*.—To 5 g. of the ketone dissolved in 100 c.c. of cold conc. H_2SO_4, the calc. quantity of $K_2Cr_2O_7$ (5 g.) in 50 c.c. of conc. H_2SO_4 was added gradually (20 min.), with ice-cooling. After 24 hr., the mixture was poured over ice and the *di*-(6-*nitro*-4-*ketobenzdioxinyl*) *ketone* (V) which separated was dried, extracted several times with small amounts of boiling AcOH to ensure its freedom from any traces of unattacked ketone, and recrystallised from hot nitrobenzene, in which it was sparingly sol., forming small, elongated, six-sided, colourless prisms, m. p. 314° (Found : C, 49·4; H, 2·05; N, 6·9. $C_{17}H_8O_{11}N_2$ requires C, 49·0; H, 1·9; N, 6·7%).

Hydrolysis. 10 G. of the ketone (V) were heated for 5 min. with 50 c.c. of 20% KOH aq. Formaldehyde was liberated and a yellow solution resulted, from which, on acidification, *di*-3 : 3′-(5-*nitrosalicylic acid*) *ketone* (VI) separated as a colourless solid. It is sparingly sol. in boiling H_2O made very slightly acid with HCl, from which it separates in colourless glistening flattened prisms which do not melt below 330° (Found : C, 46·0; H, 2·1; N, 6·9. $C_{15}H_8O_{11}N_2$ requires C, 45·9; H, 2·0; N, 7·1%).

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