CLXXXI.—*The Preparation of* 4 : 4′-*Dinitrobenzil.*

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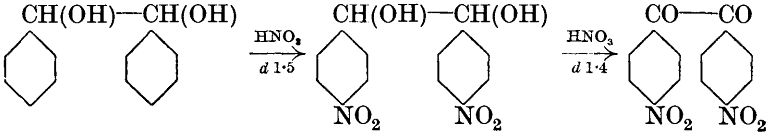
When hydrobenzoin is nitrated with fuming nitric acid at a low temperature and the product oxidised by boiling with concentrated nitric acid, 4 : 4′-dinitrobenzil is produced in considerable quantity, the group ·CH(OH)·, as in benzoin, exerting a strong para-directing influence on the nitro-group entering the nucleus to which it is attached :



4 : 4′-Dinitrobenzil forms derivatives similar to those obtained from the other five isomeric heteronuclear dinitrobenzils. On oxidation by chromic acid it yields an approximately theoretical amount of *p*-nitrobenzoic acid, a reaction which establishes its constitution.

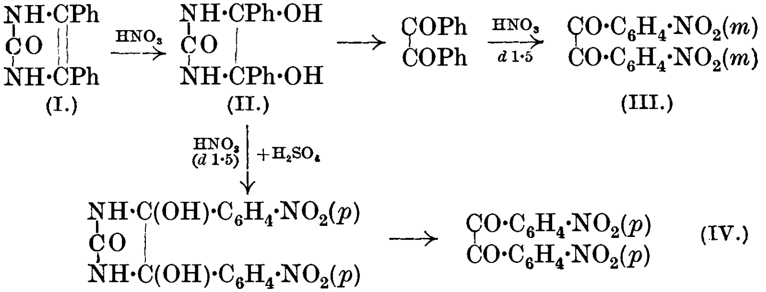
It proves to be identical with the compound obtained by Biltz

(*Annalen*, 1909, **368**, 262, footnote) by the nitration of 4 : 5-diphenylglyoxalone (I). Analysis showed the nitration product to have the composition of a dinitrobenzil and it was assumed to have the 4 : 4′-configuration, though this was not established.

As the preparation of hydrobenzoin is a troublesome operation, whereas 4 : 5-diphenylglyoxalone is very easily made by heating together benzoin and urea in acetic acid solution, the latter compound affords a convenient starting material for the production of 4 : 4′-dinitrobenzil (IV) in quantity, as from it approximately a quarter of its weight of pure 4 : 4′-dinitrobenzil can be obtained. The nitration must be effected by a mixture of concentrated sulphuric and fuming nitric acids; if fuming nitric acid alone is used, the products are only those obtained when benzil itself is nitrated.

Biltz (*Annalen*, 1909, **368**, 165) found that 4 : 5-diphenylglyoxalone was very easily oxidised by cold dilute nitric acid to 4 : 5-dihydroxy-4 : 5-diphenyldihydroglyoxalone (II), which rapidly broke down into benzil and urea. It is probably in this glycol (II) only that substitution in the two para-positions occurs, the group $\begin{matrix}\cdot\mathrm{C(OH)\cdot NH} \\ \cdot\mathrm{C(OH)\cdot NH}\end{matrix}\!\!>\!\mathrm{CO}$ exerting a directing influence similar to that of the $\cdot\mathrm{CH(OH)\cdot CH(OH)}\cdot$ group in hydrobenzoin, the 3 : 3′-dinitrobenzil (III) always formed at the same time, and to the exclusion of the 4 : 4′-isomeride if fuming nitric acid alone is used, being produced by the action of the nitric acid on the liberated benzil.

The 2 : 3′- and the 2 : 2′-isomerides are almost certainly present in the residue left after the isolation of the 4 : 4′-dinitrobenzil, but as the complete separation of such a mixture is extraordinarily tedious, it has not been exhaustively worked up. The reactions may be represented by the following scheme :



EXPERIMENTAL.

Interaction of Hydrobenzoin with Fuming Nitric Acid.—2·5 G. of hydrobenzoin, m. p. 132° (Breuer and Zincke, *Annalen*, 1879, **198**, 151, 153), were gradually added to 15 c.c. of nitric acid (*d* 1·5) at −10° to −5°. The temperature was then allowed to rise to 0° and after 2 hours the reaction mixture was diluted with 7 c.c. of water, boiled for ½ hour in order completely to oxidise the nitration product to the corresponding dinitrobenzil, and poured on ice. The semi-solid mass which separated was removed, boiled with water, and drained as completely as possible. It then solidified and after one crystallisation from acetone a product, m. p. 197—212°, was obtained; a second crystallisation raised the m. p. to 213° (constant) (yield, 1 g.). The acetone mother-liquors deposited a small amount of a friable semi-crystalline powder which was not further examined.

Oxidation of 4 : 4′-*Dinitrobenzil* (IV).—4 : 4′-Dinitrobenzil is slightly more soluble in all solvents than the 2 : 2′-isomeride but less soluble than the others. It is sparingly soluble in boiling alcohol, but fairly soluble in acetone and acetic acid and crystallises from the latter in very large, yellow, irregularly grown, elongated plates, m. p. 213° (Found : N, 9·3. Calc. for $C_{14}H_8O_6N_2$: N, 9·3%).

6·5 G. of 4 : 4′-dinitrobenzil were boiled for a short time with a slight excess of chromic acid anhydride in acetic acid and after concentration the solution was treated with a slight excess of dilute soda solution and filtered. On acidification, 0·63 g. of *p*-nitrobenzoic acid, m. p. 237°, was obtained (mixed m. p. with an authentic sample showing no depression). Yield, 87% of the theoretical.

4 : 4′-*Dinitrobenzilmonophenylhydrazone* separated when equivalent amounts of the diketone and phenylhydrazine were boiled together for a few minutes in alcoholic solution. It crystallised from acetic acid, in which it is moderately easily soluble, in very fine, hair-like, deep orange crystals, m. p. 257° (Found : N, 14·5. $C_{20}H_{14}O_5N_4$ requires N, 14·4%).

4 : 4′-*Dinitrobenzilosazone* is produced slowly and in poor yield when the diketone is boiled with phenylhydrazine in acetic acid solution, but by taking excess of phenylhydrazine and adding phosphoric oxide the formation of the osazone is greatly facilitated. It is sparingly soluble in all solvents and crystallises from acetic anhydride in tufts of small, red plates, m. p. 293° (decomp.) (Found : N, 17·3. $C_{26}H_{20}O_4N_6$ requires N, 17·5%).

2 : 3-*Di*-p-*nitrophenylquinoxaline* is very soluble in boiling acetic acid and crystallises in colourless needles, m. p. 201° (Found : N, 14·9. $C_{20}H_{12}O_4N_4$ requires N, 15·1%).

Preparation of 4 : 5-*Diphenylglyoxalone.*—Of the various methods for the preparation of this compound the best is that of Biltz (*Annalen*, 1909, **368**, 173). 50 G. of benzoin were boiled under reflux with 26 g. of urea in 200 g. of acetic acid for 6 hours. The glyoxalone crystallised from the reaction mixture on cooling and was filtered off, washed with cold acetic acid, ether, and, lastly, with boiling water, and crystallised from acetic acid. It formed colourless needles, m. p. 324° (yield, 40 g.).

Interaction of 4 : 5-*Diphenylglyoxalone with Fuming Nitric Acid.*—10 G. of 4 : 5-diphenylglyoxalone were dissolved in 20 g. of nitric acid (*d* 1·5), cooled to 0°. The solution was kept over-night and then poured into water. The yellow semi-solid mass obtained was well washed with hot water and recrystallised from acetone, 4 g. of pure 3 : 3′-dinitrobenzil, m. p. 132°, being isolated. No formation of 4 : 4′-dinitrobenzil was observed.

Interaction of 4 : 5-*Diphenylglyoxalone with Sulphuric and Fuming Nitric Acids.*—27 G. of 4 : 5-diphenylglyoxalone were dissolved in 315 g. of concentrated sulphuric acid cooled to —5° and 90 g. of nitric acid (*d* 1·5) were slowly added, the temperature being kept below 0° during the addition. The reaction mixture was kept at the ordinary temperature for 3 days; considerable effervescence took place and a flocculent, yellow mass separated from the solution. The whole was then poured on ice and the yellow, semi-solid mass was removed, boiled repeatedly with water, and drained as completely as possible. After three crystallisations from acetic acid the product yielded 7 g. of pure 4 : 4′-dinitrobenzil, m. p. 213°, identical with a specimen made from hydrobenzoin.

The acetic acid mother-liquors slowly deposited a yellow, moss-like mass of crystals, which were removed and crystallised four times from acetone, 10 g. of pure 3 : 3′-dinitrobenzil, m. p. 132°, being obtained (identical with a specimen made from benzil; compare J., 1926, 1070).

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