LXXXVII.—*The Nitration of Benzil. 3 : 5 : 3′ : 5′-Tetranitrobenzil.*

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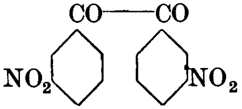
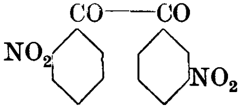
IT has recently been shown (Chattaway and Coulson, J., 1926, 1070) that when benzil is nitrated, a mixture of three isomeric dinitrobenzils is obtained, whether the nitration is effected by fuming nitric acid or by a mixture of potassium nitrate and sulphuric acid. The crude product, although consisting largely of 3 : 3′-dinitrobenzil (I), contains considerable amounts of the 2 : 3′- (II) and 2 : 2′-dinitrobenzil (III).

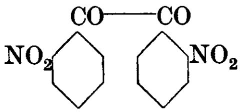
(I.)



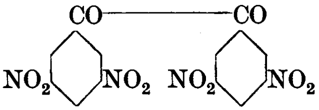
(II.)



(III.)



(IV.)



Barnett and Kay, who regarded this crude mixture as pure 3 : 3′-dinitrobenzil, were unable to nitrate it further (*Chem. News*, 1922, **125**, 57), whilst Christie and Kenner (J., 1926, 470) found no difficulty in doing this, and obtained a tetranitro-derivative (m. p. 168°) which must have been a mixture of isomerides.

3 : 3′-Dinitrobenzil having been isolated in a pure state, the further action of nitric acid upon it has been studied.

On nitration by a mixture of fuming nitric acid and sulphuric acid it yields 3 : 5 : 3′ : 5′-*tetranitrobenzil* (IV), m. p. 179°.

The only other substance produced in any recognisable quantity in the nitration is 3 : 5-dinitrobenzoic acid, which is formed in considerable amount as a by-product. That the entering nitro-groups take up the vacant *meta*-positions is shown by the production of an approximately theoretical amount of 3 : 5-dinitrobenzoic acid when the tetranitrobenzil is oxidised by chromic acid.

EXPERIMENTAL.

Isolation of 3 : 3′-*Dinitrobenzil* (I).—3 : 3′-Dinitrobenzil is most readily isolated from the product of the direct nitration of benzil (which melts at about 109°) by cooling rapidly a saturated acetone solution. A pulpy mass of crystals, melting not very sharply near 122°, separates, and a further crop of the 3 : 3′-isomeride, somewhat less pure, is obtained by distilling off part of the acetone from the mother-liquor. The process can be repeated several times until the 2 : 3′- and 2 : 2′-isomerides are seen among the crystals separating.

The various crops of crystals are then mixed and the process is repeated five or six times, until the melting point has been raised to about 129°. The final purification is best effected by recrystallising the material from acetic acid until the crystals melt sharply at 132°.

3 : 3′-*Dinitrobenzil monophenylhydrazone*,

$$NO_2·C_6H_4·C(N·NHPh)·CO·C_6H_4·NO_2,$$

separates as a pulpy mass of yellow crystals when an alcoholic solution of 3 : 3′-dinitrobenzil (1 mol.) and phenylhydrazine (1 mol.) is boiled for about an hour. It crystallises from boiling acetic acid, in which it is easily soluble, in very slender, yellow prisms, m. p. 171° (Found : N, 14·7. $C_{20}H_{14}O_5N_4$ requires N, 14·4%).

3 : 3′-*Dinitrobenzil osazone*,

$$NO_2·C_6H_4·C(N·NHPh)·C(N·NHPh)·C_6H_4·NO_2,$$

although formed only in very small amount when an alcoholic or acetic acid solution of 3 : 3′-dinitrobenzil or its monophenylhydrazone is boiled with a great excess of phenylhydrazine, separates in considerable amount when phosphorus pentoxide is added to the reaction mixture.

1·5 G. of 3 : 3′-dinitrobenzil (1 mol.) was boiled with 1·5 g. of phenylhydrazine (3 mols.) and 2 g. of phosphorus pentoxide in acetic acid for an hour. On cooling, the osazone separated free from the monohydrazone. It crystallises from boiling acetic acid, in which it is only slightly soluble, in long, slender, bright yellow prisms, which, after drying on the water-bath, contain 1 mol. of acetic acid. This is lost when the compound is heated to 130—140°, the crystals becoming opaque and lighter in colour (Found : loss after heating at 140°, 10·9. $C_{26}H_{20}O_4N_6,CH_3·CO_2H$ requires loss, 11·1%). The osazone melts at 269° (Found : N, 17·2. $C_{26}H_{20}O_4N_6$ requires N, 17·5%).

2 : 3-*Di*(3′-*nitrophenyl*)*quinoxaline* separates when a solution of equivalent amounts of *o*-phenylenediamine and 3 : 3′-dinitrobenzil in acetic acid is heated. It dissolves sparingly in boiling acetic acid and separates in very pale yellow, rhombic plates, m. p. 213° (Found : N, 15·0. $C_{20}H_{12}O_4N_4$ requires N, 15·1%).

3 : 5 : 3′ : 5′-*Tetranitrobenzil* (IV).—3 : 3′-Dinitrobenzil is so easily nitrated that the action, unless carefully controlled, may become very violent.

A solution of 10 g. of 3 : 3′-dinitrobenzil in 72 g. of concentrated sulphuric acid was heated to 100° and 60 g. of nitric acid (*d* 1·5) were slowly added, the temperature being kept between 100° and 110°. The mixture was then heated on a water-bath for a few hours, cooled, and poured over crushed ice. The yellow, viscid mass that separated was boiled repeatedly with water to extract the considerable amount of 3 : 5-dinitrobenzoic acid which it contained. The brittle, yellow, crystalline mass melting at about 174° thus obtained was practically pure 3 : 5 : 3′ : *5′-tetranitrobenzil*, the amount being about one-third of the weight of 3 : 3′-dinitrobenzil used. The aqueous extracts on condensation yielded 3 : 5-dinitrobenzoic acid, m. p. 205°, identical with the dinitrobenzoic acid obtained by nitrating *m*-nitrobenzoic acid (*Z. Chem.*, 1870, 641) and giving no depression of melting point when mixed with it.

3 : 5 : 3′ : 5′-Tetranitrobenzil is sparingly soluble in boiling alcohol and benzene, moderately easily soluble in boiling acetic acid, and separates from these solvents in bright yellow, six-sided, rhombic prisms, m. p. 179° (Found : C, 42·8; H, 1·7; N, 14·4. $C_{14}H_6O_{10}N_4$ requires C, 43·1; H, 1·5; N, 14·4%).

Oxidation of 3 : 5 : 3′ : *5′-Tetranitrobenzil.*—A solution of 1 g. of 3 : 5 : 3′ : 5′-tetranitrobenzil in 50 c.c. of boiling acetic acid was gradually treated with 0·5 g. of chromium trioxide and boiled gently for a few minutes; the excess of chromic acid was then reduced with alcohol, and the whole evaporated to small bulk. Addition of hot dilute caustic soda solution in slight excess, filtration, and acidification of the filtrate gave 0·85 g. of 3 : 5-dinitrobenzoic acid, m. p. 205°; a further 0·12 g. was obtained from the mother-liquor (total yield, 87% of the theoretical).

3 : 5 : 3′ : *5′-Tetranitrobenzil monophenylhydrazone*,

$$C_6H_3(NO_2)_2{\cdot}C({:}N{\cdot}NHPh){\cdot}CO{\cdot}C_6H_3(NO_2)_2,$$

is produced when equivalent amounts of the tetranitrobenzil and phenylhydrazine are heated together in alcohol. It is very sparingly soluble in boiling alcohol and benzene, but more soluble in boiling acetic acid, from which it separates in small, yellow, rhombic crystals, m. p. 236° (Found : N, 17·4. $C_{20}H_{12}O_9N_6$ requires N, 17·5%).

Boiling the tetranitrobenzil for a long time with an excess of phenylhydrazine, either alone or in alcohol or acetic acid, or in acetic acid with phosphorus pentoxide, does not produce an osazone.

2 : 3-*Di*(3′ : *5′-dinitrophenyl)quinoxaline* separates when equivalent amounts of *o*-phenylenediamine and 3 : 5 : 3′ : 5′-tetranitrobenzil are heated together in acetic acid solution. It is slightly soluble in boiling acetic acid and separates in short, irregular, colourless prisms which contain 1 mol. of acetic acid. This is lost by drying on the water-bath (Found : loss at 110°, 11·3. Calc. : loss, 11·5%), and the crystals become opaque and melt at 285° (Found : N, 18·5. $C_{20}H_{10}O_8N_6$ requires N, 18·2%).

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