

CXXXVII.—*The Nitration of Benzil.*

By FREDERICK DANIEL CHATTAWAY and EDWARD AUTY  
COULSON.

ALTHOUGH benzil is scarcely attacked by ordinary strong nitric acid, it is readily nitrated by fuming nitric acid. The reaction was first carried out by Zinin (*Annalen*, 1864, Suppl. **3**, 153), who recognised that a new compound distinct from benzil and *p*-nitrobenzil was formed, but did not pursue the investigation further.

It was next studied by Zagumenny (*J. Russ. Phys. Chem. Soc.*, 1872, 4, 278), who, by crystallising the crude viscid product from alcohol, obtained a moss-like mass of irregular needles melting at 107°, in which after some weeks two different kinds of crystals made their appearance and could be picked out. He thus obtained two substances crystallising respectively in yellow octahedra, m. p. 131°, and in faintly yellow, rectangular plates, m. p. 147°. Analyses showed that all these substances had the composition of dinitrobenzil, but Zagumenny expressed no opinion as to their nature. His observations were apparently overlooked, for much later Klinger and Martinoff (*Annalen*, 1912, 389, 232) claim to have obtained an almost theoretical yield of pure *mm'*-dinitrobenzil, m. p. 108·5—109°, by nitrating benzil with a large excess of cold fuming nitric acid, and more recently Barnett and Kay (*Chem. News*, 1922, 125, 57), after remarking that the preparation of dinitrobenzil is much simpler than would be gathered from the literature, state that a nearly theoretical yield of practically pure *mm'*-dinitrobenzil, m. p. 109°, can be obtained by dissolving or suspending benzil in concentrated sulphuric acid and adding slowly an equal weight of potassium nitrate.

The products described by Zagumenny (m. p. 107°), by Klinger and Martinoff (m. p. 108·5—109°), and by Barnett and Kay (m. p. 109°) appear from their melting points to have been the same, and a re-examination of the crude substances obtained by each of the three methods proves that they are substantially identical.

A closer examination of the nitration product, however, shows that it is not a single substance but a mixture of at least three isomeric dinitrobenzils. These have been separated, mainly by fractional recrystallisation, but partly by mechanical assortment of the crystals.

The crude nitration product, which melts not very sharply at about 107°, has been thus shown to consist of approximately 70% of *mm'*-dinitrobenzil, m. p. 132°, 20% of *om'*-dinitrobenzil, m. p. 149°, and about 10% of *oo'*-dinitrobenzil, m. p. 208°.

The constitutions of the first two isomerides have been established by their oxidation to the corresponding nitrobenzoic acids, whilst the third has been shown to be identical with the *oo'*-dinitrobenzil obtained by Kliegl and Haas (*Ber.*, 1911, 44, 1213) by the oxidation of *oo'*-dinitrotolane.

#### EXPERIMENTAL.

*Nitration of Benzil.*—Preliminary experiments in which benzil was heated with fuming nitric acid as described by Zagumenny showed that the product very closely resembled those obtained

when the nitration was effected by a large excess of cold fuming nitric acid as described by Klinger and Martinoff or by a mixture of cold strong sulphuric acid and potassium nitrate as described by Barnett and Kay. The crude products were identical in appearance, and the moss-like, fluffy crystals obtained by cooling saturated solutions in boiling alcohol had a similar appearance and were of approximately the same melting point, although this varied somewhat and was never sharp. All three products were similar mixtures of isomerides. The behaviours of the moss-like masses of yellow crystals, which separated when solutions of the crude products in boiling alcohol were cooled, on recrystallisation from acetone were similar, and the proportions of the various constituents of the mixture, separated as described later, were as far as could be judged about the same.

*Preparation of the Crude Mixture of Isomeric Dinitrobenzils.*—Benzil (120 g.) and 240 g. of nitric acid (*d* 1.52) were slowly heated in a litre Jena flask with a ground-in air condenser and allowed to boil gently for about 5 hours. The mixture was then poured on to crushed ice, when a viscid, yellow mass separated. The aqueous supernatant liquid was decanted off and the yellow product, which collected together and could be easily separated, was repeatedly extracted with boiling water. In this way the nitrobenzoic acids formed as by-products were removed. The warm, yellow, plastic mass was then drained as completely as possible and allowed to cool, when it slowly solidified. The yield of crude product was about 150 g. (about 80% of the theoretical). The dry product was finely powdered and dissolved in boiling acetone. On cooling, a moss-like, crystalline mass separated in which larger, definitely-shaped crystals slowly made their appearance. On allowing the crystalline mass to remain for some days in the mother-liquor at the ordinary temperature, the quantity of compact crystals appeared to increase, and under the microscope they were seen to be of different kinds.

The whole crude product was therefore systematically fractionally crystallised from acetone and was thus separated into three fractions of very different appearance and solubility.

The three fractions were finally repeatedly crystallised until their behaviour and appearance remained unchanged after several crystallisations from different solvents. The least soluble fraction was *oo'*-dinitrobenzil, the fraction of intermediate solubility was *om'*-dinitrobenzil, whilst the most soluble constituent was *mm'*-dinitrobenzil.

*mm'*-Dinitrobenzil,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , is moderately easily soluble in boiling alcohol and very easily soluble in boiling

acetic acid, benzene, chloroform, or acetone. It separates from each of these solvents in tufts of pale yellow, irregular, slender, prismatic crystals, m. p. 132°. These crystals in the mother-liquor have a moss-like appearance (Found : C, 56.2; H, 2.8; N, 9.5. Calc. for  $C_{14}H_8O_6N_2$ , C, 56.0; H, 2.7; N, 9.3%). When dissolved in boiling acetic acid and oxidised by adding chromic acid from time to time, it is converted into *m*-nitrobenzoic acid only (yield 52—55% of the theoretical).

*om'*-Dinitrobenzil is much less soluble in all solvents than the *mm'*-isomeride, but is somewhat more soluble than the *oo'*-isomeride. It is sparingly soluble in boiling acetic acid, chloroform, benzene, or acetone, and separates from the last in pale yellow, short, compact, six-sided prisms, m. p. 149°, showing a tendency to aggregate in warty-looking crusts. The crystals are phototropic and on exposure to light assume a green colour (Found : C, 56.0; H, 2.7; N, 9.4%). On oxidation by chromic acid, a mixture of *m*- and *o*-nitrobenzoic acids was obtained.

In the early stages of the fractional crystallisation of the crude product of intermediate solubility, clear, transparent crystals of a much deeper shade of yellow than the others make their appearance. These apparently are the crystals described as yellow octahedra by Zagumenny. In spite of their characteristic shape and colour, however, they prove to be, not a fourth isomeride, but mixed crystals containing the *oo'*- and the *mm'*-isomerides. On heating, they soften at about 129°, but do not melt completely till a temperature in the neighbourhood of 190° is reached, and if recrystallised from acetone can be separated into *mm'*-dinitrobenzil and *oo'*-dinitrobenzil.

*oo'*-Dinitrobenzil is very sparingly soluble in boiling alcohol and only sparingly soluble in boiling acetone, acetic acid, chloroform, or benzene. From solutions in these solvents, it separates in small, compact, pale yellow, six-sided prisms with basal ends, m. p. 208° (Found : C, 55.9; H, 2.8; N, 9.2%). It is phototropic and becomes green when exposed to light. It is scarcely attacked by chromic acid and can be recovered practically unchanged after prolonged boiling with chromic acid in acetic acid solution. Its constitution was established by comparing it with *oo'*-dinitrobenzil prepared by the oxidation of *oo'*-dinitrotolane (Kliegl and Haas, *loc. cit.*). The two specimens were identical in colour, appearance, and properties. They melted at the same temperature, 208°, alone and when mixed together, and were similarly phototropic and resistant to oxidation.