

CXXXVII.—*The Mononitrobenzils and the Heteronuclear Dinitrobenzils.*

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WHEN benzil is nitrated, three of the six possible heteronuclear dinitrobenzils are formed, 3 : 3'-dinitrobenzil in largest amount and 2 : 3'-dinitrobenzil and 2 : 2'-dinitrobenzil in smaller quantities, the group  $\cdot\text{CO}\cdot\text{CO}\cdot$  directing the entering nitro-groups into meta- and ortho-positions only (Chattaway and Coulson, J., 1926, 1070). The group  $\cdot\text{CH}(\text{OH})\cdot$ , however, which is present in benzoin, is

para-ortho-directing and, although the viscid product of the regulated nitration of benzoin cannot itself be crystallised and separated, the three theoretically possible mononitrobenzils can be isolated from the mixture obtained when it is oxidised by ordinary concentrated nitric acid. 4-Nitrobenzil (I) is thus obtained in considerable amount and 3- and 2-nitrobenzils (II and III) in much smaller quantities.

Each of these three mononitrobenzils can be further nitrated by fuming nitric acid, the second entering nitro-group being directed by the  $\cdot\text{CO}\cdot\text{CO}\cdot$  group as before mainly into the meta- and to a much smaller extent into the ortho-position in the unsubstituted nucleus. Two of the three heteronuclear dinitrobenzils previously unknown are thus formed as well as the three previously obtained.

In no case has even a slight amount of para-substitution been observed.

It is not, however, necessary to isolate these mononitrobenzils to obtain the new heteronuclear dinitrobenzils, for when a solution of benzoin or acetylbenzoin in excess of fuming nitric acid is kept at the ordinary temperature, dinitration, followed by oxidation, occurs. From the product the two heteronuclear dinitrobenzils previously wanting to complete the series, the 2 : 4'- and the 3 : 4'-dinitrobenzils (V and IV), can be isolated as well as a very small amount of the 4 : 4'-isomeride (VI). The formation of the 4 : 4'-isomeride is possibly due to the orienting influence of the  $\cdot\text{CH}(\text{OH})\cdot$  group of the benzoin being slightly effective in the nucleus to which it is only indirectly attached. A small amount of the 2 : 3'-isomeride previously obtained by the nitration of benzil itself is also formed.

The six theoretically possible heteronuclear dinitrobenzils have thus been obtained by the nitration of benzil and of benzoin.

3 : 4'-Dinitrobenzil is dimorphic; the form unstable at the ordinary temperature is of deeper colour and lower melting point than the stable form.

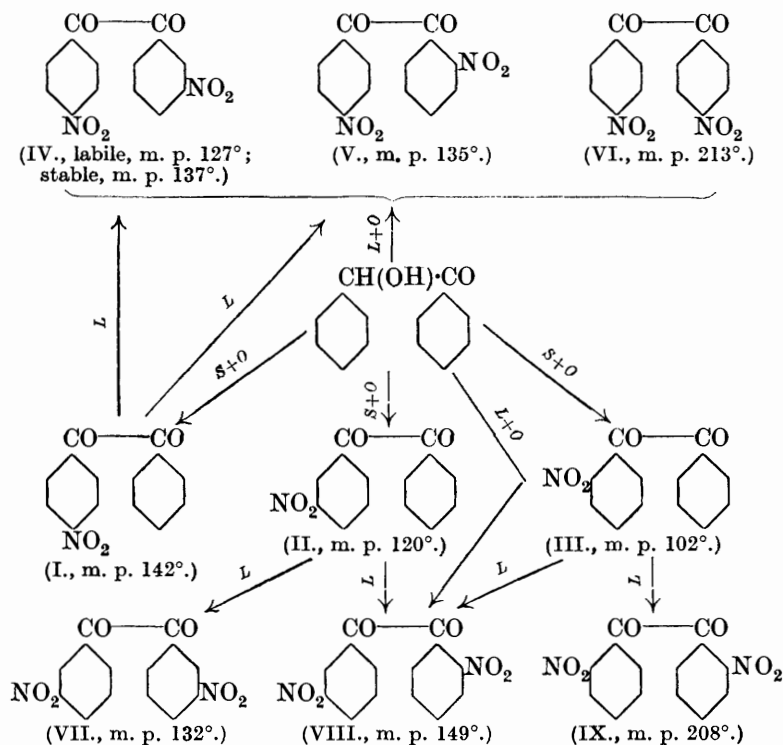
The constitutions of these compounds have been established by oxidising them with chromic acid to the corresponding nitrobenzoic acids. A number of derivatives of each have been prepared serving for their identification.

No dinitrobenzil containing an *o*-nitro-group forms an osazone and both the 2 : 2'- and the 2 : 3'-dinitrobenzil form a monohydrazone only with difficulty.

2 : 2'-Dinitrobenzil also does not form a quinoxaline and is the only one of the mono- and di-nitrobenzils which is not readily oxidised by chromic acid. These peculiarities of behaviour may be ascribed either to the steric or to the polarity effects of the *o*-nitro-groups on the adjacent keto-groups. Both the 4-nitrobenzil and the

2 : 4'-dinitrobenzil yield pairs of apparently structurally isomeric monohydrazone, but from the other unsymmetrical heteronuclear dinitro-benzils in each case only a single monohydrazone has been obtained.

The following scheme shows the mode of formation of the various mono- and heteronuclear di-nitrobenzils : *S* = regulated nitration in acetic anhydride; *L* = long interaction with anhydrous nitric acid (*d* 1.5); *O* = oxidation with ordinary nitric acid (*d* 1.4).



#### EXPERIMENTAL.

*The Regulated Nitration of Benzoin.*—By nitration of benzoin (Zinin, *Annalen*, 1864, Suppl. 3, 153; Hausmann, *Ber.*, 1890, **23**, 532) or acetylbenzoin (Francis and Keane, *J.*, 1911, **99**, 344) with fuming nitric acid, followed in the latter case by oxidation, it was found impossible to get a good yield of 4-nitrobenzil, the product of nitration being gummy and uncrystallisable. The following method, however, gave a good result.

100 G. of benzoin, dissolved in 500 c.c. of acetic anhydride containing 100 g. of concentrated sulphuric acid (whereby the

benzoin was probably first acetylated), were slowly treated at  $-10^{\circ}$  with 55 g. of finely powdered potassium nitrate; the temperature was not allowed to rise above  $0^{\circ}$ . After remaining for 2 days at the ordinary temperature, the reaction mixture was poured on ice. The cream-coloured, semi-solid mass that separated was removed, drained, and oxidised by boiling with concentrated nitric acid ( $d$  1.5; 3 parts by wt.). When no more nitrous fumes were evolved, the solution was poured on ice, and the yellow viscid mass that separated was well washed with boiling water and crystallised twice from acetone and once from alcohol, 50 g. of pure 4-nitrobenzil, m. p.  $142^{\circ}$ , being obtained (yield 42%).

The acetone mother-liquors were diluted with alcohol, and a yellow friable mass of crystals, m. p.  $103-106^{\circ}$ , slowly separated, which contained 3- and 2-nitrobenzils. The former, being less soluble, was obtained by extracting the mixture with insufficient boiling alcohol completely to dissolve it and then crystallising the residue from acetone or alcohol till it melted sharply at  $120^{\circ}$  (yield, 1 to 2 g. of 3-nitrobenzil). When no more 3-isomeride could be separated, the final residue was crystallised six or seven times from alcohol and yielded 1 g. of pure 2-nitrobenzil, m. p.  $102^{\circ}$ .

*Oxidation of 4-Nitrobenzil (I).*—A solution of 1 g. of 4-nitrobenzil in acetic acid containing chromic anhydride was boiled for a few minutes, concentrated, and extracted with warm dilute aqueous caustic soda. The filtered extract yielded on acidification 0.94 g. of a mixture of *p*-nitrobenzoic and benzoic acids. The latter was separated by sublimation and had m. p.  $121^{\circ}$ ; the residue on crystallisation from water had m. p.  $235^{\circ}$  (wt. 0.4 g.). Both were identified by mixed m. p. determinations.

*Isomeric Monophenylhydrazones of 4-Nitrobenzil.*—4-Nitrobenzil (2.45 g.) was warmed with a solution of 1.1 g. of phenylhydrazine in 30 c.c. of alcohol until it dissolved; on cooling, there was obtained a mixture of two substances, which were separated by fractional crystallisation. The less soluble, which was present in greater amount, crystallises in yellow, elongated, rhombic plates, m. p.  $200^{\circ}$  (Found: N, 12.3.  $C_{20}H_{15}O_3N_3$  requires N, 12.2%). The other isomeride crystallises in orange, rhombic plates, m. p.  $162^{\circ}$  (Found: N, 12.0%). The m. p. of a mixture of the two showed a depression and they appear to be structurally isomeric *monophenylhydrazones* of the formulæ  $NO_2 \cdot C_6H_4 \cdot C(N \cdot NHPh) \cdot COPh$  and  $NO_2 \cdot C_6H_4 \cdot CO \cdot C(N \cdot NHPh)Ph$ .

No evidence on which to assign these formulæ more exactly was obtained.

4-Nitrobenzilozazone was obtained by boiling the diketone with an excess of phenylhydrazine and phosphoric oxide. It crystallised

from hot acetic acid in very small, orange-coloured needles, m. p.  $216^{\circ}$  (Found : N, 15.8.  $C_{26}H_{21}O_2N_5$  requires N, 16.0%).

2-*p*-Nitrophenyl-3-phenylquinoxaline crystallised from boiling acetic acid, in which it is very soluble, in large, irregular, colourless plates which became opaque and fell to powder when removed from the mother-liquor (probably owing to loss of loosely combined acetic acid), and melted at  $161^{\circ}$  (Found : N, 13.0.  $C_{20}H_{13}O_2N_3$  requires N, 12.8%).

*Oxidation and Nitration of 3-Nitrobenzil* (II).—3-Nitrobenzil is readily soluble in boiling alcohol and very readily soluble in boiling acetic acid, acetone, chloroform, and benzene. It crystallises from alcohol in pale yellow, rhombic plates, m. p.  $120^{\circ}$  (Found : N, 5.4.  $C_{14}H_9O_4N$  requires N, 5.5%).

This isomeride on oxidation (for method see p. 1083) gave benzoic and *m*-nitrobenzoic acids, which were separated by sublimation of the former.

The difficulty of preparing 3-nitrobenzil in a perfectly pure state has hindered the investigation of its derivatives, but it has been found to be readily nitrated to give a mixture of 3 : 3'- and 3 : 2'-dinitrobenzils. A solution of 1 g. of 3-nitrobenzil in 2 g. of fuming nitric acid (*d* 1.5) was boiled a few minutes and then diluted with water. The yellow, viscid, semi-solid product, after being boiled with water, drained, and dried, soon solidified. It was crystallised three times from boiling acetone and 0.4 g. of 3 : 3'-dinitrobenzil, m. p.  $132^{\circ}$  (m. p. of mixture with 3 : 3'-dinitrobenzil prepared from benzil not depressed), was obtained. The acetone mother-liquors deposited a mixture of crystals of 3 : 3'- and 3 : 2'-dinitrobenzils. By washing these with cold acetone, the former were dissolved away, leaving 0.1 g. of the 3 : 2'-isomeride which, after one crystallisation from acetic acid, had m. p.  $149^{\circ}$  (m. p. of mixture with 3 : 2'-dinitrobenzil prepared from benzil not depressed).

*Oxidation and Nitration of 2-Nitrobenzil* (III).—This isomeride is similar in appearance to the 3-isomeride, but is rather more soluble in all solvents, and the pale yellow rhombic crystals become green on exposure to light (thus resembling the three heteronuclear dinitrobenzils containing one or more *o*-nitro-groups). When pure, this substance has m. p.  $102^{\circ}$  (Found : N, 5.5%). List, who first prepared it from *o*-nitrodeoxybenzoin (*Ber.*, 1893, **26**, 2453), gave m. p.  $98^{\circ}$ .

On oxidation as before, a mixture of benzoic and *o*-nitrobenzoic acids was produced, from which the latter was obtained pure by sublimation of the benzoic acid.

2-Nitrobenzil was nitrated in a similar way to the 3-isomeride with fuming nitric acid (*d* 1.5), and the product from 1 g. yielded

0.5 g. of pure 3 : 2'-dinitrobenzil, m. p. 149°, and a smaller amount of 2 : 2'-dinitrobenzil, m. p. 208°, after fractional crystallisation from acetone.

*Nitration of 4-Nitrobenzil: Preparation of 3 : 4'- and 2 : 4'-Dinitrobenzils.*—The best method of preparing 3 : 4'- and 2 : 4'-dinitrobenzils in quantity is by the nitration of pure 4-nitrobenzil, since a product is obtained which contains little besides these two isomerides and is consequently much easier to crystallise fractionally than the more complicated mixture of isomerides obtained by dinitration and subsequent oxidation of benzoin or acetylbenzoin.

A solution of 13 g. of 4-nitrobenzil in 26 g. of fuming nitric acid (*d* 1.5) was slowly heated and finally boiled gently for 15 minutes. It was then poured on ice. The yellow semi-solid product, which hardened after being washed with boiling water, drained, and dried, was powdered and extracted with insufficient boiling chloroform completely to dissolve it. The small residue, on repeated crystallisation, yielded only 3 : 4'-dinitrobenzil, m. p. 137°, thus showing that no 4 : 4'-dinitrobenzil had been formed in the nitration, for this isomeride is much less soluble in chloroform than any other that could have been present.

The chloroform extract, when rapidly cooled, deposited deep yellow, compact crystals of the unstable polymorph of 3 : 4'-dinitrobenzil fairly free from 2 : 4'-dinitrobenzil. The processes of solution in chloroform and rapid cooling were repeated till the m. p. of the product, after one crystallisation from acetic acid, was 137°, showing it to be quite pure. The chloroform mother-liquors were diluted with alcohol and the mixture of 3 : 4'- and 2 : 4'-dinitrobenzils precipitated was further fractionally crystallised from chloroform; eventually a product was obtained so rich in 2 : 4'-dinitrobenzil that crystals of this substance, which is much paler in colour than the 3 : 4'-isomeride, could be seen to separate when the chloroform solution was cooled.

Pure 2 : 4'-dinitrobenzil was obtained from the residue, after partial separation of the 3 : 4'-isomeride as just described, by dissolving it in boiling acetic acid, cooling the solution carefully so that no crystals separated, and inoculating it with a crystal of this isomeride. The first crop of crystals, consisting largely of 2 : 4'-dinitrobenzil, was rapidly filtered off and recrystallised from acetic acid. When the amount of 2 : 4'-isomeride in the residues had been diminished, a further quantity of 3 : 4'-dinitrobenzil was removed by fractional crystallisation from chloroform. By using the two methods alternately, the crude nitration product from 13 g. of 4-nitrobenzil was separated into 7.4 g. of pure 3 : 4'-dinitrobenzil, 1.7 g. of pure 2 : 4'-dinitrobenzil, and a small residue.

*Long Interaction of Benzoin and Acetylbenzoin with Fuming Nitric Acid.*—A solution of 20 g. of benzoin in 60 g. of nitric acid (*d* 1.5) was kept at 25—30° for 6 hours and then poured on ice. The yellow gummy product was removed and boiled with 60 g. of nitric acid (*d* 1.4) and when nitrous fumes were no longer given off the solution was poured on ice. The bright yellow viscid mass which separated was well washed with boiling water, drained, and recrystallised from acetone; it then yielded 4 g. of 3 : 4'-dinitrobenzil, m. p. 137°.

The acetone mother-liquor was concentrated, and the crystals obtained, which were seen to be of more than one kind, were removed, powdered, and extracted with boiling chloroform; the residue, when recrystallised from acetic acid, yielded 0.2 g. of 4 : 4'-dinitrobenzil, m. p. 213°. (A more complete investigation of this compound being in progress, its description is reserved.) The mother-liquor deposited on concentration 0.5 g. of 3 : 2'-dinitrobenzil, m. p. 149°.

When the chloroform extract (see above) was cooled, the first crop of crystals to separate consisted entirely of the 3 : 4'-isomeride; these were filtered off and the mother-liquor deposited a second crop containing crystals of 2 : 4'-dinitrobenzil as well. Pure 2 : 4'-dinitrobenzil (0.5 g.), m. p. 135°, was obtained by recrystallisation of the second crop from acetic acid.

Acetylbenzoin under similar conditions of nitration, followed by oxidation, yielded a similar mixture of the same isomeric dinitrobenzils, which were separated by identical methods.

*Polymorphism and Oxidation of 3 : 4'-Dinitrobenzil (IV).*—3 : 4'-Dinitrobenzil is soluble in boiling alcohol, more easily soluble in boiling acetic acid, acetone, chloroform, and benzene. It can be obtained in two polymorphic forms; the unstable form is deposited on chilling a chloroform solution or by seeding supersaturated solutions in other solvents with the unstable form, as deep yellow, rhombic crystals which become opaque when heated to 100°, or if allowed to remain for very long periods at the ordinary temperature, and change into the stable form. The latter usually crystallises at once when solutions in alcohol, acetic acid or acetone are cooled, as tufts of pale yellow, irregularly formed needles or elongated plates, similar in appearance to the 3 : 3'-isomeride but rather deeper in colour. The m. p. of the stable form is 137°; the unstable form, if rapidly heated, melts at 127°, sets again at once, and finally melts at 136—137° (Found : N, 9.25.  $C_{14}H_8O_6N_2$  requires N, 9.3%).

5 G., oxidised by the method previously employed, yielded 5 g. of a mixture of *m*- and *p*-nitrobenzoic acids, which were separated by taking advantage of the greater solubility of the former in chloroform and of the sparing solubility of its barium salt. 2 G. of

*p*-nitrobenzoic acid, m. p. 235°, and 1 g. of *m*-nitrobenzoic acid, m. p. 141°, were obtained (the m. p.'s of mixtures of these acids with authentic samples showed no depression).

**3 : 4' - Dinitrobenzilmonophenylhydrazone.**—When equivalent amounts of the dinitrobenzil and phenylhydrazine were boiled together for a few minutes in alcohol, the *hydrazone* separated in good yield; it crystallised from alcohol as a mass of orange-coloured, felted needles, m. p. 182°, very soluble in boiling acetic acid (Found : N, 14.4.  $C_{20}H_{14}O_5N_4$  requires N, 14.4%). It appeared to be a single individual, but no evidence was obtained to show which keto-group condenses with the phenylhydrazine.

The *osazone* can be obtained by boiling the dinitrobenzil or its monohydrazone with a great excess of phenylhydrazine and phosphoric oxide in acetic acid solution. It is sparingly soluble in acetic acid and crystallises from acetic anhydride in orange-red, rhombic plates, m. p. 287° (decomp.) (Found : N, 17.3.  $C_{26}H_{20}O_4N_6$  requires N, 17.5%).

**2-*m*-Nitrophenyl-3-*p*-nitrophenylquinoxaline** crystallises from boiling acetic acid in small, colourless plates, m. p. 221° (Found : N, 15.0.  $C_{20}H_{12}O_4N_4$  requires N, 15.1%).

**Oxidation of 2 : 4' - Dinitrobenzil (V).**—2 : 4' - Dinitrobenzil appears to be slightly more soluble in acetone and chloroform than the 3 : 4' - isomeride, but otherwise closely resembles it in solubility in these and other solvents. It crystallises well from acetone or acetic acid in well-formed, pale yellow needles, m. p. 135°, which are phototropic and turn green when exposed to sunlight (Found : N, 9.1%).

1 G. yielded on oxidation 0.4 g. of *p*-nitrobenzoic acid, m. p. 235°, and 0.2 g. of *o*-nitrobenzoic acid, m. p. 143°, which were separated by fractional crystallisation from water.

**Isomeric Monophenylhydrazones of 2 : 4' - Dinitrobenzil.**—When 2 : 4' - dinitrobenzil was boiled for a few minutes with an equivalent amount of phenylhydrazine in alcohol there separated a mixture of orange-coloured and yellow crystals. The latter were the less soluble and were obtained pure by recrystallisation from boiling acetic acid as bright yellow needles, m. p. 224° (Found : N, 14.5.  $C_{20}H_{14}O_5N_4$  requires N, 14.4%).

The orange-coloured substance, being the denser, was separated by agitating the mixture with alcohol and pouring off the suspension of the yellow substance. From solution in boiling acetic acid it crystallised in four-sided plates or flattened prisms, m. p. 201° (Found : N, 14.3%).

The two substances appear to correspond to the two possible structures  $(o)NO_2 \cdot C_6H_4 \cdot C(:N \cdot NHPh) \cdot CO \cdot C_6H_4 \cdot NO_2(p)$  and  $(o)NO_2 \cdot C_6H_4 \cdot CO \cdot C(:N \cdot NHPh) \cdot C_6H_4 \cdot NO_2(p)$ ,

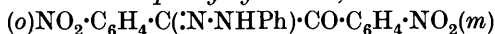


but no evidence on which to assign the structures more exactly was obtained.

*2-o-Nitrophenyl-3-p-nitrophenylquinoxaline* crystallised from boiling acetic acid, in which it is easily soluble, in small, well-shaped, colourless needles, m. p.  $186^{\circ}$  (Found: N, 15.1.  $C_{20}H_{12}O_4N_4$  requires N, 15.1%).

*Derivatives of 2:2'- and 2:3'-Dinitrobenzil.*—The monophenylhydrazone of the former compound is formed only slowly when the diketone is boiled with an excess of phenylhydrazine in alcoholic or acetic acid solution. It crystallises from boiling acetic acid, in which it is fairly readily soluble, in large, deep yellow, octahedral crystals, m. p.  $199^{\circ}$  (Found: N, 14.3.  $C_{20}H_{14}O_5N_4$  requires N, 14.4%).

*2:3'-Dinitrobenzilmonophenylhydrazone,*



or  $(o)NO_2 \cdot C_6H_4 \cdot CO \cdot C(:N \cdot NHPh) \cdot C_6H_4 \cdot NO_2(m)$ , separates gradually on prolonged boiling of 2:3'-dinitrobenzil with an excess of phenylhydrazine in alcoholic solution. The product appears to be a single individual, crystallising from acetic acid, in which it is fairly readily soluble, in deep yellow prisms, m. p.  $193^{\circ}$  (decomp.) (Found: N, 14.3%).

*2-m-Nitrophenyl-3-o-nitrophenylquinoxaline* crystallises from boiling acetic acid in small, colourless or very pale yellow, rhombic prisms, m. p.  $168^{\circ}$  (Found: N, 15.2.  $C_{20}H_{12}O_4N_4$  requires N, 15.1%).

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