XLIV.—*The Nitration of Acetylbenzoin and of Stilbenediol Diacetates.*

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THE object of this investigation has been to obtain some unsymmetrical derivatives of benzoin, such as the nitro-compounds, with the view of examining their stereochemical and desmotropic relations. The action of nitric acid on benzoin and some allied compounds offers several points of interest. Benzoin itself, as is well known, is oxidised to benzil when heated with ordinary concentrated nitric acid, but with fuming nitric acid at 0° *p*-nitrobenzil is also obtained.

Benzil is less readily nitrated; on heating it with fuming nitric acid, two nitro-groups are introduced to form two isomeric dinitro-compounds, melting respectively at 131° and 147° (Zagumenny, *J. Russ. Phys. Chem. Soc.*, 1873, **4**, 278); mononitrobenzils have not been obtained directly from benzil. The action of nitric acid on acetyl- and on benzoyl-benzoin has been studied by Zinin (*Annalen*, 1857, **104**, 116). From acetylbenzoin he obtained a mixture of two nitro-compounds, neither of which, however, appears to have been isolated in a pure state or submitted to more than a preliminary investigation. The nitrobenzoyl compound he obtained pure, and isolated it in rhombic tablets, melting at 137° .

With the object of preparing nitrobenzoin, attempts were first made to hydrolyse nitrobenzoylbenzoin, but it was not found possible to effect this decomposition with any hydrolytic agents, as complex condensation products, which are still under investigation, invariably resulted. In order to obtain a less stable ester, *p*-nitroacetylbenzoin was prepared, but condensation products were similarly formed on hydrolysis, and all attempts to obtain *p*-nitrobenzoin by the action of hydrolytic agents from it were unsuccessful. Attention was then directed to the nitration of the geometrically isomeric stilbenediol diacetates prepared by Thiele (*Annalen*, 1899, **306**, 142). These compounds are so readily hydrolysed to benzoin that it appeared probable that by effecting the nitration in absence of hydrolytic agents, nitro-compounds of the diacetyl isomerides might be obtained, from which nitrobenzoin could be prepared. The experiments conducted with this object in view resulted in the formation of benzoin mononitrate and a small quantity of a substance, possibly nitrobenzoin, which is still under examination, together with benzil. Both the α -stilbenediol diacetate melting at 153° and the β -compound melting at 110° act similarly towards nitric acid, except for the fact that the isomeride of lower melting point is partly converted into the α -compound under the conditions described below. The action of nitric acid may be represented by the following equations, the final formation of benzoin nitrate being due to a molecular rearrangement, as in the preparation of benzoin from the stilbenediol diacetates:

This difference in the behaviour of acetylbenzoin, benzoylbenzoin,

and of the stilbenediol diacetates towards nitric acid is shared by several other reagents, and similar differences have also been observed with some of their derivatives. These reactions are under further investigation.

EXPERIMENTAL.

Nitration of Acetylbenzoin.

Zinin (*Annalen*, 1857, **104**, 120), Jena and Limprecht (*ibid.*, 1870, **155**, 92), and Pöpcke (*Ber.*, 1888, **21**, 1336) have all prepared acetylbenzoin, but give different melting points for the compound, namely, below 100°, 75°, and 83° respectively. It is best prepared as follows: 200 grams of benzoin are added in successive small quantities to a mixture of 25 c.c. of concentrated sulphuric acid and 500 c.c. of acetic anhydride kept cold in running water; the mixture is kept for some time, poured into water, the precipitate collected, and recrystallised from 90 per cent. alcohol. The product thus prepared melts at 83°, agreeing with the value given by Pöpcke. A practically quantitative yield is obtained by this method of preparation.

Two methods of nitration were employed.

Method I.—For the nitration by this method, 400 grams of fuming nitric acid are cooled to 0° in a freezing mixture of ice and salt, and 200 grams of finely powdered acetylbenzoin gradually added. The acetyl compound must be thoroughly dry, free from odour of acetic acid, and finely powdered, and the temperature must be kept within a degree or so of 0°; if it falls much below this temperature, considerable quantities of benzoin are formed, and above this temperature the amount of benzil formed is increased. The deep red solution thus obtained is poured at once into ice-cold water, when a pale green oil separates, which is well washed by decantation with water. After some time this sets to a semi-solid mass, from which the nitro-compound is separated by treatment with successive small quantities of ether, whereby the adherent oil is removed. The residue is recrystallised from 90 per cent. alcohol. A yield of 20 per cent. on the weight of acetylbenzoin taken is obtained.

Method II.—Five grams of acetylbenzoin are treated with 25 c.c. of acetic anhydride, 4 c.c. of concentrated sulphuric acid, and 1.7 grams of recently fused and finely powdered nitre at a temperature of -15°. The nitration is carried out as in the case of the stilbenediol diacetates described below. A yield of 40 per cent. on the weight of the acetylbenzoin taken is obtained.

p-Nitroacetylbenzoin crystallises from 90 per cent. alcohol in brilliant, almost colourless leaflets, and melts at 125° (uncorr.). It

is sparingly soluble in ether or light petroleum, readily so in chloroform, acetone, or benzene, and somewhat less so in boiling 90 per cent. alcohol or glacial acetic acid. It is decomposed by alkalis in either aqueous or alcoholic solution, with the formation of acidic condensation products, as stated above:

0.2064 gave 0.4846 CO₂ and 0.0834 H₂O. C=64.03; H=4.48.

0.5640 „, 24.0 c.c. N₂ (moist) at 20° and 755 mm. N=4.83.

0.7421, in 20 c.c. alcohol, gave E=0.19°. M.W.=305.

C₁₆H₁₃O₅N requires C=64.20; H=4.35; N=4.68 per cent.

M.W.=299.

When heated with nitric acid (D 1.40), *p*-nitrobenzil, melting at 140°, is formed. (Found, N=5.34. Calc., N=5.49 per cent.)

When oxidised with a mixture of sulphuric acid (25 grams of concentrated sulphuric acid in 25 c.c. of water) and an approximately normal solution of potassium dichromate, it is completely hydrolysed and oxidised to acetic acid, benzoic acid (melting at 122°), and *p*-nitrobenzoic acid (melting at 237°). Care must be taken to have always an excess of dichromate present during the oxidation, otherwise acidic condensation products result. Benzoin, under precisely the same conditions, yields molecular proportions of benzaldehyde and benzoic acid. From this it follows that the nitro-group is in the para-position in the phenyl radicle connected with the carbon atom of the secondary alcohol group, so that the nitroacetylbenzoin has the structural formula:

The identity of the *p*-nitrobenzoic acid formed in the oxidation was confirmed by titration with alkali. (Found, M.W.=166.4. Calc., M.W.=167.)

Nitration of the Stilbenediol Diacetates (α , melting at 153°, and β , melting at 110°).

Forty c.c. of concentrated sulphuric acid are added, drop by drop, to 250 c.c. of acetic anhydride kept cold in a freezing mixture of ice and salt; when the temperature has fallen to -15°, 45 grams of the finely powdered β -stilbenediol diacetate (melting at 110°) are added, and then 17 grams of recently fused and finely powdered nitre in small portions at a time and with constant shaking, care being taken to keep the temperature at -15°. If the diacetate be added to the mixed acid, anhydride, and nitre, no benzoin nitrate is formed. When all the nitre has been added, the solution, which is clear and red in colour, is poured into the bath liquor, cooled to -15°, and the whole stirred until solid. The supernatant acid liquid is then decanted, the residue being thoroughly washed by

decantation, and collected. The bulk of the benzil present is removed by washing with ether, and the residue purified by fractional crystallisation from 90 per cent. alcohol. The products isolated consisted of: (1) benzoin mononitrate, melting at 167° , 3 grams; α -stilbenediol diacetate, melting at 153° , 3 grams; and the substance, melting at 188° , 1 gram.

The amount of α -stilbenediol diacetate formed increases with decrease of temperature; at 0° , 5 per cent. of the β -diacetate used is obtained, at -15° , 7 per cent., at -25° , 10 per cent., whilst no benzoin nitrate is formed either at 0° or at -25° .

The α -diacetate, melting at 153° , gives a somewhat better yield of benzoin nitrate, 25 grams yielding 2 grams of benzoin nitrate, melting at 167° , and 2 grams of unchanged α -diacetate, melting at 153° . None of the β -isomeride is formed in the reaction.

Benzoin mononitrate crystallises from 90 per cent. alcohol in beautiful, colourless plates, and melts at 167° (uncorr.). It is very sparingly soluble in ether, light petroleum, or cold 90 per cent. alcohol, but dissolves fairly readily in boiling 90 per cent. alcohol. On hydrolysis with potassium hydroxide, it yields benzoin and potassium nitrate, and on heating with concentrated nitric acid it gives benzil. The complete combustion of the nitrate is exceedingly difficult, as it burns explosively; the analytical results, however, leave no doubt as to the composition of the compound:

0.1461 gave 0.3482 CO_2 and 0.0732 H_2O . $\text{C}=65.0$; $\text{H}=5.56$.

0.1891 „ 8.70 c.c. N_2 (moist) at 15° and 762 mm. $\text{N}=5.41$.

0.2090 „ 9.25 c.c. N_2 „ „ 14° „ 763 mm. $\text{N}=5.23$.

0.4838, in 20 c.c. alcohol, gave $\text{E}=0.16^{\circ}$. $\text{M.W.}=238$.

$\text{C}_{14}\text{H}_{11}\text{O}_4\text{N}$ requires $\text{C}=65.37$; $\text{H}=4.28$; $\text{N}=5.45$ per cent.

$\text{M.W.}=257$.

The substance melting at 188° is very sparingly soluble in 90 per cent. alcohol, but can be obtained crystalline from this solvent in fine, light yellow needles. It is unchanged by boiling with potassium hydroxide, and is therefore not a nitrate; its composition corresponds with that of nitrobenzoin:

0.3482 gave 16.4 c.c. N_2 (moist) at 13° and 760 mm. $\text{N}=5.57$.

$\text{C}_{14}\text{H}_{11}\text{O}_4\text{N}$ requires $\text{N}=5.45$ per cent.

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