

*The Benzoin Reaction with Terephthalaldehyde.*

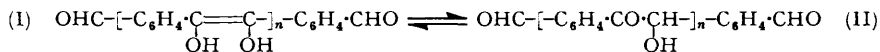
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A polymer containing benzoin units is obtained by self-condensation of terephthalaldehyde. Certain of its derivatives have been prepared and on oxidation with nitric acid it gives a polymer containing benzil units.

THE benzoin condensation of dialdehydes appears to have been studied only by Grimaux (*Compt. rend.*, 1876, **83**, 826) and Oppenheimer (*Ber.*, 1886, **19**, 1814) who worked with terephthalaldehyde. A re-investigation of the product obtained in 90% yield by treatment of terephthalaldehyde with potassium cyanide has shown that it is polymeric. Although not of very high molecular weight, it is not the dimer  $\text{OHC}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  as claimed by Oppenheimer. Its insolubility in most organic solvents has precluded precise determination of the chain length. The polymer is almost colourless and softens and melts at 170—200°, giving a viscous red liquid which sets on cooling to a brittle glass.

In the early stages of the reaction an intense red colour develops, which fades as reaction proceeds and is rapidly removed by treatment with acid and restored by alkali. The red colour is more persistent when the reaction is carried out in an atmosphere of nitrogen. These facts would find a ready explanation in terms of the coloured enediol (I) and colourless "benzoin" (II); however, stable dienols are known only for hindered 2:6-disubstituted benzoin (Ide and Buck, "Organic Reactions," Wiley, New York, 1948, Vol. IV, p. 269) and for the benzoin of pyridine-2-aldehyde where the dienol is stabilised by hydrogen bonding with the pyridine nitrogen atom (Hensel, *Angew. Chem.*, 1953, **65**, 491; Cramer and Krum, *Ber.*, 1953, **86**, 1586).



The analytical data for the polymer suggest that some oxidation, possibly of the aldehyde end-groups, also takes place during the reaction if the system is exposed to the atmosphere.

The polymer dissolved in concentrated aqueous alkali and from the product obtained on acidification some terephthalic acid was isolated (cf. the cleavage by alkali of benzoin; Sharpe and Miller, *J. Amer. Chem. Soc.*, 1952, **74**, 5643). This acid was obtained in good yield when an alkaline solution of the polymer was oxidised with hydrogen peroxide.

Oxidation with nitric acid furnished a bright yellow amorphous material with properties and elementary composition suggesting the structure  $\text{HO}_2\text{C}\cdot[\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}]_n\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ . It had an indefinite melting point ( $\sim 350^\circ$ ), was insoluble in the common solvents but soluble in aqueous alkali, formed derivatives with hydroxylamine and phenylhydrazine, and gave a colourless product on reductive acetylation.

Phthalaldehyde and isophthalaldehyde appear to undergo condensations analogous to those of terephthalaldehyde.

#### EXPERIMENTAL

*"Benzoin" Reaction of Terephthalaldehyde.*—A few drops of potassium cyanide solution (10 g. in 20 ml.) were added to a 10% solution of the aldehyde (*Org. Synth.*, 20, 92) in ethanol at room temperature. A red colour developed immediately and in a short time the solution became cloudy, a dark red precipitate then coagulating. This became colourless overnight, but was more readily decolorised when washed with very dilute acid. The product, obtained in 90% yield, was an off-white, amorphous solid softening and melting in the range  $170\text{--}200^\circ$ , almost insoluble in normal organic solvents, ethylene carbonate being the only solvent [Found: C, 70.0; H, 4.6. Calc. for  $(\text{C}_8\text{H}_6\text{O}_2)_n$ : C, 71.8; H, 4.4%]. If only the terminal aldehyde groups had been oxidised, the analysis approximates to that of a polymer comprising seven terephthalaldehyde units with two terminal carboxylic acid groups (Calc.: C, 70.0; H, 4.3%).

When the condensation was carried out in an atmosphere of nitrogen the red colour persisted for up to 20 hr. On addition of a few drops of mineral acid the colour changed to yellow and on addition of dilute sodium hydroxide solution this reverted to red. This change was reversible. Admission of air caused a gradual fading of the red colour. When the reaction was carried out under oxygen only a very pale red colour was observed.

The polymer dissolved in boiling phenylhydrazine. Pouring the solution into 2N-hydrochloric acid precipitated a yellowish-brown solid which dissolved in acetone and was reprecipitated by alcohol and water. It had an indefinite m. p.  $\sim 250^\circ$  (Found: C, 74.5; H, 5.8; N, 6.0%). Partial conversion into a phenylhydrazone had taken place.

The polymer dissolved in aqueous caustic alkalis, and the concentration of the alkali solution did not seem to be critical. In 10% sodium hydroxide solution the material first blackened and dissolved, giving a clear red solution. On acidification a white solid was obtained from which some terephthalic acid was extracted and characterised as the dimethyl ester, m. p.  $139^\circ$ .

To the polymer (0.5 g.) dissolved in 5% sodium hydroxide solution (100 ml.), hydrogen peroxide (5 ml.; 30-vol.) was added and the solution was gently heated until it became colourless; then it was acidified. The product (0.5 g.) was shown to be terephthalic acid by conversion *via* the acid chloride into dimethyl terephthalate, m. p.  $139^\circ$  (0.4 g.).

*Oxidation to the "Benzil" Polymer.*—The aldehydic polymer (2 g.) was heated with water (1 ml.) and concentrated nitric acid (10 ml.) on a steam-bath for 2 hrs. Dissolution occurred and later a bright yellow compound was precipitated. More of this was obtained on dilution with water, giving a total yield of 90% (Found: C, 70.0; H, 3.3%). It had m. p.  $\sim 350^\circ$  after preliminary charring and was insoluble in all organic solvents tried, including ethylene carbonate. It was not soluble in sodium hydrogen carbonate solution, but dissolved readily in sodium hydroxide solution giving a very dark solution. If the acid polymer has the structure suggested, a value  $n = 5$  demands: C, 70.1; H, 3.1%, in close agreement with the values found. A value  $n = 0$  (*i.e.*, for  $\text{C}_{16}\text{H}_{10}\text{O}_6$ ) requires C, 64.4; H, 3.3%. Therefore the initial product is not the dimer postulated by Oppenheimer (*loc. cit.*).

The oxidised polymer dissolved in excess of hot phenylhydrazine, yielding, as above, a dull yellow amorphous product, m. p.  $\sim 260^\circ$  after softening at  $220^\circ$ , soluble in acetone, less soluble in ethanol (Found: C, 73.2; H, 4.30; N, 11.6. A *monohydrazone* with  $n = 5$  requires C, 73.6; H, 4.4; N, 11.2%).

An amorphous "oxime" (Found: N, 7.1%), m. p.  $210\text{--}230^\circ$ , was also obtained.

This work, published by permission of the Director of this Laboratory, was largely carried out by P. B. Tinker of the University of Sheffield under the vacation-student scheme of the Department of Scientific and Industrial Research in 1952. A complete study of the problem was not possible and it is not proposed to pursue the investigation.