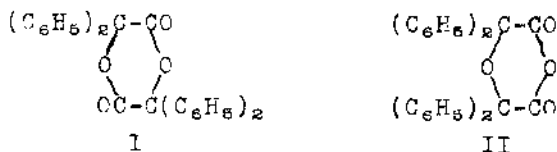


BENZILIDE AND ITS REDUCTION BY LITHIUM ALUMINUM HYDRIDE

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ABSTRACT - Three known methods for converting benzilide into benzilide gave identical material. A new reaction of benzilide supporting inner ester structure for its reduction with LiAlH_4 to produce 1,1-diphenyl-1,2-ethanediol in essentially quantitative yield. This diol was readily cleaved by periodic acid into benzophenone and formaldehyde. No support for Stolle's acid anhydride structure for benzilide was found.

Two structures (I, II) have been proposed for benzilide. Wasserman (1950) used the infrared spectrum to prove that their sample of benzilide was of structure I, not II, but



they failed to mention the source of their I. Certainly, however, (Wasserman, 1960) it was not via diphenylchloroacetic anhydride, $(\text{Ph}_2\text{CClCO})_2\text{O}$ (III), which was the intermediate that was claimed by Stolle (1910) for his synthesis of II.

Stollé made his III from benzoic acid, $\text{Ph}_2\text{C}(\text{OH})\text{COOH}$ (IV), and thionyl chloride in hot carbon tetrachloride, then heated the product in benzene with yellow mercuric oxide. In efforts to duplicate this work, we only obtained benzophenone. No III was obtained. Comparably, Wasserman (1960) obtained only benzophenone. It is known (Meyer, 1901) that thionyl chloride vigorously converts benzoic acid into benzophenone.

That II could not be the structure of benzilide should have been evident from data reported in Klinger and Standke's original paper (1889) on benzilide. The compound was crystallized from ethanol for purification. An acid anhydride of structure II would instead have reacted with ethanol to form

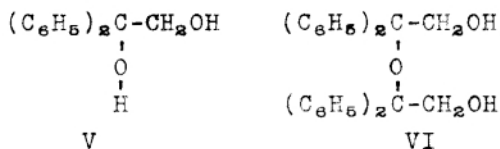
an acid ester. Neither Stolle nor Staudinger (1911), who accepted II, called attention to this fact.

SOURCES

To obtain further critical evidence regarding the structure we reduced benzilide with lithium aluminum hydride. For this purpose we prepared benzilide of m.p. 193-196° by directions given by Einhorn (1902), Staudinger (1911), and Arnold (1949). These methods all support structure I by following the pattern of "acid plus alcohol" since, respectively, these are reactions of IV with phosgene and pyridine; heating IV at 155-165° (15 mm) for 12 hr; refluxing a solution of IV in xylene in the presence of a little p-toluenesulfonic acid. Yields following the first two methods were only 9-13% but that of the third method was 65% which corresponded to the stated yield. Mixture m.p. determinations of the several samples showed no depression, and the infrared spectrum of each showed a single strong carbonyl peak at 1762-1759 cm⁻¹ confirming Wasserman and Zimmerman (1950).

RESULTS

Glycol V should arise by reduction of inner ester I, whereas a quite different diol, VI, should arise from II.



Each of our three samples of benzilide was refluxed in a slurry of dry ether for 24 hr with LiAlH₄, followed by alkaline hydrolysis (Amundsen, 1951). Each sample gave rise to an essentially quantitative yield of 1,1-diphenyl-1,2-ethanediol (V), m.p. 119-120°. No VI was found. An authentic sample of the glycol was prepared by reaction of phenylmagnesium bromide and ethyl glycolate (Paal, 1906). Its m.p. was 118-119° and its mixed m.p. with each of the three products of m.p. 119-120° was 118-119°.

It was established that V was readily cleaved into benzophenone and formaldehyde by use of periodic acid solution. Alcohol/water (about 1:1) was used as solvent for V since it was insoluble in water. Just enough alcohol was used to maintain solubility. Otherwise, the directions of Reeves (1941) were followed.

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