The Structure of Benzilide

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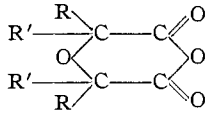
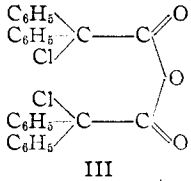
The pyrolysis of α-hydroxy acids which may result in polyester or lactide formation[1,2,3] has yielded products which, in certain instances, have been formulated as ether-anhydrides. For example, it has been proposed[4] that in the pyrolysis of mandelic acid and benzilic acid, the anhydrides (I) and (II), respectively, are formed. The interaction of two moles of α-hydroxy acid in this manner (head-to-head elimination of water from the two hydroxyl groups) has been ascribed[4] to the enhanced reactivity of the benzyl-type alcohol, where there is aryl substitution on the hydroxyl-bearing carbon.



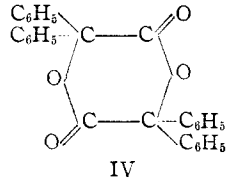
I R = H, R′ = C_6H_5

II R = R′ = C_6H_5

In the case of benzilide (derived from benzilic acid) the assignment of an ether-anhydride structure (II) to the pyrolysis product is based primarily on synthetic evidence reported by Stollé.[5] When α,α'-dichlorotetraphenylacetic anhydride (III) was heated with mercuric oxide in boiling benzene, benzilide, identical with the pyrolytic product, was isolated. In this reaction, substitution of oxygen for the two chlorine atoms would yield the anhydride (II); Stollé assumed that a lactide structure (IV) could result only by rearrangement.



III



IV

On the basis of the purely chemical evidence, such as the ready hydrolysis of benzilide to benzilic acid, the cleavage to benzophenone, diphenylketene and carbon dioxide by slow distillation, and the formation of diphenylacetic acid anilide by heating with aniline, one cannot distinguish between the two possibilities, (II) and (IV). However, infrared data, reported here, clearly indicate that benzilide has the lactide structure (IV).

Both *meso*-lactide and benzilide exhibit a single intense band in the lactone region of the infrared at 5.66–5.69 μ (Fig. 1), whereas glutaric anhydride shows the typical anhydride splitting in the carbonyl region, with absorption maxima at 5.55 and 5.68 μ. It may thus be concluded that the lack of correspondence between benzilide and the model

(1) Drechsel, *Ann.*, **127**, 154 (1863); Fittig and Thomson, *ibid.*, **200**, 79 (1879).

(2) Krafft and Dyes, *Ber.*, **28**, 2591 (1895).

(3) Bischoff and Walden, *Ann.*, **279**, 100 (1894).

(4) Hurd, "The Pyrolysis of Carbon Compounds," A. C. S. Monograph Series, 1929, p. 433.

(5) Stollé, *Ber.*, **43**, 2473 (1910).

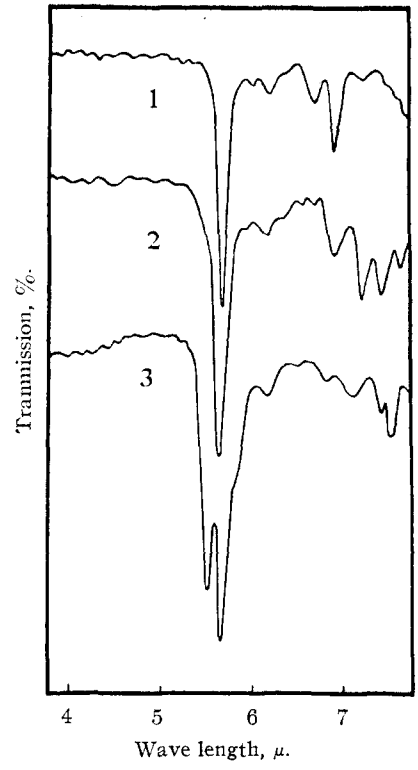


Fig. 1.—Infrared absorption spectra in chloroform: (1) benzilide; (2) meso-lactide; (3) glutaric anhydride.

six-membered cyclic anhydride in the infrared makes the ether-anhydride formulation extremely unlikely, whereas the good agreement between the spectra of benzilide and the related symmetrical lactide model represents convincing evidence in favor of the lactide structure (IV).

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Micro Syntheses with Tracer Elements. IV. The Synthesis of Hexestrol Labeled with Tritium[1]

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Information was desired regarding the stability of organic compounds containing the isotope tritium in place of hydrogen. Since a higher concentration of radioactivity can be imparted to an organic compound by means of tritium than with almost any other element, this method of labeling should prove to be ideal for those chemical entities which produce profound biologic changes in the living system when present in exceedingly small concentrations.

A group of compounds having such an effect are the sex hormones. Minute amounts of these chemical entities can bring about deep seated

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