Anal. Calcd. for $C_{16}H_{10}O_3Br_2$: C, 46.74; H, 2.46; Br, 38.9. Found: C, 47.1; H, 2.44; Br, 38.9.

Summary

The synthesis of 1,4-diphenylbutane-1,2,4-trione enol is described. The enol exists in two forms which are regarded as stereoisomers of dibenzoylethenol. The structures and configurations are discussed on the basis of a preliminary study which includes isomerization, hydrolysis, ozonization and alkylation with diazomethane.

The structure, configurations, and some reactions of the dibenzoylethenol ethers are considered.

The formation and hydrolysis of dibenzoylaminoethylene is described and the structure established by ozonization.

The alkylation of 1,4-diphenylbutane-1,2,4-trione enol by alcohol and acids and by means of dialkyl sulfates leads to the enol alkyl ethers of 1,4-diphenyl-1,2-diketo-3-butene-4-ol, rather than of dibenzoylethenol. The reactions and determination of structure of these ethers are considered.

The enol reacts with acetic anhydride and acetyl chloride (with sulfuric acid) like a typical unsaturated 1,4-diketone, giving furans.

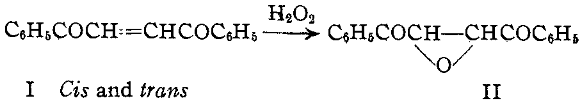
UNIVERSITY, VIRGINIA RECEIVED JUNE 5, 1934

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, NO. 135]

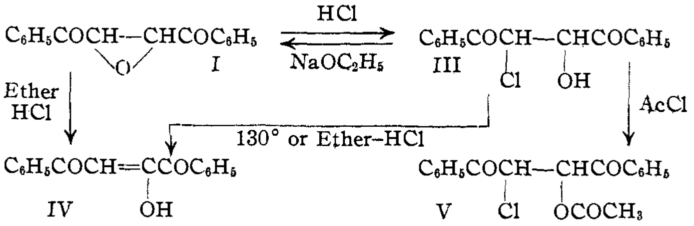
Dibenzoylethylene Oxide and Chlorohydrin

BY ROBERT E. LUTZ AND FRANK N. WILDER

Dibenzoylethylene oxide II is of interest as an oxido-1,4-diketone and because of its relation to saturated and unsaturated 1,4-diketones and the 1,2,4-triketones, particularly with respect to a convenient method of preparing dibenzoylethenol IV.[1] It is prepared from both *cis* and *trans* dibenzoylethylenes I by the action of hydrogen peroxide and is transformed by means of ethereal hydrogen chloride into dibenzoylethenol IV, and by hydrochloric acid in 80% ethanol into the chlorohydrin III. The chlorohydrin is stable under ordinary conditions and gives a monoacetyl derivative (V); when heated at 130° it gives dibenzoylethenol and hydrogen chloride; the action of sodium ethylate converts it back into the oxide. These various reactions are typical and establish the structures of both the oxide and chlorohydrin.



$$\underset{\text{I \textit{Cis} and \textit{trans}}}{C_6H_5COCH{=}CHCOC_6H_5} \xrightarrow{H_2O_2} \underset{\text{II}}{\underset{\diagdown O \diagup}{C_6H_5COCH{-}CHCOC_6H_5}}$$



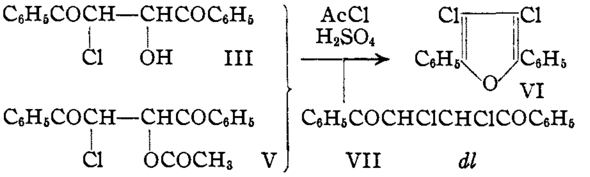
The mechanism of the transformation of dibenzoylethylene oxide into dibenzoylethenol by the action of ethereal hydrogen chloride probably involves the chlorohydrin III which is similarly converted into the ethenol under these conditions. A different and unstable chlorine containing compound is isolated, however, on evaporation at room temperature of the ethereal hydrogen chloride solutions resulting from the action of this reagent both on the chlorohydrin and also on the enol. This product is apparently a hydrogen chloride addition compound of the enol IV or its tautomer, $C_6H_5COCOCH{=}C(OH)C_6H_5$; it loses hydrogen chloride spontaneously on standing or on warming with solvents to give dibenzoylethenol; it gives no simple derivatives and reacts in the same sense as dibenzoylethenol and hydrogen chloride, the products of spontaneous decomposition. When heated for a short time with methyl or ethyl alcohol it is converted into the enol ethers, $C_6H_5COCOCH{=}C(OR)C_6H_5$. The latter are obtained also directly from the oxide and from the enol[1] by the action of alcoholic hydrogen chloride.

Both the chlorohydrin III and its acetate V react with acetyl chloride and sulfuric acid to give 2,5-diphenyl-3,4-dichlorofuran VI which is known.[2]

---

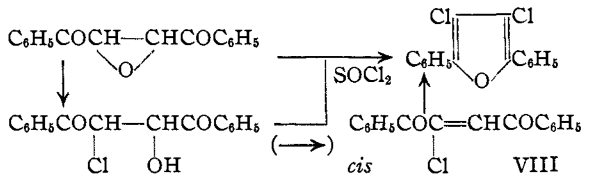
(1) Lutz, Wilder and Parrish, THIS JOURNAL, **56**, 1980 (1934).

(2) Conant and Lutz, *ibid.*, **47**, 881 (1925). The action of acetic anhydride and sulfuric acid gives, instead of diphenylacetoxychlorofuran, a new product which is now under investigation.



The reaction involves replacement of the hydroxyl and acetoxy groups as well as dehydration to the furan. The introduction of the second chlorine must take place prior to furan ring closure because otherwise 2,5-diphenyl-3-acetoxy-4-chlorofuran (known[1]) would have been formed and isolated since it is stable under these conditions. The reaction possibly involves replacement of the hydroxyl or acetoxy group with chlorine giving *dl*-dibenzoyldichloroethane VII which reacts similarly. The *meso* isomer and *cis* and *trans* dibenzoylchloroethylenes do not give the dichlorofuran under these conditions and therefore cannot be intermediates. It is noteworthy that the *dl*-dibenzoyldichloroethane is dehydrated to the furan easily under these conditions in contrast with the *meso* isomer which is stable.[3]

The action of phosphorus pentachloride or thionyl chloride both on the chlorohydrin III and on the oxide gives diphenyldichlorofuran VI instead of the expected *dl* or *meso* dibenzoyldichloroethanes VII both of which are stable under the reaction conditions and therefore are not intermediate products. It is noteworthy that it has not been possible to replace the hydroxyl group of the chlorohydrin directly with chlorine without furan formation, as can be done in the case of dibenzoylhydroxyethane.[4]



The mechanism of the reactions possibly involves conversion of the oxide to a chlorohydrin (or a derivative) and dehydration of the chlorohydrin either directly to a furan, or, as is more likely, to the *cis* dibenzoylchloroethylene VIII which gives the dichlorofuran under these conditions.[4]

Experimental Part

1,2-Dibenzoylethylene Oxide (II).—A 20% solution of hydrogen peroxide (prepared[5] by adding 40 g. of sodium peroxide slowly to 325 cc. of ice and water, and adding 71 cc. of concd. hydrochloric acid at 5° and then 50 cc. of alcohol) was added quickly with vigorous stirring to a suspension of 60 g. of finely crystallized dibenzoylethylene in 1200 cc. of ethanol (obtained by chilling a hot solution to 40°). The yellow color was quickly bleached. The mixture was cooled and the colorless oxide filtered off (nearly pure). A small amount was recovered from the filtrate on dilution with water; yield 50–55 g. (78–86%); recrystallized from ethanol, m. p. 128–129° (corr.).

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.24; H, 4.78. Found: C, 75.82, 75.61; H, 4.86, 4.73.

The oxide is stable toward acetyl chloride or acetic anhydride (with sulfuric acid), boiling glacial acetic acid, and thionyl chloride (25°). It reacts with phosphorus pentachloride at 100° (but not at 25°) giving a yield of 25% of 2,5-diphenyl-3,4-dichlorofuran. Refluxing for one hour with thionyl chloride gave a nearly quantitative yield of this furan.

Hydrolysis of the oxide with alcoholic sodium methylate or hydroxide was without result.

1,2-Dibenzoylethylene Chlorohydrin (IV).—A suspension of 10 g. of the above oxide in a mixture of 200 cc. of 20% absolute ethanolic hydrogen chloride and 35 cc. of water was allowed to stand six days. The solvent was then evaporated in a current of air at room temperature and the residue crystallized from ethanol; yield 7 g.; m. p. 102° (corr.).

Anal. Calcd. for $C_{16}H_{13}O_3Cl$: Cl, 66.5; H, 4.54; Cl, 12.3. Found: C, 66.3; H, 4.41; Cl, 12.2.

The chlorohydrin reacted with acetyl chloride and sulfuric acid under the following conditions which were used as standard in this work. A solution of the compound (0.5 g.) in 5 cc. of acetyl chloride containing 5–6 drops of concd. sulfuric acid was allowed to stand for fifteen to thirty minutes at room temperature and was then decomposed in water. The supernatant liquid was decanted from the coagulated residue which was then crystallized from ethanol and identified as 2,5-diphenyl-3,4-dichlorofuran by mixed m. p.; yield 0.4 g. The action of an excess of phosphorus pentachloride (room temperature) and of thionyl chloride (refluxing for one hour) also gave this product in similar yields.

The chlorohydrin (1 g.), when warmed with a solution of 0.2 g. of sodium in 15 cc. of methanol, gave 0.65 g. of the oxide.

Pyrolysis of 1 g. at 125–130° for fifteen minutes gave fumes of hydrogen chloride. The residue, when crystallized from ethanol, gave 0.5 g. of dibenzoylethenol (the product was difficult to free from halogen, and probably contained a trace of dibenzoylchloroethylene).

1,2-Dibenzoylethylene Chlorohydrin Acetate (V).—Prepared by the action of cold acetyl chloride (one hour) on the chlorohydrin; crystallized from ethanol; m. p. 71.5° (corr.).

Anal. Calcd. for $C_{18}H_{15}O_4Cl$: C, 65.34; H, 4.57; Cl, 10.72. Found: C, 65.52; H, 4.79; Cl, 10.92.

With acetyl chloride and sulfuric acid (the standard procedure) 0.5 g. gave 0.4 g. of the dichlorofuran.

The Conversion of the Oxide into Dibenzoylethenol.—Fifty grams of the oxide II was suspended in 300 cc. of

---

[3] *Cf.* the analogous difference in the ease of dehydration of the *d,l* and *meso* dibenzoyldibromoethanes [Lutz, THIS JOURNAL, **48**, 2916 (1926)].

[4] Lutz and Wilder, *ibid.*, **56**, in press (1934).

[5] *Cf.* Kohler, Richtmyer and Hester, *ibid.*, **53**, 213 (1931).

ether (previously saturated at 0° with hydrogen chloride) and allowed to stand for twenty-four hours or longer, with occasional shaking, until all of the oxide was dissolved. A yellow solution resulted. The solvent was then evaporated under reduced pressure and the residue heated at 75° under water pump vacuum until the hydrogen chloride was completely expelled (about three hours). The residue was recrystallized from ethyl acetate–petroleum ether mixtures; yield 40 g. of pure ethenol (80%) of m. p. 88–89° (corr.). Repeated crystallizations by this method and also from ethanol did not change the melting point nor remove the last faint trace of halogen (flame test). Chlorine analyses showed, respectively, 0.0 and 0.1% chlorine, which is negligible.

Dibenzoylethenol or dibenzoylethylene chlorohydrin (IV) react with ethereal hydrogen chloride in the same way as the oxide and may be substituted in the above reactions.

The intermediate chlorohydrin is unstable and loses hydrogen chloride spontaneously with such ease that the compound has not yet been isolated in a pure state. When the ethereal hydrogen chloride solution (above) was allowed to evaporate in a current of air it was obtained as a colorless crystalline residue which was recrystallized from ether by adding petroleum ether; it melted at 75–80°, and gave a chlorine analysis of 7.9% (calcd., 12.3). On further crystallizations, or when warmed gently alone or in solvents, it loses hydrogen chloride, going finally into dibenzoylethenol. When refluxed in methanol or ethanol it gives nearly theoretical yields, respectively, of 1,4-diphenyl-4-methoxy-3-butene-1,2-dione and the ethoxy analog. (Dibenzoylethenol reacts similarly with methanol or ethanol containing a small amount of hydrogen chloride.)

Stability of *dl* and *meso* Dibenzoyldichloroethanes toward Phosphorus Pentachloride, Thionyl Chloride and Acetyl Chloride.—These tests were made because of their importance in connection with the mechanism of reaction between these reagents and various saturated and unsaturated 1,4 diketones. These dichlorides were recovered nearly quantitatively, unchanged, (a) when heated for one hour at 100° with phosphorus pentachloride, with or without added phosphorus oxychloride and gaseous hydrogen chloride, and (b) when heated in thionyl chloride (with a stream of hydrogen chloride and sulfur dioxide passing through), refluxing for one hour.

The *meso* dichloride was recovered unchanged upon standing for fifteen minutes in 10 cc. of acetyl chloride containing 5–6 drops of concd. sulfuric acid, but the *dl* isomer under these conditions was converted nearly quantitatively into diphenyldichlorofuran.

Summary

The preparation and typical reactions of dibenzoylethylene oxide and chlorohydrin are described, including their conversion into dibenzoylethenol.

UNIVERSITY, VIRGINIA

RECEIVED JUNE 5, 1934

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

Some Physical Constants of Anabasine

BY O. A. NELSON

Anabasine, an isomer of nicotine, and present to the extent of approximately 2% in *Anabasis aphylla* L., has been found to be toxic to a number of insects.[1,2] In view of the available supply and its promise as a valuable insecticide it was considered advisable to prepare a sample of high purity, and to determine some of the more important physical constants.

Purification of Material.—The commercial material from which the anabasine was obtained was a solution containing approximately 44% total alkaloids in water. The solute consisted of 72% anabasine, the remainder being lupinine, other alkaloids and miscellaneous plant materials not identified.

The mixture was treated with strong caustic solution and centrifuged. The resulting mixture of alkaloids and other impurities was separated from anabasine by converting the latter into the nitroso derivative, after which the anabasine was recovered by treatment with hydrochloric acid followed by sodium hydroxide.

The dark brown product obtained at this stage was freed from tarry material by distillation at 10–15 mm. pressure, and an attempt was made to purify it further by fractionation in a 23-plate column under pressure of 2–2.5 mm., at which pressure about 88% distilled at a temperature of 104 ± 1°. It was observed, however, that the distillate was not miscible in all proportions with water, as it should have been, indicating that some change had taken place during the fractionation. The plates of the fractionation column were made from nickel gauze, therefore dehydrogenation may have taken place. The composition of the water-insoluble compound was not ascertained, but it was found to be readily removed by extracting the aqueous solution with ether, which took up very little of the anabasine.

Final purification was accomplished by means of a Hickman still at a temperature of 40–50° and under a pressure of 4×10^{-4} to 2.5×10^{-4} mm. The anabasine obtained was water white and on cooling in a carbon dioxide–alcohol trap solidified to a viscous mass which appeared to crystallize after remaining at the low temperature overnight.

The pure anabasine was miscible in all proportions in water, and showed the following constants: specific gravity $^{20}_{20}$ 1.0481; n^{20}_{D} 0.5443; $[\alpha]^{20}_{D}$ −59.66°. A. Oréchoff

---

(1) F. L. Cambell, W. N. Sullivan and C. R. Smith, *J. Econ. Entomol.*, **26**, 500 (1933).

(2) P. Garman, *Conn. Agr. Exp. Sta. Bull.*, **349**, 433 (1933).