2-Bromodecene-1.—A mixture of 45 g. of 2-bromo-decene, 400 ml. of ammonia, and 200 ml. of ether was vigorously agitated and treated with a solution of 12 g. of sodium in 200 ml. of ammonia. On working up the product two fractions were obtained: Fraction I, 16 g., b. p. 75–78° at 30 mm., n_D^{25} 1.4215, d_{25} 0.743; Fraction II, 10 g., b. p. 138–146° at 23 mm., n_D^{24} 1.4296. Fraction I was soluble and Fraction II insoluble in ethanol. Fraction I is undoubtedly decene-1 as indicated by the following values recently reported[10] for this compound: b. p. 171–173°, d_{20} 0.7447, n_D^{20} 1.4259. Fraction I did not give even the slightest opalescence with alkaline mercuric cyanide solution. On bromination the decene took the calculated quantity of bromine and gave 27 g. of material: b. p. 145–160° at 18 mm., d_{25} 1.324, n_D^{24} 1.4891. On treatment with sodamide[11] in liquid ammonia the bromide gave a good yield of decyne-1.

(10) Waterman, van't Spijker and von Westen, *Rec. trav. chim.* **48,** 1097 (1929).

(11) Vaughn, Vogt and Nieuwland, to be published.

Fraction II was refractionated and gave 7 g. of material: b. p. 142.5° at 28 mm., n_D^{23} 1.4308, d_{25} 0.7636, γ_{25} 26.46 dynes/cm. The material was insoluble in ethanol, water and hydrochloric acid and reacted very slowly or not at all with bromine in carbon tetrachloride. It gave no precipitate with alkaline mercuric cyanide solution.

Summary

1. Six organic halides which give acetylenes when dehydrohalogenated have been treated with sodium in liquid ammonia. In some cases the halogen was replaced by hydrogen and in others acetylenes were obtained.

2. Acetylenes prepared by dehydrohalogenation with sodium in ammonia are contaminated by hydrogenation products.
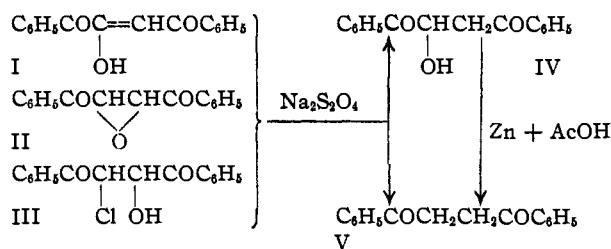
NOTRE DAME, INDIANA   RECEIVED JUNE 4, 1934

The Reduction of Dibenzoylethenol and of Dibenzoylethylene Oxide and Chlorohydrin

BY ROBERT E. LUTZ AND FRANK N. WILDER

The reduction of dibenzoylethenol (I) and dibenzoylethylene oxide II and chlorohydrin III with zinc and glacial acetic acid gives largely dibenzoylethane V. With sodium hydrosulfite, however, there are obtained mixtures of dibenzoylethane and dibenzoylhydroxyethane IV; the latter is stable under these conditions and is therefore an independent end-product of the reaction, but it is reduced further to dibenzoylethane by means of zinc and glacial acetic acid.

C_6H_5COC=$CHCOC_6H_5$
I   OH
$C_6H_5COCHCHCOC_6H_5$
II   \O/
$C_6H_5COCHCHCOC_6H_5$
III   Cl OH

$C_6H_5COCHCH_2COC_6H_5$
        OH   IV
$Na_2S_2O_4$
                  Zn + AcOH

$C_6H_5COCH_2CH_2COC_6H_5$
V

Dibenzoylethenol in some instances appears to function in the sense of the tautomeric enol form, $C_6H_5COCOCH$=$C(OH)C_6H_5$.[1] On the basis of this formulation reduction to dibenzoylhydroxyethane would be expected, but the loss of the oxygen during the sodium hydrosulfite reduction would be difficult to account for. The
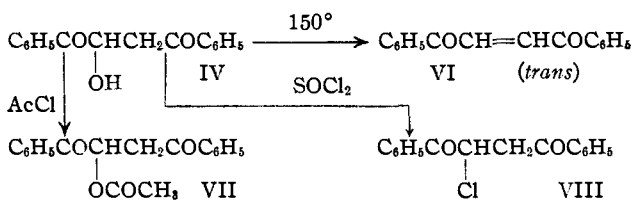
(1) Lutz, Wilder and Parrish, THIS JOURNAL, **56**, 1980 (1934).

ease of reduction of dibenzoylethenol is comparable with that of its alkyl ethers, C_6H_5COC-(OCH_3)=$CHCOC_6H_5$, whereas the isomeric methyl and ethyl ethers, $C_6H_5COCOCH$=C-$(OR)C_6H_5$, are attacked by these same reducing agents only under considerably more drastic conditions and are not affected by sodium hydrosulfite or by zinc and glacial acetic acid under the usual conditions. It is evident, therefore, that only the enol form I, dibenzoylethenol, is involved.
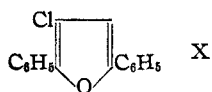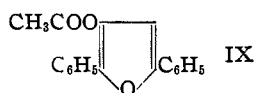
Dibenzoylhydroxyethane was shown to have the structure IV by the various transformations which are illustrated in (2). It is converted into an acetyl derivative (VII) by the action of cold acetyl chloride or acetic anhydride at 70°. When heated with acetyl chloride, however, it behaves like a tertiary alcohol, the hydroxyl group being replaced by chlorine giving dibenzoylchloroethane VIII. The latter reaction is accomplished easily, also using benzoyl chloride or thionyl chloride. The methoxyl group in dibenzoylmethoxyethane, $C_6H_5COCH(OCH_3)CH_2COC_6H_5$, is similarly replaced by chlorine with phosphorus pentachloride (a reaction which confirms this structure[2]). Pyrolysis, or the action of boiling acetic anhy-

(1) ... (2) Cf. Lutz, *ibid.*, **51**, 3008 (1929).

dride, converts dibenzoylhydroxyethane into *trans* dibenzoylethylene VI.

$$C_6H_5COCHCH_2COC_6H_5 \xrightarrow{150°} C_6H_5COCH=CHCOC_6H_5$$

$$\underset{OH}{|} \quad IV \quad SOCl_2 \quad VI \quad (trans)$$

AcCl |

$$C_6H_5COCHCH_2COC_6H_5 \qquad C_6H_5COCHCH_2COC_6H_5$$

$$\underset{OCOCH_3}{|} \; VII \qquad \underset{Cl}{|} \; VIII$$

As saturated 1,4 diketones, dibenzoylhydroxyethane and its acetate are readily converted into furans; with acetic anhydride and sulfuric acid they give 2,5-diphenyl-3-acetoxyfuran IX, and with acetyl chloride and sulfuric acid, 2,5-diphenyl-3-chlorofuran X.

$$C_6H_5-\underset{\overset{||}{O}}{\overset{2}{C}}-\underset{\overset{|}{OH}}{\overset{3}{C}}=\overset{4}{C}H-\underset{\overset{||}{O}}{\overset{5}{C}}C_6H_5 \xrightarrow[\text{addition}]{1,4} \left[C_6H_5C=C=CHCOC_6H_5 \atop \underset{OH}{|} + H_2O \right] \quad (3)$$

1,6-addition ↓

$$\left[C_6H_5C=C-CH=CC_6H_5 \atop \underset{OH\;OH}{|\;\;|} \quad \underset{OH}{|} \right]$$

$$C_6H_5COCH(OH)CH_2COC_6H_5 \qquad \qquad [C_6H_5COCH=CHCOC_6H_5]$$

↓

$$C_6H_5COCH_2CH_2COC_6H_5$$

$$\underset{C_6H_5 \diagdown \diagup C_6H_5}{\overset{CH_3COO}{\bigcirc}} \; IX \qquad \underset{C_6H_5 \diagdown \diagup C_6H_5}{\overset{Cl}{\bigcirc}} \; X$$

**The Mechanism of the Reductive Elimination of Functional Groups.**—The formation of dibenzoylethane during sodium hydrosulfite reduction of dibenzoylethenol calls to mind the elimination of chlorine from dibenzoylchloroethylene, $C_6H_5COC(Cl)=CHCOC_6H_5$, XI, during reduction with titanous chloride.[3] Since in both of these cases the expected primary reduction products are stable under the conditions involved, the functional groups must have been eliminated either before or simultaneously with (but not after) the saturation of the double bond. Loss of the groups beforehand would involve a simple 1,2-reaction, but the. alternate supposition must entail a more complicated process which may be interpreted in terms of 1,4-addition of hydrogens to the two electronegative elements located at the ends of the system O=C—C—O(or Cl).[4] In favor of the 1,4-mechanism is the fact that the ease of the reduction (involving relatively mild reducing agents in homogeneous solution) is of the same order as that of unsaturated 1,4-dike-

tones where the analogous 1,6-mechanism is involved.[2,5]

(2) The sodium hydrosulfite reduction of dibenzoylethenol, therefore, seems most reasonably interpreted in terms of competing 1,4- and 1,6-additions of hydrogen as outlined in (3), and the first step in the titanous chloride reduction of dibenzoylchloroethylene as exclusively a 1,4-reduction.
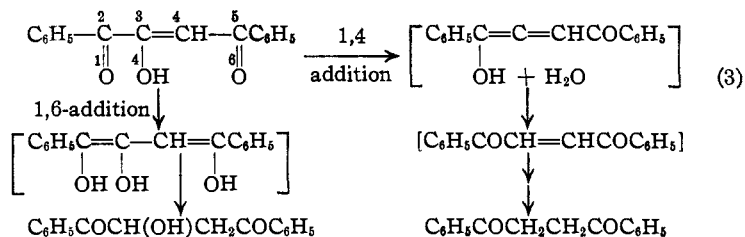
The sodium hydrosulfite reduction of dibenzoylethylene oxide (1) involves two competing processes. One of these, the reductive scission of the oxide ring, may be regarded either as a 1,2-addition of hydrogen directly to the ring, or as a 1,4-reduction of the system O=C—C—O of the α-oxido ketone, giving $C_6H_5C=CHCHCOC_6H_5$,

$$\underset{OH \qquad OH}{| \qquad \qquad |}$$

an enol form of dibenzoylhydroxyethane (IV), as an intermediate. The other reaction, reductive elimination of the oxido oxygen, involves the direct addition of two hydrogens to the oxygen (in a sense a 1,4-addition).

The reduction of dibenzoylethylene chlorohydrin, involving elimination of both the halogen and hydroxyl, may be interpreted as a 1,4-reduction of the system Cl—C—C—O, generating water, hydrogen chloride, and dibenzoylethylene (the latter being quickly reduced to dibenzoylethane). The electrolytic reduction of chlorodihydrocodide XII[4b] is an analogous reaction, wherein the same system of linkages is involved, but where the unsaturated primary reduction product XIII (corresponding with the intermediate dibenzoylethylene in the reduction of the chlorohydrin) is stable and is isolated as the end-product, the oxygen being retained in the

(3) Conant and Lutz, THIS JOURNAL, **47**, 881 (1925). For examples of somewhat analogous reductions see Houben, "Methoden der org. Chem.." 1925, Vol. II. p. 234, and also the reductive elimination of the enol oxygen from certain enol acetates and methyl carbonates during catalytic hydrogenation [Roll and Adams, *ibid.*, **53**, 3470 (1931); Michael and Ross. *ibid.*, **54**, 392 (1932); Boese and Major, *ibid.*, **56**, 950 (1934)].

(4) Here the double bond is conjugated with the C–O (or C–halogen) linkage. For examples, see reduction of pseudocodeine types [(a) Lutz and Small, *ibid.*, **54**, 4715 (1932); (b) **56**, 1738 (1934): (c) **56**, 1741 (1934)], cyclic β-bromobenzoylcrotonic ester [(d) Lutz, *ibid.*, **56**, 1378 (1934)], and cinnamyl alcohols [(e) Klages, *Ber.*, **39**, 2587 (1906)].

(5) The reductive elimination of amino from dibenzoylamino-ethylene and of halogen. hydroxyl and alkoxyl from substituted saturated 1,4-diketones such as dibenzoyl-hydroxy, chloro, alkoxy and aroxyethanes may also be interpreted as 1,4-additions. The loss of bromine in sodium hydrosulfite reduction of 2,4,6-tribromo-resorcinol, if it involves the pseudoquinoid form, would be better interpreted as 1,6-reduction of the system O=C—C=C—C—Br, or as direct 1,2-reduction of the aliphatic C–Br group, rather than as the 1,4-addition suggested by Davis and Harrington [THIS JOURNAL, **56**, 129 (1934)].

molecule by its second point of attachment to the morphine skeleton, at position 4.

XII   Chlorodihydrocodide

XIII   Dihydrodesoxycodeine-C
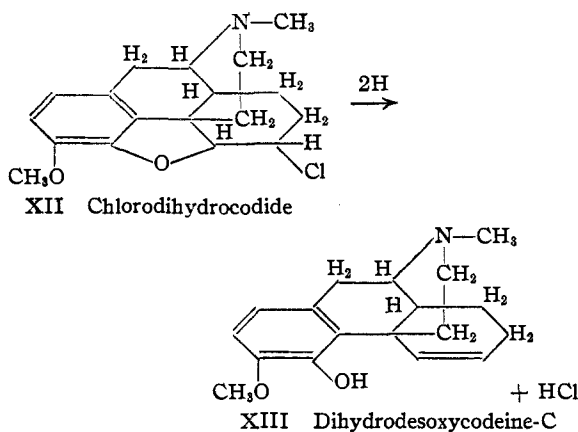
Experimental Part

Reduction with Zinc and Glacial Acetic Acid.—Dibenzoylethylene oxide was reduced to dibenzoylethane in yields averaging 75% when a solution of the substance in glacial acetic acid was treated with a large excess of zinc dust at 30–35° for fifteen minutes to two hours. Higher temperatures gave poorer yields and increasingly large amounts of resinous by-products. Dibenzoylethylene chlorohydrin acetate, reacting at refluxing temperature for fifteen minutes, gave dibenzoylethane in 80% yield. Dibenzoylhydroxyethane at 35° in fifteen minutes was reduced almost quantitatively to dibenzoylethane. In every case the product was isolated, after filtering off the zinc dust, by diluting the solution with water, crystallizing the precipitated organic material from ethanol, and identifying by mixed melting points.

In some of the reductions under mild conditions small amounts of dibenzoylhydroxyethane were found.

Reduction of dibenzoylethenol and dibenzoylethylene oxide, and chlorohydrin with titanous chloride in acetone at 20° and at refluxing temperature gave only resinous products.

Reductions with Sodium Hydrosulfite.—The reduction of dibenzoylethylene oxide (10-g. samples) in 200 cc. of 85% ethanol with 30 g. of sodium hydrosulfite at refluxing temperature for four hours gave a nearly theoretical yield of mixtures of dibenzoylethane and dibenzoylhydroxyethane from which the pure products were isolated in a ratio of yields of approximately 2–1. When the reaction was carried out at 60° with mechanical stirring the yield of dibenzoylhydroxyethane was much higher (in one instance 70%). At lower temperatures the reactions were incomplete. The crude product was isolated in crystalline form by diluting the reaction mixture with water. The two constituents were separated by laborious fractional crystallizations from ether or alcohol, dibenzoylethane being the less soluble. The products were identified in every case by mixed melting points.

Reduction of dibenzoylethenol and dibenzoylethylene chlorohydrin (as above, refluxing for one hour) gave nearly equal yields of dibenzoylethane and dibenzoylhydroxyethane.

Dibenzoylhydroxyethane in a typical reduction experiment as above (with 5 times by weight of sodium hydrosulfite, and refluxed for one hour), was recovered unchanged.

1,2-Dibenzoylhydroxyethane (IV).—Prepared as above by the sodium hydrosulfite reduction in 85% ethanol at 50–60°; crystallized from chloroform–ligroin mixtures; m. p. 87.5° (corr.).

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.55; H, 5.55. Found: C, 75.60; H, 5.67.

Samples of the above, allowed to react (a) with benzoyl chloride (standing overnight or heating at 50°) and (b) with thionyl chloride (refluxing for several minutes or standing at 25°), gave 80–85% yields of dibenzoylchloroethane.

Pyrolysis (thirty minutes at 150°) of 1 g. gave a residue from which 0.7 g. of *trans*-dibenzoylethylene was isolated on recrystallization from ethanol. Moisture condensed in the side arm and gave blue color with anhydrous copper sulfate.

Acetic anhydride (refluxing for one hour) converted the above into *trans*-dibenzoylethylene in 82% yield; standing at room temperature gave no reaction; at 75° it gave the acetate (see below).

Acetyl chloride (10 cc.) with 3 drops of concd. sulfuric acid on 1 g. (standing for ten minutes and decomposed in ice) gave 0.9 g. of diphenylchlorofuran (identified by mixed m. p.). The use of acetic anhydride instead of acetyl chloride gave 0.7 g. of diphenylacetoxyfuran. Acetyl chloride and sulfuric acid under these conditions were without effect on diphenylacetoxyfuran. Thionyl chloride at 25° was without effect on the acetate (VII).

1,2-Dibenzoylacetoxyethane (VII).—Prepared from 1-g. samples of IV by (a) standing in 5 cc. of acetyl chloride for thirty minutes and (b) heating in 10 cc. of acetic anhydride at 75° for one hour. It was isolated by decomposing the mixtures in ice and recrystallizing the precipitated organic material from ethanol; yields 80%; m. p. (sublimed in vac.) 116° (corr.).

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.90; H, 5.41. Found: C, 72.73; H, 5.45.

The action of acetyl chloride and sulfuric acid (above procedure) gave diphenylchlorofuran (identified by mixed m. p.).

Summary

The sodium hydrosulfite reduction of dibenzoylethenol and dibenzoylethylene oxide and chlorohydrin gives mixtures of dibenzoylethane and dibenzoylhydroxyethane. The reduction of the latter, and other typical reactions including pyrolysis, acetylation, and furan formation, are described.

The mechanism of reductive elimination of functional groups from certain of the substituted saturated and unsaturated 1,4-diketones is interpreted in terms of 1,4-addition.