when the oxide was added to the glycol, an exothermic reaction occurred at temperatures much lower than those required for condensation of the glycol directly to the dioxane. Some of the glycol was undoubtedly converted to the corresponding dioxane by self-condensation at higher temperatures.

Neutralization of the acidic reaction mixture with sodium bicarbonate before distillation decreased the yields of the substituted dioxanes by preventing the acid catalyzed cyclization which would have occurred during distillation. For example, only a 4% yield of trimethyl dioxane and a 9% yield of phenyl dioxane was obtained compared with 12% and 20–27% yields from identical reaction mixtures distilled without neutralization. This indicates that part of the ring closure which would have taken place in acidic media during the distillation did not occur after neutralization. Instead over 60% of the weight of the reaction mixture consisted of high boiling distillation residues and unreacted glycol.

CLEVELAND, OHIO

[CONTRIBUTION FROM MELLON INSTITUTE]

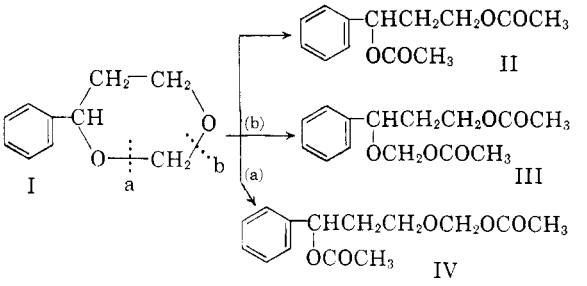
Reaction of 4-Phenyl-1,3-dioxane with Acetic Anhydride

H. MOE AND B. B. CORSON

Received June 26, 1959

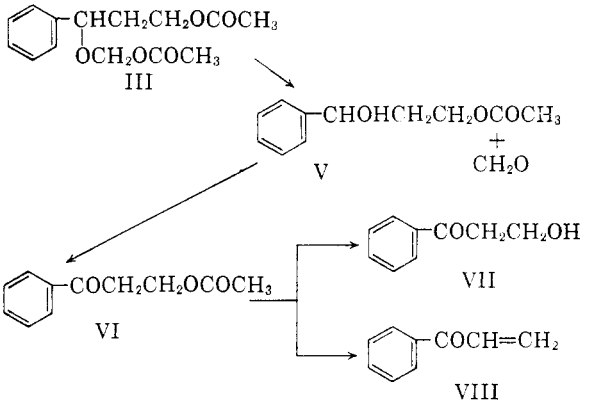
The acetylation of 4-phenyl-1,3-dioxane yields 1,5-diacetoxy-3-phenyl-2-oxapentane—not 1,3-diacetoxy-1-phenylpropane as has been elsewhere reported.

Shorygina[1] reports, without evidence, that the reaction between 4-phenyl-1,3-dioxane (I) and acetic anhydride results in the formation of 1,3-diacetoxy-1-phenylpropane (II). On the contrary, we find under the experimental conditions described by Shorygina, that the product is 1,5-diacetoxy-3-phenyl-2-oxapentane (III) obtained by cleavage at position *b*. No evidence was found for the presence of isomeric 1,5-diacetoxy-5-phenyl-2-oxapentane (IV) which would result from ring opening at position *a*.



Our results are in agreement with those of Senkus[2] who reports that the acetylation of several 4- and 5-substituted 1,3-dioxanes gives diacetylated products which retain the methylene group, and of Ness, Hann, and Hudson[3] who describe the acetylation of cyclic formals to yield products in which the acetoxy group is attached to the primary carbon atom and the acetoxymethoxy to the secondary carbon atom.

The reaction of 4-phenyl-1,3-dioxane (I) with acetic anhydride yielded a diacetate product from which was obtained, after crystallization followed by distillation, an 80% yield (based on I consumed) of 99.0–99.5 mole % pure diacetate (III). Preferential hydrolysis of the purified diacetate yielded formaldehyde plus 3-acetoxy-1-phenyl-1-propanol (V). The latter was oxidized to β-acetoxypropiophenone (VI).



Acidic hydrolysis of VI yielded β-hydroxypropiophenone (VII) whose identity was established by conversion to its known semicarbazone, α-naphthylurethane and pyrazoline derivatives.

Alkaline hydrolysis of VI with sodium hydroxide resulted in a hydrolytic product containing benzoylethylene (VIII), identified by the preparation of its dibromo derivative. The formation of benzoylethylene from VI is an example of a base-catalyzed olefin-forming elimination reaction.[4]

(1) N. V. Shorygina, *J. Gen. Chem.* (*U.S.S.R.*), **26**, 1643 (1956).

(2) M. Senkus, *J. Am. Chem. Soc.*, **68**, 734 (1946).

(3) A. T. Ness, R. M. Hann, and C. S. Hudson, *J. Am. Chem. Soc.*, **65**, 2215 (1943).

(4) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, Chap. VIII.

EXPERIMENTAL

All boiling points and melting points are uncorrected. The freezing temperature of 1,5-diacetoxy-3-phenyl-2-oxapentane (III) was determined by extrapolation of its freezing curve, temperature being measured by a certified platinum resistance thermometer and G-2 Mueller bridge, purity being estimated from the shape of the curve.

1,5-Diacetoxy-3-phenyl-2-oxapentane (III). A solution of 164 g. (1.0 mole) of 4-phenyl-1,3-dioxane[5] (I), 224 g. (2.2 moles) of acetic anhydride and 10 ml. of concentrated hydrochloric acid was stirred at 80° for 5 hr., then cooled, neutralized with aqueous sodium hydroxide and extracted with ether. The dried extract was concentrated and the residue distilled to yield 29 g. (18%) of recovered 4-phenyl-1,3-dioxane and 200 g. (93% based on dioxane consumed) of diacetate product. The latter was crystallized once out from 2150 ml. of petroleum ether (b.p. 40–45°) to yield 170 g. of solid which was distilled to yield 160 g. (80% based on dioxane consumed) of 99.0–99.5 ± 0.5 mole % pure 1,5-diacetoxy-3-phenyl-2-oxapentane; b.p. 137°/0.8 mm., n_D^{25} 1.4850; f.t. 34.41°.

Anal. Calcd. for $C_{14}H_{18}O_5$: C, 63.14; H, 6.81; mol. wt. 266. Found: C, 63.47; H, 6.64; mol. wt., 264.

3-Acetoxy-1-phenyl-1-propanol (V). To a solution of 133 g. (0.50 mole) of diacetate (III) in 1 l. of absolute ethanol was added a solution of 26.5 g. (0.25 mole) of sodium carbonate in 750 ml. of water. The mixture was stirred for 1.5 hr. at 25°, filtered, and the filtrate evaporated at 25°/1 mm. to a 500-ml. aqueous concentrate which was saturated with sodium chloride and extracted with ether. The dried extract was concentrated and the residue distilled to yield 70 g. (72%) of 3-acetoxy-1-phenyl-1-propanol (V); b.p. 115–122°/0.4 mm., n_D^{25} 1.5100–1.5125. Redistillation through a 60-cm. spinning band column at 30/1 reflux ratio gave a 40-g. heart cut; b.p. 123–124°/0.45 mm., n_D^{25} 1.5125.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 68.26; H, 7.48.

A second hydrolytic experiment, similar to the one above, but on $^1/_{10}$ the scale, was made and the product reacted with Brady's reagent[6] (a solution of 2,4-dinitrophenylhydrazinium sulfate in aqueous ethanol containing excess sulfuric acid) to yield 9.3 g. (88%) of formaldehyde 2,4-dinitrophenylhydrazone, melting point and mixture melting point with an authentic specimen 164–166°.

β-Acetoxypropiophenone (VI). *Method* A. To 21 g. (0.11 mole) of 3-acetoxy-1-phenyl-1-propanol (V) was added, in one portion, a mixture of 42 g. (0.14 mole) of sodium dichromate dihydrate, 35 ml. (0.66 mole) of concentrated sulfuric acid and 400 ml. of water. The temperature was held at 55–60° by swirling in an ice bath. When the temperature no longer tended to rise, the mixture was extracted with benzene. The extract was dried and concentrated to give a solid residue which was crystallized twice from petroleum ether (b.p. 40–45°) to yield 5.7 g. (27%) of β-acetoxypropiophenone, m.p. 53.5–54.0°.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30. Found: C, 68.68; H, 6.00.

β-Acetoxypropiophenone (VI). *Method* B. Ten grams (0.10 mole) of chromium trioxide was added during 1.5 hr. to a stirred solution of 19.4 g. (0.10 mole) of 3-acetoxy-1-phenyl-1-propanol (V) in 250 ml. of acetic acid. The temperature rose from 25 to 45°. The solution was stirred for an additional 3 hr., then poured into excess aqueous sodium carbonate and extracted with ether. The extract was dried and concentrated to give a solid residue which was crystallized once from petroleum ether (b.p. 40–45°) to yield 5.5 g. (27%) of β-acetoxypropiophenone, m.p. 51–54°.

2,4-Dinitrophenylhydrazone of β-acetoxypropiophenone. Orange needles from ethanol, m.p. 174–175°.

Anal. Calcd. for $C_{17}H_{16}N_4O_6$: C, 54.83; H, 4.33; N, 15.05. Found: C, 55.65; H, 4.28; N, 14.66.

β-Hydroxypropiophenone (VII). A solution of 19.2 g. (0.10 mole) of β-acetoxypropiophenone (VI), 200 ml. of water, 200 ml. of methanol and 100 ml. of concentrated hydrochloric acid was stirred for 2 hr. at 35°, then neutralized by the addition of solid sodium carbonate. Methanol was evaporated at 10 mm. and the residual solution saturated with sodium chloride and extracted with ether. The dried extract was concentrated to yield 11.5 g. (77%) of β-hydroxypropiophenone, n_D^{25} 1.5408. Distillation gave a heart cut boiling at 90°/0.15 mm.; n_D^{25} 1.5444 (lit.[7] b.p. 98°/0.2 mm., n_D^{20} 1.5450).

α-Naphthyl carbamate of β-hydroxypropiophenone. White crystals from carbon tetrachloride, m.p. 116–117° (lit.[7] m.p. 115–116°).

Semicarbazone of β-hydroxypropiophenone. White needles from aqueous methanol, m.p. 160–161° (lit.[7] m.p. 160–161°). Shorygina[1] reports 194–195° as the melting point.

1,3-Diphenyl-2-pyrazoline. Prepared by condensing β-hydroxypropiophenone with phenylhydrazine, yellow plates from aqueous methanol, melting point and mixture melting point with an authentic specimen 151–153° (lit.[8] m.p. 151–152°). Authentic 1,3-diphenyl-2-pyrazoline was prepared by reacting β-dimethylaminopropiophenone hydrochloride with phenylhydrazine.

Benzoylethylene (VIII). A mixture of 9.6 g. (0.05 mole) of β-acetoxypropiophenone (VI), 2.0 g. (0.05 mole) of sodium hydroxide and 200 ml. of water was stirred at 30° for 0.5 hr., then saturated with sodium chloride and extracted with carbon tetrachloride. The presence of benzoylethylene was demonstrated as follows: to the cold, dry extract was slowly added a cold solution of bromine in carbon tetrachloride until the appearance of a faint yellow color. The solvent was evaporated and the residue crystallized from petroleum ether (b.p. 40–45°) to yield 4.5 g. (31%) of α,β-dibromopropiophenone, melting point and mixture melting point with an authentic specimen 52–54° (lit. m.p. 53°,[9] 58°[10]). Authentic α,β-dibromopropiophenone was prepared from benzoylethylene obtained from β-dimethylaminopropiophenone hydrochloride.[11]

Acknowledgment. This work was done by the Monomers Fellowship sustained by Koppers Company, Inc.

PITTSBURGH 13, PA.

(5) M. G. J. Betts, *Rec. trav. chim.*, **70**, 20 (1951); R. L. Shriner and P. R. Ruby, *Org. Syntheses*, **33**, 72 (1953).

(6) O. L. Brady, *J. Chem. Soc.*, 757 (1931).

(7) M. G. J. Beets and L. G. Heeringa, *Rec. trav. chim.*, **74**, 1096 (1955).

(8) H. O. House and R. L. Wasson, *J. Org. Chem.*, **22**, 1157 (1957).

(9) H. Jager and M. Arenz, *Ber.*, **83**, 182–5 (1950).

(10) E. P. Kohler, *Am. Chem. J.*, **42**, 375 (1909).

(11) C. Mannich and G. Heilner, *Ber.*, **55**, 356 (1922).