The aminoethylene is stable toward the action of boiling alcoholic sodium acetate and alcoholic hydrogen chloride. It was not easily hydrolyzed with alcoholic alkali; however, 0.85 g., when refluxed with 15 cc. of ethanol and 0.1 g. of sodium hydroxide for five hours, gave 0.8 g. of di-(trimethylbenzoyl)-ethanol. Hydrolysis of 0.5 g. by refluxing with 10 cc. of alcohol, 10 cc. of concd. hydrochloric acid and 10 cc. of water for two and a half hours gave 0.48 g. of the enol (identified by mixed m. p.).

1,2-Di-(2,4,6-trimethylbenzoyl)-ethenol I, is best prepared by the action of boiling 80% methanol containing an excess of sodium hydroxide on di-(trimethylbenzoyl)-dibromoethane; m. p. 112–113° (corr.) (*cf.* Ref. 1a). It is not affected by exposure to sunlight (in ethanol), or when refluxed with alcoholic ammonia. The keto form is readily enolized by the latter reagent, or by refluxing with alcoholic hydrogen chloride. Titration by the K. Meyer method showed the enol to be completely enolized and the keto form not at all.[6] Both keto and enol forms are sublimed easily *in vacuo* at air-bath temperatures of 140–150°.

The sodium salt[6] of I was prepared by heating 2.0 g. of di-(trimethylbenzoyl)-dibromoethane with 25 cc. of 80% methanol until dissolved. On cooling 1.28 g. of the sodium salt crystallized (m. p. 308–310°); recrystallized from alcohol in which it is difficultly soluble; very difficultly soluble in water.

Anal. Calcd. for $C_{22}H_{23}O_3Na$: C, 73.7; H, 6.45. Found: C, 73.6; H, 6.43.

The enol was liberated from the salt upon treating the solid material directly with dilute acid.

Summary

Di-(trimethylbenzoyl)-ethenol and the *cis* and *trans* methyl and ethyl ethers have been studied, and evidence given for their structures and configurations.

UNIVERSITY, VIRGINIA RECEIVED APRIL 16, 1934

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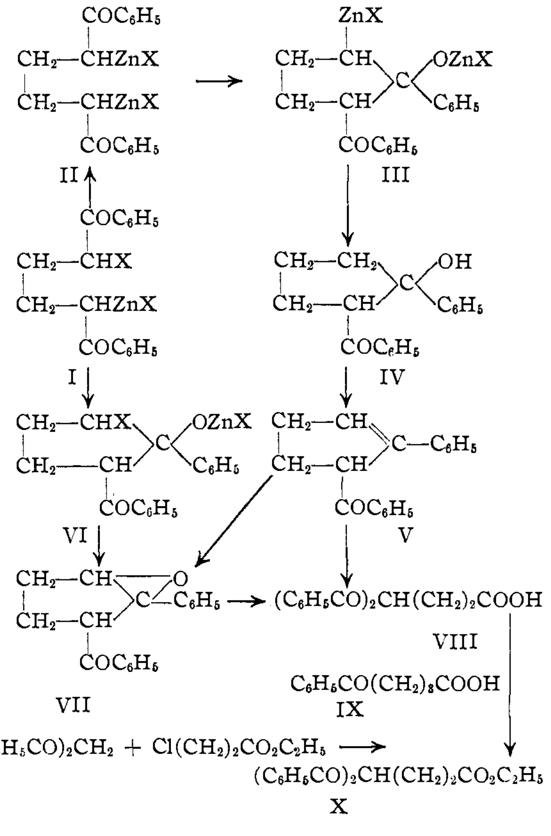
[6] These experiments were carried out by Dr. C. I. Parrish.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Action of Zinc on 1,4-Dibromo-1,4-dibenzoylbutane. An Intramolecular Reformatsky Reaction

BY REYNOLD C. FUSON AND MARK W. FARLOW

In a study of the action of zinc on 1,4-dibromo-1,4-dibenzoylbutane it has become apparent that the reaction proceeds in a most unusual and unexpected manner, for no compound containing the cyclobutane ring is produced. Instead, *cyclopentane derivatives* are formed. From a consideration of the structure of the products it appears probable that the reaction involves the intermediate formation of an organo zinc compound which undergoes an intramolecular Reformatsky condensation. These transformations are summarized in the following chart.



The evidence for these reactions derives from the character of the compounds obtained. Three primary reaction products have been isolated and identified.[1] One of these, 1,4-dibenzoylbutane, is apparently a hydrolysis product of an intermediate of the type illustrated by II in which both bromine atoms have been replaced by the metal.

1-Phenyl-5-benzoyl-1-cyclopentene (V).—A second product was an unsaturated compound melting at 99–100°. From the melting point it appeared that the compound might be 1-phenyl-5-benzoyl-1-cyclopentene which has been reported

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[1] A fourth compound proved to be a rearrangement product of one of the others and has not been included in the present report.

by Bauer[2] as melting at 98°. Analysis and comparison with a sample prepared by the method of Bauer proved this surmise to be correct. Moreover, this structure was confirmed by ozonization. The products of this reaction are described below. The formation of the pentene from II through III and IV as intermediates seems probable.

1 - Phenyl - 5 - benzoyl - 1 - cyclopentene Oxide (VII).—The main product of the reaction was found to melt at 169.5–170°. Analyses and molecular weight determinations showed the formula to be $C_{18}H_{16}O_2$. Attempts to prepare carbonyl derivatives with hydroxylamine, phenylhydrazine and semicarbazide were unsuccessful. Although the compound did not decolorize bromine water or permanganate, it was readily attacked by ozone which converted it into an acid melting at 117.5–118.5° and having the formula $C_{18}H_{16}O_4$. This acid has been shown to be γ,γ-dibenzoylbutyric acid (VIII). Alkaline hydrolysis converted it into benzoic acid and γ-benzoylbutyric acid (IX). That the second benzoyl group is in the γ and not the α position (these two positions alone would permit the observed hydrolysis) is shown by the fact that the diketo acid does not readily lose carbon dioxide. The structure of VIII was confirmed by converting it to the ethyl ester (X) which was synthesized by the condensation of ethyl β-chloropropionate with dibenzoylmethane.[3]

The molecule of the parent compound contains two less oxygen atoms than its ozonization product and is saturated. It contains one oxygen atom more than does V *and gives the same ozonization product*. This suggested formula VII which has proved to be correct. The confirming evidence was the synthesis of VII from V by treatment of the latter with perbenzoic acid.

The formation of the pentene oxide (VII) is evidently due also to an intramolecular condensation of the Reformatsky type. The transformation of II into III and of I into VI, while entirely hypothetical, offers a satisfactory interpretation of the facts presented.

Experimental

Action of Zinc on 1,4-Dibromo-1,4-dibenzoylbutane.—The general procedure of Conant and Lutz[4] was followed. A mixture of 100 g. of the dibromide, 50 g. of zinc dust and 150 g. of sodium iodide was covered with acetone and allowed to react for thirty minutes. The heat of reaction caused the acetone to boil. At the end of about one and one-half hours the reaction had subsided and the mixture had cooled to room temperature.[5] The zinc sludge was removed and extracted in a Soxhlet apparatus with fresh acetone. Evaporation of the acetone from the combined solutions from the filtration and extraction gave a residue which, after several recrystallizations from ethyl acetate, gave 8 g. of **1-phenyl-5-benzoyl-1-cyclopentene oxide** melting at 169.5–170°.[6] An additional 8 g. of this solid was obtained by concentration of the mother liquors from the above purification. The compound was halogen-free; it did not decolorize potassium permanganate in acetone, and it reacted only slowly with bromine in carbon tetrachloride, with the evolution of hydrogen bromide.

Anal. Calcd. for $C_8H_{16}O_2$: C, 81.8; H, 6.1; mol. wt., 264. Found: C, 81.8; H, 6.2; mol. wt., 267, 258 (Rast).

The mother liquors from the preceding purification processes gave a solid residue which by recrystallization from methanol yielded 11 g. of **1,4-dibenzoylbutane** melting at 106–107°. Its identity was confirmed by a mixed melting point with an authentic specimen.

The methanol mother liquors yielded a solid residue which, when extracted with hot petroleum ether, left an insoluble solid. This compound as indicated above is a rearrangement product of **the oxide**; it has been investigated separately and its identification will be reported elsewhere.

From the petroleum ether used in the extraction previously mentioned was obtained 1-phenyl-5-benzoyl-1-cyclopentene, melting (from methyl alcohol or petroleum ether) at 99–100°. It decolorized permanganate in acetone; bromine in carbon tetrachloride reacted instantly without the evolution of hydrogen bromide. The identification was confirmed by a mixed melting point determination with a sample of the pentene made by the method of Bauer.[2]

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.1; H, 6.5. Found: C, 87.0; H, 6.5.

Oxidation of the Oxide (VII).—Oxidation of 1 g. of the oxide with permanganate in alkali gave 0.44 g. of pure benzoic acid.

Ozonization of the Oxide (VII).—Treatment with ozone converted the oxide into a mixture of substances from which, by suitable manipulations, two were isolated in pure form. One of these was a neutral solid melting at 123.5–124° (from methanol) and is **an isomer of the oxide.** This compound is under investigation.

The other product, after numerous recrystallizations from dilute methanol, melted at 117.5–118° and proved to be **γ,γ-dibenzoylbutyric acid.**

This acid was also prepared by ozonization of 1-phenyl-5-benzoyl-1-cyclopentene prepared by the method of Bauer.[2]

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 73.0; H, 5.4. Found: C, 72.7, 72.9; H, 5.5, 5.6.

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[2] Bauer, *Compt. rend.*, **155**, 288 (1912).

[3] This work was done by Mr. R. L. Walker.

[4] Conant and Lutz, THIS JOURNAL, **49**, 1090 (1927). The compound (m. p. 163°) reported by these authors is probably identical with the rearrangement product mentioned above.

[5] Runs made under comparatively anhydrous conditions gave results similar to that obtained with hydrated sodium iodide.

[6] All melting points reported in this paper are corrected.

A sample of the diketo acid was heated for thirty minutes with a 15% potassium hydroxide solution. γ-Benzoylbutyric acid (m. p. 126–127°) was isolated from the reaction mixture. The acid was identified by comparison with an authentic specimen.

Synthesis of Ethyl γ,γ-Dibenzoylbutyrate.—This ester was obtained in two ways—by esterification of the acid and by the condensation of ethyl β-chloropropionate with dibenzoylmethane. The latter process was carried out according to the following procedure. To a cold solution of 1 g. of metallic sodium in 30 cc. of absolute ethyl alcohol was added, with stirring, 10 g. of dibenzoylmethane. After the mixture had become homogeneous 8.7 g. of ethyl β-chloropropionate was added gradually. The mixture was allowed to stand, with occasional stirring, for eighty-six hours. The product, after recrystallization from alcohol, melted at 95–95.5°.

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.0; H, 6.2. Found: C, 74.2; H, 6.3.

Synthesis of the Oxide (VII).—Two grams of 1-phenyl-5-benzoyl-1-cyclopentene was dissolved in chloroform containing the theoretical amount of perbenzoic acid. After twenty-four hours the chloroform solution was washed with aqueous sodium bicarbonate and allowed to evaporate. The solid residue when recrystallized from ethyl acetate melted at 169–169.5° and when mixed with a sample of the oxide described above caused no lowering of the melting point.

Summary

The action of zinc (in acetone) on 1,4-dibromo-1,4-dibenzoylbutane gives rise to a mixture of products of which the principal is 1-phenyl-5-benzoyl-1-cyclopentene oxide (VII). The corresponding pentene (V) and 1,4-dibenzoylbutane are also formed. Structure proofs are presented for V and VII.

A mechanism which involves an intramolecular Reformatsky condensation is suggested to explain the formation of the two cyclic compounds.

URBANA, ILLINOIS RECEIVED APRIL 16, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

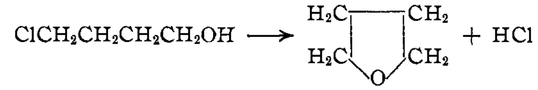
Reduction of Furan and the Preparation of Tetramethylene Derivatives

BY DONALD STARR[1] AND R. M. HIXON

A convenient method for the preparation of δ-chlorovaleronitrile was desired in order that the reaction developed for the α-substituted pyrrolines and pyrrolidines[2] could be used for the synthesis of the α-substituted tetrahydropyridines and piperidines. In spite of the large number of investigations leading to the preparation of various tetramethylene derivatives, no reference to δ-chlorovaleronitrile could be found in the literature.

Tetramethylene bromide and bromohydrin have previously been prepared from tetrahydrofuran,[3] which should be a more convenient source of tetramethylene derivatives than its analog, pyrrolidine.[4] The practicability of using tetrahydrofuran for the synthesis of δ-chlorovaleronitrile depended upon finding an efficient method for reducing furan.[3,5] The catalytic reduction using platinic oxide-platinum black catalyst[6] was found to be very unsatisfactory, but palladous oxide-palladium black[7] made possible a quantitative conversion of furan to tetrahydrofuran.

Tetramethylene chlorohydrin[8] has been reported as being unstable when distilled at temperatures appreciably above 85°. Presumably, the reaction is



This reaction has been studied in the reverse direction to determine its applicability in the preparation of tetramethylene chlorohydrin. The splitting of tetrahydrofuran with hydrogen chloride was studied first in the vapor phase since the partial pressure of the tetramethylene chlorohydrin was so much less than that of the tetrahydrofuran that there was slight probability of a secondary reaction occurring to form tetramethylene chloride. Experience showed that there was very little difference in the yield of chlorohydrin if the reaction occurred in the liquid phase. The reaction in the liquid phase is about three times as rapid as in the gaseous phase. The compound partially breaks down at about 106° in both cases,

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[1] Research Fellow, Rockefeller Fluid Research Fund.

[2] Craig, Bulbrook and Hixon, THIS JOURNAL, **53**, 1831 (1931); Starr, Bulbrook and Hixon, *ibid.*, **54**, 3971 (1932).

[3] Bouguignon, *Bull. soc. chim. Belg.*, **22**, 87 (1908).

[4] Von Braun and Besche, *Ber.*, **39**, 4119 (1906).

[5] Smyth and Walls, THIS JOURNAL, **54**, 3231 (1932). Furan was reduced catalytically in butyl alcohol but no details were reported.

[6] "Organic Syntheses," Vol. VIII, p. 92.

[7] Shriner and Adams, THIS JOURNAL, **46**, 1683 (1924).

[8] Bennett and Heathcoate, *J. Chem. Soc.*, 268 (1929); Kirner and Richter, THIS JOURNAL, **51**, 2503 (1929).