

once when immersed in a bath at 250°, but melts at 262–262.5° when heated slowly.

The dianhydride was obtained as straw colored needles, m. p. 262.5–263°, by crystallization of the tetrabasic acid from glacial acetic acid containing a few drops of acetic anhydride.

Anal. Calcd. for C₁₄H₄O₆: C, 62.68; H, 1.50. Found: C, 62.52; H, 1.71.

A dimethyl ester anhydride was obtained on treating 0.2 g. of the tetrabasic acid with diazomethane in ether (six hours at 0° with occasional shaking). The residue left on evaporation when crystallized twice from benzene formed glistening colorless plates, m. p. 219.5–220.5°.

Anal. Calcd. for C₁₆H₁₀O₇: C, 61.16; H, 3.21. Found: C, 61.03; H, 3.40.

Summary

Liquid hydrogen fluoride is an excellent reagent for the cyclization of a number of γ -arylbutyric acids and β -arylpropionic acids. A particularly significant use of the reagent is in the preparation of 1,2-benz-10-anthrones by the cyclization of appropriate acids, for these important intermediates in the synthesis of carcinogenic hydrocarbons

are thereby rendered readily available in the pure keto form.

Certain intermolecular hydrocarbon acylations with free acids, anhydrides, or acid chlorides also can be brought about under the influence of hydrogen fluoride at room temperature. The reaction is not general under these conditions for negative results have been obtained with several common hydrocarbons. Acenaphthene reacts readily, giving benzoyl, acetyl, and succinoyl derivatives in good yield. In most cases the orientation is the same as in the Friedel and Crafts reaction, but the condensation with acetic acid takes a different course. Due to this fortunate circumstance and to favorable solubility relationships, the hitherto unknown 1-acetoacenaphthene can be prepared easily in 25% yield.

Acenaphthene reacts smoothly with crotonic acid in the presence of hydrogen fluoride to give 1'-methyl-3'-keto-2,3-cyclopentenoacenaphthene.

CONVERSE MEMORIAL LABORATORY

CAMBRIDGE, MASS.

RECEIVED FEBRUARY 15, 1939

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

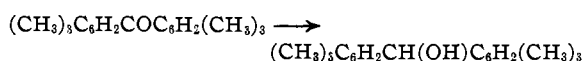
The Reduction of α -Diketones

BY R. B. THOMPSON

Since dimesityl diketone was first synthesized,¹ several papers have appeared showing that it fails to undergo many of the reactions typical of α -diketones. Thus Kohler and Baltzly¹ found that it forms a monoxime with difficulty, and does not undergo a benzilic acid rearrangement, give a quinoxaline derivative with *o*-phenylenediamine, react with Grignard reagents, or undergo reduction by hydrogen and platinum. Shortly afterward Fuson and Gray² prepared the diketone by a different method and confirmed its inertness toward the usual reagents.

A priori, there is no reason why reduction of dimesityl diketone should be difficult, since the hydrogen may add to the ends of the conjugated system. Numerous experiments have shown that the failure of mesityl compounds to participate in addition reactions is confined to those reactions in which the atoms attached to the ring are involved. Thus mesityl carboxylic acid is esterified with difficulty, but, in contrast, mesityl acetic

acid reacts readily.³ Even if reduction does not proceed through a 1,4-mechanism, 1,2-addition is entirely possible, since it has been shown that dimesityl ketone, in which hindrance to the carbonyl is at a maximum, is not especially difficult to reduce.¹



Actually the reduction of dimesityl diketone proceeds readily in absolute methyl alcohol in the presence of platinum. The reaction stops when one mole of hydrogen has been absorbed, and the solution becomes colorless; in contact with air, however, it becomes yellow at once, and concentration of the solution gives the diketone in 95% yield.⁴

The only explanation for this anomaly is that the ene-diol II, in contrast with most compounds of its type, is unusually persistent.⁵ The presence

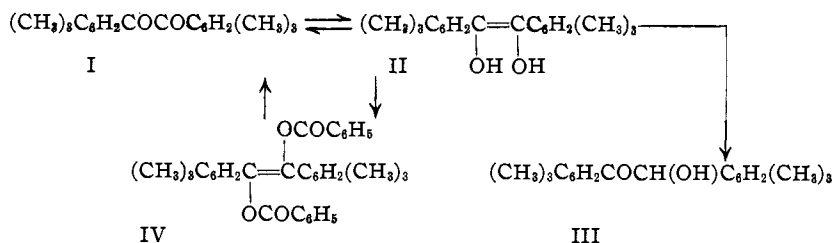
(3) Meyer, *Ber.*, **27**, 510 (1894); Meyer and Sudborough, *ibid.*, **27**, 1587 (1894).

(4) This experiment was completed in January, 1937, while the author was working under the direction of the late Professor E. P. Kohler.

(5) Fuson and Corse, *THIS JOURNAL*, **61**, 975 (1939).

(1) Kohler and Baltzly, *THIS JOURNAL*, **54**, 4015 (1932).

(2) Fuson and Gray, *ibid.*, **56**, 739 (1934).



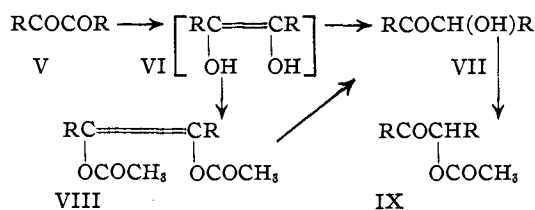
of the ene-diol is confirmed by the facile reduction of 2,6-dichloroindophenol, since freshly reduced solutions decolorize the dye as rapidly as do the well-known ene-diols, reductone and ascorbic acid.

Further evidence for the remarkable persistence of the ene-diol was shown by the fact that at least 60% of it was still present in alcoholic solution containing piperidine after standing at 40° for a week. This ene-diol is, therefore, much more persistent than that obtained by Kohler and Thompson⁶ or that observed by Lutz and Wood,⁷ both of which changed to the hydroxy ketones in a short time. This difference must be ascribed to the effect of mesityl radical as compared to the less bulky substituents present in the other ene-diols.

It was further found that upon reduction in moderately concentrated solution, the ene-diol crystallized spontaneously and could be isolated in an atmosphere of nitrogen, but slowly turned yellow when exposed to air. When treated with benzoyl chloride and pyridine, a dibenzoate was formed, and, as expected, hydrolysis of this diester led to the diketone¹ rather than the hydroxy ketone III. The ene-diol melting at 149–151° yields, with benzoyl chloride and pyridine, a dibenzoate melting at 235°, and is stereoisomeric with Fuson's ene-diol⁶ which melts at 143–144° and yields a dibenzoate melting at 188–189°.

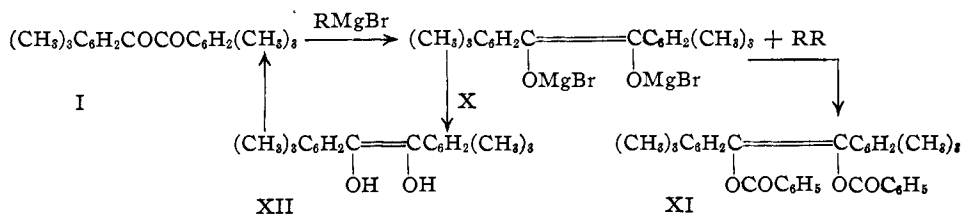
Heretofore all of the evidence for the 1,4-addition of catalytically activated hydrogen to α -diketones has been confined to those compounds bearing notoriously bulky residues.^{5,6} To show the generality of this mode of reaction, however, the work has been extended to cover the phenyl

homologs of dimesityl and mesityl benzhydryl diketones. When these compounds are reduced in methyl alcohol, there is no indication of the ene-diol resulting from 1,4-addition. But, if the reduction takes place in solutions containing an active acetylating agent, at least 90% of the product is the diacetate of the ene-diol VIII. This diac-



tate cannot arise from the hydroxy ketone VII, since acetylation of the latter leads exclusively to the monoacetate IX. Unlike the diester IV resulting from the ene-diol II, the diester VIII has no bulky groups to stabilize the ene-diol VI, and hydrolysis of the latter ester leads to the hydroxy ketone VII. Thus the divergence in the products of reduction is attributable to the relative rates of ketonization, not to the actual mode of addition of hydrogen.

Since this reaction has shown that dimesityl and mesityl benzhydryl diketones behave similarly, an investigation of the behavior of the former ketone toward Grignard reagents seemed worth while. Mesityl benzhydryl diketone is reduced by ethylmagnesium bromide to the dienolate⁶ just as benzil is reduced with triphenylmethylmagnesium bromide.⁸ Here, too, the two mesityl diketones are similar, both giving dienolates which lead to diesters when acylated.



(6) Kohler and Thompson, *THIS JOURNAL*, **59**, 887 (1937).

(7) Lutz and Wood, *ibid.*, **60**, 708 (1938).

This conclusion was supported by the Zerewitinoff

(8) Bachmann, *ibid.*, **53**, 2758 (1931).

determination in which dimesityl diketone yielded one mole of gas and consumed two moles of reagent.

Experimental

Reduction of Dimesityl Diketone.—The diketone was prepared by the method of Fuson and Gray.² The yellow solid (0.5 g.), dissolved in 20 cc. of methyl alcohol absorbed 1 mole of hydrogen, during thirty minutes, in the presence of 0.04 g. of platinum oxide, to give a colorless solution. In air, the product is the diketone (95%), but in an atmosphere of nitrogen the ene-diol II (70%) melting at 149–151° was obtained.

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.1; H, 8.11. Found: C, 81.0; H, 8.11.

Benzoylation.—The ene-diol (0.3 g.) dissolved in benzoyl chloride (2 cc.) and pyridine (10 cc.) gave 0.3 g. of the dibenzoate IV melting at 235° after crystallization from a mixture of benzene-petroleum ether.

Anal. Calcd. for $C_{38}H_{42}O_4$: C, 80.9; H, 6.39. Found: C, 80.5; H, 6.23.

Hydrolysis with dilute alcoholic potassium hydroxide yielded the diketone.

The isomeric dibenzoate XI, melting at 188–189°, was prepared by treating the di-enolate X, prepared according to Fuson⁵ by the action of a magnesium-magnesium iodide couple on the diketone I, with benzoyl chloride, and a mixed melting point with an authentic sample prepared by Kohler and Baltzly¹ proved that this dibenzoate was identical with their hexamethyl isobenzil.

2,2',4,4',6,6'-Hexamethyl Benzoin, III.—After forty-five hours, a solution of the ene-diol in methyl alcohol (platinum was still present) containing piperidine yielded only the diketone, when the product was isolated in air, and a similar solution after standing one week at 40° yielded 60% of the diketone, but a solution containing piperidine acetate after two weeks at 40° gave the benzoin melting at 130°,⁹ although an appreciable quantity of ene-diol was still present.

Reduction of Benzil.—The procedures for reducing benzil and benzhydryl phenyl diketone were identical. A mixture of benzil (1 g.), platinum oxide (0.06 g.), fused zinc chloride (1 g.) and hydrochloric acid (3 drops of 12 *N*), dissolved in acetic anhydride (12 cc.), absorbed one mole of hydrogen in four to five hours. The filtered solution,

(9) Fuson, Emerson and Weinstock, *THIS JOURNAL*, **61**, 413 (1939), give the melting point as 130.5–131°.

after hydrolysis of the excess anhydride, yielded a solid (90%), which crystallized from methyl alcohol in prisms melting at 107–108°. Hydrolysis with alcoholic potassium hydroxide gave benzoin melting at 133°. Acetylation of benzoin with a mixture of acetic anhydride-zinc chloride gave benzoin acetate melting at 82–83°.¹¹

Reduction of Phenyl Benzhydryl Diketone.—The diketone was prepared by the method of Kohler and Weiner.¹² The yellow diketone (1.4 g.) reduced in the same way as benzil gave a 90% yield of diacetate, melting at 132.5–133.5° after crystallization from methyl alcohol.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 77.7; H, 5.70. Found: C, 77.8; H, 5.66.

Hydrolysis of the diacetate gave phenyl (diphenylacetyl) carbinol melting at 126–127°, which was identical with an authentic sample prepared according to Kohler and Weiner.¹² Acetylation of this hydroxy ketone gave a monoacetate melting at 67–68°.

Anal. Calcd. for $C_{28}H_{20}O_3$: C, 80.2; H, 5.81. Found: C, 79.8; H, 5.84.

Reduction of Dimesityl Diketone with Ethylmagnesium Bromide.¹³—The diketone (1.5 g.) was added to ethylmagnesium bromide prepared from 0.45 g. of magnesium, and gave a dark red color which rapidly disappeared as gas was evolved. The mixture was boiled for thirty minutes, 2.6 g. of benzoyl chloride in 40 cc. of dry benzene added, and most of the ether distilled. After boiling for two hours, the mixture was treated with dilute hydrochloric acid, distilled with steam, the residue extracted with ether, the extract washed with bicarbonate, and the dried solution concentrated yielding the dibenzoate XI melting at 188–189°.

Summary

The production of ene-diols resulting from primary 1,4-addition in the catalytic reduction of α -diketones has been demonstrated.

s-Dimesityl dihydroxyethylene, stereoisomeric with the ene-diol of Fuson, has been isolated in a pure condition.

CAMBRIDGE, MASSACHUSETTS

RECEIVED MARCH 27, 1939

(10) Thiele, *Ann.*, **306**, 142 (1899), gives the melting point of his β -diacetate as 110°.

(11) Meisenheimer, *Ber.*, **38**, 877 (1905).

(12) Kohler and Weiner, *THIS JOURNAL*, **56**, 434 (1934).

(13) Mr. J. F. Ege, Jr., assisted in this experiment.