from acetone–cyclohexane to give a 70% yield of free naphtholic lactone (VIII) melting at 191–192°. Subsequent recrystallization from aqueous acetone (with 10% loss) raised the melting point to 192–193° (microscopic crystals).

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.48, 75.59; H, 6.84, 6.77.

3-Hydroxy-2,2-dimethyl-1-(6-methoxynaphthyl-2)-1-propanone (IX).—Four-tenths of a gram of chloro ketone (V), m.p. 85.0–85.5°, was dissolved in 13 ml. of methanol plus 3 ml. of 26% potassium hydroxide and the resulting solution refluxed on the steam-bath for 2 hours. The hot solution was diluted with water (to turbidity) and left overnight in the ice-box. The resulting crystals were filtered and washed with water. Recrystallization from aqueous acetone gave 0.12 g. of product melting at 105–107°. A recrystallization from acetone–Skellysolve B followed by a recrystallization from Skellysolve F–ethyl ether gave 0.04 g. of silky needles (IX), m.p. 119°. This melting point was not improved upon subsequent recrystallization.

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.39; H, 7.03. Found: C, 74.05, 74.19; H, 6.73, 6.67.

Alkaline Degradation of 3-Chloro-2,2-dimethyl-1-(6-methoxynaphthyl-2)-1-propanone (V) to 6-Hydroxy-2-naphthoic Acid.—To 0.28 g. of pure chloro ketone (V) was added a solution of 10 g. of 85% potassium hydroxide in 10 ml. of water plus 30 ml. of ethanol. The alkaline solution was heated under reflux for 2 hours, cooled, and then acidified with dilute sulfuric acid. After 24 hours at room temperature, the precipitated acid was filtered, washed with water, and dried in the oven. The yield was 0.12 g. of crude 6-methoxy-2-naphthoic acid. This was demethylated by fusing with pyridine hydrochloride at 190° for 2 hours. The cooled fusion mixture was diluted with 100 ml. of water and, after a few hours, filtered from a dark brown precipitate. The filtrate, upon standing in the ice-box overnight, deposited 52 mg. of white crystals, m.p. 235–239°. Recrystallization of these white crystals from aqueous methanol and from benzene–Skellysolve B raised the melting point to 241–242°. Butler and Royle[10] record a melting point of 240–241° for 6 hydroxy-2-naphthoic acid.

Anal. Calcd. for $C_{11}H_8O_3$: C, 70.21; H, 4.29. Found: C, 70.15; H, 4.36.

The ethyl ester of this acid, prepared according to Butler and Royle,[10] melted sharply at 110°. (Butler and Royle record 111–112°.)

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.20; H, 5.59. Found: C, 72.01; H, 5.87.

Acknowledgment.—The support of this research by G. D. Searle and Company is gratefully acknowledged.

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(10) C. Butler and F. A. Royle, *J. Chem. Soc.*, 1654 (1923).

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[CONTRIBUTION FROM THE THOMPSON LABORATORY OF THE PHILLIPS EXETER ACADEMY]

The Tautomeric Forms of Some 1,1-Diaroylethanes

BY CHARLES L. BICKEL AND ROBERT MORRIS(1)

This report describes the preparation of the enolic forms of four diaroylethanes. These substances easily revert to the parent diketones but may be recrystallized without change from ether. The bromo derivatives of the enols have also been prepared and these have, in turn, been converted into the parent diketones by the use of hydriodic acid.

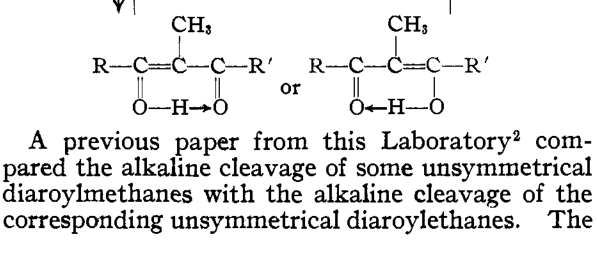
The investigation of a large number of diaroylmethanes has shown that these substances are completely enolic in solution, indicating that the enolic forms are more stable than the tautomeric ketonic forms.

Conversely, fragmentary reports on diaroylethanes indicate that the introduction of the methyl group suppresses the enolization almost completely.[2–4] These compounds give no coloration with ferric chloride and there is no evidence of bromine addition or copper salt formation. By the acidification of a sodium alcoholate solution of 1-anisoyl-1-benzoylethane, Weygand[5] obtained a solid which appeared to be the enolic form of the diaroylethane but which reverted to the diketone upon recrystallization.[6] Dieckmann[7] applied the same method to 1,1-dibenzoylethane and obtained a substance which gave the characteristic reactions of the enol but which reverted to the keto form on standing in alcoholic solution.

This paper reports the preparation of the pure enolic forms of four diaroylethanes by the action of an alcoholic solution of potassium hydroxide on the ethanes, followed by the addition of an excess of hydrochloric acid. Each of the enols can be recrystallized from ether without ketonization; in one case the enol was recovered unchanged after standing for several months in ether solution. The enols revert to the tautomeric diketones when heated in ordinary glass melting point tubes so that the melting points must be determined on a metal block. At the melting point the enols revert fairly rapidly to the diketones.

Chloroform solutions of the enols instantaneously absorb the calculated quantity of bromine, liberating hydrogen bromide and giving the corresponding 1,1-diaroyl-1-bromoethanes. These bromine compounds are quantitatively converted by potassium iodide and acid into the diaroylethanes from which the enols were prepared.

The above changes are summarized structurally



A previous paper from this Laboratory[2] compared the alkaline cleavage of some unsymmetrical diaroylmethanes with the alkaline cleavage of the corresponding unsymmetrical diaroylethanes. The

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(1) The 1,1-diaroylethanes used in this problem were prepared by Robert Morris, a senior in the Phillips Exeter Academy during the school year 1949–1950.

(2) Bickel, THIS JOURNAL, **67**, 2204 (1945).

(3) Kohler, Tishler and Potter, *ibid.*, **57**, 2518 (1935).

(4) Sprague and Adkins, *ibid.*, **56**, 2672 (1934).

(5) Weygand, *Ber.*, **61**, 687 (1928).

(6) Weygand reported a melting point of 80° for this solid. The pure enol melts at 112° while the diketone melts at 72°. The solid obtained by Weygand was, therefore, undoubtedly a mixture of the tautomeric forms.

(7) Dieckmann, *Ber.*, **55**, 2481 (1922).

direction of the cleavage was shown to be independent of the presence or absence of the methyl group. The conclusion was then drawn that the enolization of the diketones was not a deciding factor in the cleavage, on the assumption that the diaroylethanes were not enolized. The results presently reported quite clearly indicate extensive enolization of diaroylethanes in the presence of alcoholic potassium hydroxide. The above conclusion is therefore invalidated.

This investigation was assisted by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Experimental[8]

1,1-Dibenzoylethane, 1-anisoyl-1-benzoylethane, 1-(*p*-chlorobenzoyl)-1-benzoylethane and 1-(*p*-bromobenzoyl)-1-benzoylethane were prepared as previously described.[2,9]

Preparation of the Enols.—A chilled solution of 7 g. of potassium hydroxide in 50 ml. of methanol was poured quickly with stirring into a chilled solution of 5 g. of the diaroylethane in 100 ml. of methanol. After standing for not more than 15 seconds, the resulting yellow solution was poured into a large excess of iced hydrochloric acid, giving a voluminous white or pale yellow precipitate which was extracted with ether. The ether solution was washed free of acid and then shaken with saturated cupric acetate solution. The precipitated copper salt was washed with ether, then suspended in ether and shaken with hydrochloric acid in order to regenerate the free enol. The enol was recovered from the ether solution in the usual way.

In each case unchanged diaroylethane was recovered from the filtrate from the copper salt. The yields of enols given below are based on the amounts of diaroylethanes not recovered.

Each of the enols is much less soluble in ether than is the parent diketone. Moreover, each enol reverted more or less completely to the diketone at the melting point. In every case the remelting of a once melted and solidified sample gave the pure keto form. Repeated recrystallization of the enols from ether, however, gave no evidence of ketonization. Alcoholic solutions of the enols gave a violet coloration with ferric chloride.

The enol of 1,1-dibenzoylethane, obtained in 95% yield, crystallizes as colorless, flat, elongated plates and melts at 105°.[10] The copper salt separates as green needles and melts at 215°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.7; H, 5.9. Found: C, 80.6; H, 6.1. Calcd. for $C_{32}H_{26}O_4Cu$: C, 71.4; H, 4.9. Found: C, 71.5; H, 5.1.

The enol of 1-anisoyl-1-benzoylethane, obtained in 90% yield, crystallizes as pale yellow, flat, elongated plates and melts at 112°. The copper salt separates as green needles and melts at 195°.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.2; H, 6.0. Found: C, 76.1; H, 6.1. Calcd. for $C_{34}H_{30}O_6Cu$: C, 68.2; H, 5.1. Found: C, 68.3; H, 5.1.

The enol of 1-(*p*-chlorobenzoyl)-1-benzoylethane, obtained in 95% yield, crystallizes as very pale yellow, glistening long, thin plates and melts at 128–129°. The copper salt separates as pale green needles and melts at 235°.

Anal. Calcd. for $C_{16}H_{13}O_2Cl$: C, 70.5; H, 4.8. Found: C, 70.5; H, 5.0. Calcd. for $C_{32}H_{24}O_4Cl_2Cu$: C, 63.3; H, 4.0. Found: C, 63.2; H, 4.2.

The enol of 1-(*p*-bromobenzoyl)-1-benzoylethane, obtained in 95% yield, crystallizes as very pale yellow, flat, elongated plates and melts at 130–131°. The copper salt separates as pale green needles and melts at 240°.

Anal. Calcd. for $C_{16}H_{13}O_2Br$: C, 60.6; H, 4.1. Found: C, 60.4; H, 4.1. Calcd. for $C_{32}H_{24}O_4Br_2Cu$: C, 55:3; H, 3.5. Found: C, 55.3; H, 3.6.

Bromination of the Enols.—A solution of bromine (slight excess) in 10 ml. of chloroform was poured into a solution of 2 g. of the enol in 15 ml. of chloroform. There was an immediate exothermic reaction accompanied by the evolution of hydrogen bromide gas. The chloroform solution was evaporated by a current of air and the product crystallized from a mixture of ether and low-boiling petroleum ether. A quantitative yield of the bromodiaroylethane was realized in each of the four brominations.

The bromo compounds are very soluble in ether and only slightly soluble in petroleum ether.

1,1-Dibenzoyl-1-bromoethane crystallizes as massive, colorless prisms and melts at 68°.

Anal. Calcd. for $C_{16}H_{13}O_2Br$: C, 60.6; H, 4.1. Found: C, 60.6; H, 4.1.

1-Anisoyl-1-benzoyl-1-bromoethane crystallizes as colorless prisms and melts at 82°.

Anal. Calcd. for $C_{17}H_{15}O_3Br$: C, 58.8; H, 4.4. Found: C, 58.8; H, 4.4.

1-(*p*-Chlorobenzoyl)-1-benzoyl-1-bromoethane crystallizes as colorless plates and melts at 67°.

Anal. Calcd. for $C_{16}H_{12}O_2ClBr$: C, 54.6; H, 3.4. Found: C, 54.8; H, 3.7.

1-(*p*-Bromobenzoyl)-1-benzoyl-1-bromoethane crystallizes as colorless needles and melts at 75–76°.

Anal. Calcd. for $C_{16}H_{12}O_2Br_2$: C, 48.5; H, 3.1. Found: C, 48.8; H, 3.0.

Action of Hydrogen Iodide on the Bromo Compounds.—A mixture of 1 g. of the diaroylbromoethane, 3 g. of potassium iodide, 5 ml. of 6 *N* hydrochloric acid and 40 ml. of alcohol-free acetone was boiled for about five minutes, let stand for about fifteen minutes and then poured into ether and water. The ether extract was washed with water, then with sodium thiosulfate solution to remove the free iodine, again with water and then dried over anhydrous sodium sulfate. In each case a quantitative recovery of the diaroylethane was realized from the ether solution, the diaroylethanes being identified by mixed melting points with authentic specimens.

EXETER, N. H.

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[8] The melting points of the enols and their copper salts were determined on an aluminum block.

[9] Bickel, THIS JOURNAL, **67**, 2045 (1945).

[10] Dieckmann[7] reported a melting point of 110° which the present authors have been unable to duplicate.