

p-Ethylphenylphosphonic Acid.—1-Ethyl-4-nitrobenzene (Eastman P 2996) was redistilled and the fraction boiling at 139–143 at 25 mm. was collected. It was readily reduced with Raney nickel and hydrogen at 40 lb. pressure to *p*-ethylamine, b.p. 115–120° at 29 mm. *p*-Ethylbenzenediazonium fluoroborate was obtained from the amine by method IIA⁶ and used immediately for the preparation of *p*-ethylphenylphosphonic acid by the general method previously described.² The phosphonic acid was purified by Procedure A.^{2a}

Acknowledgments.—The authors wish to thank Mrs. Barbara Stanley for performing the analyses necessary for this research and Mr. Edward L. Petit for skilled technical assistance.

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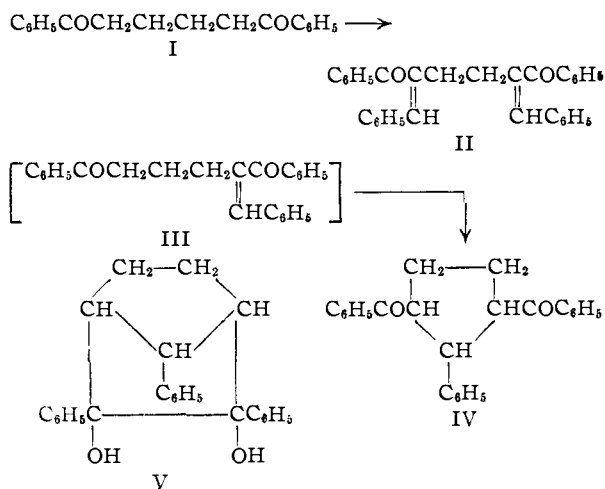
Condensation of 1,4-Diaroylbutanes with Benzaldehyde

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RECEIVED JUNE 14, 1954

In the base-catalyzed condensation of 1,4-dibenzoylbutane (I) with benzaldehyde it was discovered that the dibenzal derivative II can be made successfully only by using a large excess of the aldehyde. Smaller amounts of benzaldehyde gave instead 1,3-dibenzoyl-2-phenylcyclopentane (IV), formed presumably by cyclization of the monobenzal derivative III by an internal Michael reaction.

In the cyclopentane derivative the two benzoyl groups appear to lie on the same side of the ring because the compound yields a pinacol V when reduced by the binary mixture Mg–MgI₂.¹ The reduction is analogous to that involved in the formation of satene glycol from 1,3-diacetylcyclohexane.² Oxidation with potassium permanganate converted the 2,3-dihydroxy-2,3,7-triphenylbicyclo[2,2,1]heptane (V) to the original diketone IV.



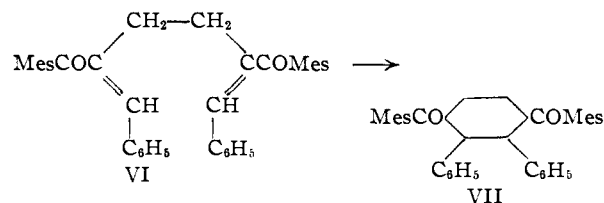
As was reported earlier,³ the dibenzal derivative VI of 1,4-dimesitylbutane is formed in satis-

(1) M. Gomberg and W. E. Bachmann, *THIS JOURNAL*, **49**, 236 (1927).

(2) L. M. Mohunta and J. N. Ray, *J. Chem. Soc.*, 1328 (1934).

(3) R. C. Fuson and R. W. Hill, *J. Org. Chem.*, **19**, 1575 (1954).

factory yield when the diketone and the aldehyde are taken in the theoretical amounts. Reduction of this compound with the binary mixture appears to occur in the conjugate manner to bring about cyclization. Although a satisfactory proof of structure was not worked out, the product is believed to be 1,4-dimesityl-2,3-diphenylcyclohexane (VII).



Experimental

1,4-Dibenzal-1,4-dibenzoylbutane (II).—A solution of 10 g. (0.0375 mole) of 1,4-dibenzoylbutane, 6.0 g. of sodium methoxide and 200 ml. of absolute ethanol was heated under reflux, with stirring, for 1.5 hours. The solution was cooled to 0°, the rate of stirring being increased to prevent clumping of the crystals which separated. To the cold mixture was added, with rapid stirring, 10 g. (0.094 mole) of benzaldehyde. After 10 minutes the ice-bath was removed and stirring continued for an additional hour at room temperature. The mixture was poured into iced acetic acid and, after the resulting mixture had been allowed to stand for an hour, it was extracted with benzene and with ether. The product, a dark yellow oil, crystallized from ethanol. The first two crops of crystals (1.5 g.) proved to be unchanged 1,4-dibenzoylbutane.

The residue from the second filtration was distilled *in vacuo*, and the oil which remained was distilled through a short-path still. Three fractions were collected; a low-boiling liquid which was found to be benzaldehyde, a middle fraction (144–159° (0.5 mm.)) which was the dibenzal derivative and a high-boiling fraction (159–220° (0.5 mm.)) which was a mixture of the dibenzal derivative with unchanged dibenzoylbutane. The pure dibenzal derivative boils at 166° (0.5 mm.); it crystallizes from an ethanol-water solution to give long, colorless needles, m.p. 39–40°.

*Anal.*⁴ Calcd. for C₂₂H₂₆O₂: C, 86.83; H, 5.92. Found: C, 86.89; H, 6.45.

The infrared spectrum⁵ shows no evidence of a hydroxyl group, but does indicate the presence of monosubstituted benzene; aromatic stretching vibrational band splitting at 1600 cm.⁻¹ indicates there is conjugation with the benzene ring. Absorption at 1647 cm.⁻¹ indicates the presence of a highly conjugated carbonyl group, and a band at 1629 cm.⁻¹ may be assigned to a conjugated carbon-carbon double bond.

1,3-Dibenzoyl-2-phenylcyclopentane (IV).—A solution of 10 g. of 1,4-dibenzoylbutane in 100 ml. of 95% ethanol was heated under reflux for 30 minutes, with stirring, with 4.2 g. of potassium hydroxide. To this mixture 5.74 g. of benzaldehyde was added rapidly, and heating was continued for one hour. The mixture was poured into iced hydrochloric acid, and the resulting mixture was treated with benzene. A high-melting solid (m.p. 238°), which was insoluble in most organic solvents, was not identified. From the filtrate 3.5 g. of a colorless crystalline solid, m.p. 158–159°, was obtained. Two more recrystallizations from benzene gave the pure compound, m.p. 162.5–163°. All the mother liquors were combined and the solvent was distilled under diminished pressure. The residual viscous, dark-brown oil was distilled *in vacuo* through a short-path still, two fractions being collected in approximately equal amounts. The first (b.p. 144° (0.3 mm.)) was the dibenzal derivative. The second (b.p. 214–225° (0.3 mm.)) was dissolved in ethanol; the solution, when allowed to stand, deposited colorless crystals of the cyclopentane derivative IV.

Anal. Calcd. for C₂₅H₂₂O₂: C, 84.72; H, 6.26. Found: C, 84.80; H, 6.23.

(4) Microanalyses by Miss L. Chang and Mr. Josef Nemeth.

(5) The infrared spectra mentioned in this paper were recorded and interpreted by Miss Helen Miklas.

The infrared spectrum has a strong, slightly unsymmetrical band at 1683 cm.^{-1} , which may be attributed to the presence of a conjugated carbonyl group. The $6\ \mu$ aromatic bands are split and relatively strong, as is usually the case when there is conjugation outside the ring.

Reduction of 1,3-Dibenzoyl-2-phenylcyclopentane (IV).—To a mixture of 1.92 g. of magnesium, 40 ml. of dry *n*-butyl ether and 80 ml. of dry toluene was added, with stirring, 9.8 g. of iodine. The mixture was heated under reflux and, when the iodine color had disappeared, 1.5 g. of 1,3-dibenzoyl-2-phenylcyclopentane was added in 40 ml. of hot dry toluene. After being heated under reflux, with stirring, for 19 hours, the reaction mixture was poured into iced hydrochloric acid. The product, crystallized from methanol, melts at $82\text{--}83^\circ$; slightly above this temperature it resolidifies and melts again at 167° .

Anal. Calcd. for $\text{C}_{26}\text{H}_{24}\text{O}_2$: CH_3OH : C, 80.83; H, 7.27. Found: C, 79.50; H, 7.17.

Since the composition of the low-melting crystals (m.p. $82\text{--}83^\circ$) corresponds approximately to that of the glycol solvated with a molecule of methanol, the compound was heated at the boiling point of acetone for four days under reduced pressure. It was then found to melt at $167\text{--}168^\circ$ without previous melting.

Anal. Calcd. for $\text{C}_{28}\text{H}_{24}\text{O}_2$: C, 84.24; H, 6.79. Found: C, 84.28; H, 7.03.

The infrared spectrum still has strong absorption between 1000 and 1100 cm.^{-1} .

Oxidation of the Glycol V.—A solution of 250 mg. of potassium permanganate in 50 ml. of reagent acetone was added, with stirring, over a period of 30 minutes to a solution of 50 mg. of the glycol in 50 ml. of reagent acetone. The excess permanganate was carefully reduced to manganese dioxide with aqueous sodium bisulfite and the mixture filtered. The organic product separated from benzene as colorless crystals, m.p. $162.5\text{--}163.5^\circ$, and was shown by a mixed melting point determination to be 1,3-dibenzoyl-2-phenylcyclopentane.

Reduction of 1,4-Dibenzal-1,4-dimesitylbutane.—A mixture of 1.92 g. of magnesium, 40 ml. of dry *n*-butyl ether, 80 ml. of dry toluene and 9.8 g. of iodine was heated under reflux until the iodine color had disappeared. A hot solution of 10.5 g. of the diketone in 40 ml. of toluene was added, and the mixture was heated for 20 hours under reflux, with stirring. After being allowed to cool, the mixture was treated with iced hydrochloric acid; the product, isolated by conventional procedures, was a viscous yellow oil which crystallized from ethanol. The crystallization occurred over a period of several days, yielding starting material as well as the cyclohexane derivative VII which, after repeated recrystallization, melted at 312° . It was observed to change its crystalline form before melting.

Anal. Calcd. for $\text{C}_{38}\text{H}_{40}\text{O}_2$: C, 86.32; H, 7.62. Found: C, 86.06; H, 7.95.

The infrared spectrum has absorption bands assignable to a hindered, unconjugated carbonyl group (at 1683 cm.^{-1}), a mesityl group (at 1611 and 852 cm.^{-1}) and monosubstituted phenyl (at 698 cm.^{-1}).

Degradation of the Cyclohexane Derivative VII.—Five hundred milligrams of the reduction product was heated at 300° *in vacuo* for one hour with a palladium-on-charcoal catalyst. During the heating a gas was evolved, a liquid was produced which could be condensed in a solid carbon dioxide trap, and a solid sublimed. The liquid separated into two layers, one of which proved to be water; it was identified by boiling point and melting point and by the fact that it converted acetyl chloride to acetic acid. The other layer had the boiling point of mesitylene.

The material which sublimed from the reaction mixture was warmed with a 10% solution of sodium bicarbonate, and the aqueous layer was extracted with benzene and then with ether. Careful acidification of the water layer yielded a solid which was shown, by the method of mixed melting points and by a comparison of infrared spectra, to be mesitoic acid. The organic layer was distilled and the residue was sublimed under diminished pressure, *in vacuo* at 50° . The solid so obtained, after further purification by resublimation, melted at $66\text{--}67^\circ$. This compound has the composition of an aromatic hydrocarbon but was not studied further.

Anal. Found: C, 92.69; H, 7.96.

The residue, which remained after the easily sublimed hydrocarbon had been removed, was sublimed at 100° *in vacuo* and recrystallized from benzene; m.p. 59° . Although the infrared spectrum of this compound is superimposable upon that of *o*-terphenyl, a mixed melting point determination with an authentic specimen of *o*-terphenyl was depressed. Analytical values show also that, if the solid is *o*-terphenyl, it is not pure. Lack of material prevents further examination of this compound.

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An Improved Synthesis of Fluorene-1-carboxylic Acid¹

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RECEIVED JULY 8, 1954

The preparation of fluorene-1-carboxylic acid from fluorenone-1-carboxylic acid by a modified Wolff-Kishner reduction has been reported recently by Bergmann and Orchin.² However, the yields in this reduction were unsatisfactory in our hands and never exceeded 30%. Nearly quantitative yields and products of satisfactory purity were obtained consistently by a modification of the Clemmensen-Martin reduction.³ The success of the method depends on the presence of sufficient glacial acetic acid (98 ml./g. of ketone) to keep the ketone in solution and on the addition of enough concentrated hydrochloric acid (2 ml./g. of zinc amalgam) over a period of 40 hours. A similar modification using glacial acetic acid to solubilize the ketone has been employed previously for the reduction of fluorenone to fluorene.⁴

The general applicability of this method to fluorenone and its derivatives is of some importance since many compounds of the fluorene series can only be prepared from the corresponding fluorenone.

Experimental

Zinc amalgam (200 g.) was prepared according to the directions of Martin⁵ and placed into a 3-liter three-necked flask fitted with a reflux condenser and a Hershberg stirrer.⁶ To the zinc amalgam were added 60 ml. of glacial acetic acid and 60 ml. of concentrated hydrochloric acid and the mixture was heated to boiling. Fluorenone-1-carboxylic acid (10.0 g.), m.p. $191\text{--}194^\circ$,⁶ was dissolved in 600 ml. of hot glacial acetic acid and introduced over a period of 15 minutes into the reaction mixture which was stirred and refluxed vigorously throughout the entire run. A total of 395 ml. of concentrated hydrochloric acid and 235 ml. of glacial acetic acid was delivered into the solution in 20–25 ml. portions during the following 18 hours. Freshly prepared zinc amalgam (60 g.) then was added, followed by a total of 330 ml. of concentrated hydrochloric acid and 100 ml. of glacial acetic acid during the next 6 hours. The addition of fresh zinc amalgam (60 g.) was repeated followed by 300 ml. of concentrated hydrochloric acid and 150 ml. of glacial acetic acid over a period of 7 hours. At the end of this time all of the zinc amalgam had been used up in the reduction. To isolate the product, the dark-green solution was then reduced to one-third of its volume by distillation under reduced pressure. The concentrated mixture was next boiled for 5 minutes and then cooled in an ice-bath. The dark-brown precipitate was collected on a Büchner funnel and washed free of acid with distilled water. It was then

(1) Supported by a grant from the Graduate School, University of Minnesota.

(2) E. Bergmann and M. Orchin, *THIS JOURNAL*, **71**, 1111 (1949).

(3) E. L. Martin, *ibid.*, **58**, 1438 (1946).

(4) J. H. Peters, unpublished experiments.

(5) E. B. Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 313 (1936).

(6) All melting points are corrected.