

ketone (1667  $\text{cm}^{-1}$ ), a monosubstituted phenyl derivative (692, 755  $\text{cm}^{-1}$ ), and a duryl group (870  $\text{cm}^{-1}$ ).

*Conversion of duryl 2-hydroxy-4-benzyl-3,4-dihydrophenyl ketone into 2,4-dibenzylphenyl duryl ketone.* The Grignard reagent prepared from 3.52 g. (0.028 mole) of benzyl chloride, 0.68 g. (0.028 g.-atom) of magnesium turnings, and 50 ml. of anhydrous ether was placed in a dropping funnel; 20 ml. of the reagent was added dropwise with stirring to a solution of 1.0 g. (0.0029 mole) of duryl 2-hydroxy-4-benzyl-3,4-dihydrophenyl ketone in 20 ml. of anhydrous ether under a nitrogen atmosphere. The reaction mixture was heated under reflux for 1 hr., and stirring was continued for 12.5 hr. After hydrolysis with dilute hydrochloric acid solution, the product was taken up in ether, and the solution washed with water and concentrated; 1.0 g. (79% yield) of a  $\text{C}_{31}\text{H}_{34}\text{O}_2$  compound precipitated as colorless crystals, m.p. 206.5–208°, dec. An analytical sample melted at 210–210.5°.

*Anal.* Calcd. for  $\text{C}_{31}\text{H}_{34}\text{O}_2$ : C, 84.89; H, 7.81. Found: C, 84.75; H, 7.74.

A mixture of 0.35 g. (0.0008 mole) of the product ( $\text{C}_{31}\text{H}_{34}\text{O}_2$ ) and 0.06 g. of 10% palladium-on-charcoal was heated at 250–275° for 1 hr. under a slow stream of nitrogen, allowed to cool, and extracted with acetone. The solution was filtered and concentrated. Crystallization of the residue from methanol and water solution gave 0.054 g. (16% yield) of 2,4-dibenzylphenyl duryl ketone, m.p. 93–95°. The melting point of a mixture of this ketone with an authentic sample<sup>9</sup> was not depressed. The intermediate compound (m.p. 210–210.5°) undergoes not only dehydrogenation when heated with palladium-on-charcoal but loses the elements of water as well; in it the hydroxyl group and one of the benzyl groups are *ortho* to the ketone group. Whether they are attached to the same carbon atom or not has not been established.

URBANA, ILL.

(9) R. C. Fuson, J. P. Freeman, and J. J. Looker, *J. Org. Chem.*, **26**, 4217 (1961).

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

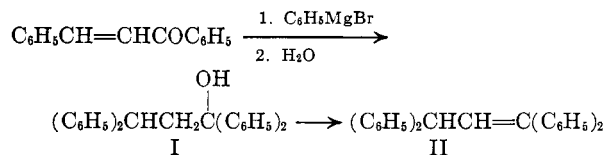
## Condensation of Benzalacetophenone with Phenylmagnesium Bromide. 2-Benzhydryl-2-hydroxy-3,3-diphenylpropionic Acid<sup>1</sup>

REYNOLD C. FUSON, THET SAN,<sup>2</sup> AND JÜRGEN DIEKMANN

Received November 3, 1961

1,1,3,3-Tetraphenyl-1-propanol (I) was formed by treating benzalacetophenone with a large amount of phenylmagnesium bromide and decomposing the reaction mixture with water. When the reaction mixture was poured on solid carbon dioxide, 2-benzhydryl-3-hydroxy-3,3-diphenylpropionic acid (IV) was produced.

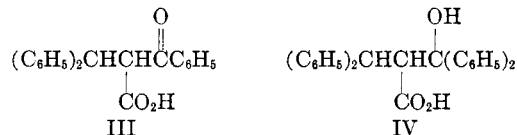
When the reaction mixture obtained by the treatment of benzalacetophenone with large amounts of phenylmagnesium bromide was hydrolyzed, 1,1,3,3-tetraphenyl-1-propanol (I), a *di-addition* product, was obtained accompanied by the 1,4-addition product,  $\beta,\beta$ -diphenylpropiophenone. Dehydration of the propanol by the use of acetic anhydride or a glacial acetic acid–hydrochloric acid mixture afforded 1,1,3,3-tetraphenylpropene (II). This propene had been made also by Vorländer and Siebert.<sup>3</sup>



*p*-Chlorobenzalacetophenone was found to undergo a similar condensation when treated with large amounts of phenylmagnesium bromide. Dehydration of the resulting carbinol gave 1,1,3,3-triphenyl-3-*p*-chlorophenylpropene. The structure of this propene was proved by synthesis. The olefin was made by adding phenylmagnesium bromide to

$\beta$ -*p*-chlorophenyl- $\beta$ -phenylpropiophenone and dehydrating the carbinol that was produced.

Treatment of benzalacetophenone with large amounts of the phenyl reagent followed by pouring the reaction mixture on solid carbon dioxide gave, in addition to  $\alpha$ -benzhydrylbenzoylacetic acid (III), an acid (in low yield) that corresponds to the addition of two moles of the Grignard reagent to the unsaturated ketone followed by carbonation. The acid has now been identified as 2-benzhydryl-3-hydroxy-3,3-diphenylpropionic acid (IV).



When a solution of the acid IV in ethanol was treated with hydrochloric acid, dehydration took place accompanied by decarboxylation, and 1,1,3,3-tetraphenylpropene (II) was isolated as the product. The formation of this hydrocarbon indicated that the acid IV probably was a  $\beta$ -hydroxy acid; such acids are known to undergo this type of reaction.<sup>4</sup> The methyl ester, prepared with the aid of diazomethane, was stable to long heating in acetic anhydride.

(1) This investigation was supported in part by a grant from the Office of Ordnance Research, U. S. Army (Contract No. DA-11-022-ORD-874).

(2) State Scholar of the Government of the Union of Burma, 1954–1957.

(3) D. Vorländer and C. Siebert, *Ber.*, **39**, 1024 (1906).

(4) D. S. Noyce, P. A. King, and G. L. Woo, *J. Org. Chem.*, **26**, 632 (1961).



78° and then under reflux for 18 hr. The mixture was then poured rapidly on pulverized Dry Ice which had been spread evenly on the bottom of a 4-l. beaker. The reaction mixture was allowed to stand overnight and decomposed with cold hydrochloric acid. The organic layer was washed with water and extracted with three 100-ml. portions of 5% sodium hydroxide. The basic extract was diluted to 800 ml. and then heated on a steam bath. The colorless  $\beta,\beta$ -diphenylpropionophenone that separated was collected by filtration, yield 4.1 g. When the filtrate was acidified with hydrochloric acid, a copious, colorless precipitate appeared. The acidified mixture was heated to 90°, and 0.9 g. of undissolved solid was collected by filtration. The solid was dissolved in hot ethanol, and the resulting solution filtered to remove insoluble impurities. When cooled the solution deposited the pure acid as a colorless solid, yield 0.4 g. (4%), m.p. 215–216°.

*Anal.* Calcd. for  $C_{28}H_{24}O_3$ : C, 82.33; H, 5.92. Found: C, 82.51; H, 6.17.

The acid was made also from  $\beta,\beta$ -diphenyl- $\alpha$ -bromopropionophenone by way of benzhydrylbenzoylactic acid. The bromo ketone (10 g., 0.027 mole) in 30 ml. of ether was added to a 0.087-mole portion of phenylmagnesium bromide solution in ether. The reaction mixture was stirred for 2 hr. and then poured into a slurry of Dry Ice in ether. A colorless salt, collected by filtration, was washed with two 100-ml. portions of ether and decomposed with dilute hydrochloric acid by prolonged shaking. The product was extracted with ether, and the organic layer was washed with water and dried. After evaporation of the ether a colorless solid remained. Two recrystallizations from an acetone-petroleum ether mixture gave the benzhydrylbenzoylactic acid as short, white needles, m.p. 127–128°, with decomposition, yield 5.8 g. (60%).

To a cooled phenylmagnesium bromide solution containing 0.03 mole of reagent was added rapidly 3.3 g. (0.01 mole) of  $\alpha$ -benzhydrylbenzoylactic acid in 30 ml. of ether. A colorless precipitate appeared immediately in the reaction mixture, which was then stirred for 4 hr. Nearly 2 g. of  $\beta,\beta$ -diphenylpropionophenone was recovered, and 0.42 g. (10%) of 2-benzhydryl-3-hydroxy-3,3-diphenylpropionic acid was ob-

tained. A mixed melting point with an authentic sample of the acid did not show a depression.

The acid (0.8 g.) was dissolved in 10 ml. of alcohol and to this solution was added 0.5 ml. of concentrated hydrochloric acid. The mixture was heated on a steam bath for 15 min. and stored overnight in a refrigerator. The product (0.65 g.) was recrystallized from alcohol, m.p. 124–126°. A mixed melting point determination and the infrared spectral data indicate that the product is 1,1,3,3-tetraphenylpropene.

*Methyl 2-benzhydryl-3-hydroxy-3,3-diphenylpropionate.* To a solution of 0.4 g. (0.001 mole) of 2-benzhydryl-3-hydroxy-3,3-diphenylpropionic acid in 30 ml. of an ether-benzene mixture was added an ether solution of diazomethane prepared from 1 g. of *N*-nitrosomethylurea.<sup>10</sup> The solution was kept in an ice bath for 1 hr. and then allowed to warm to room temperature. After 8 hr. it had turned nearly colorless, and the solvent was evaporated. The ester, isolated as a colorless solid (0.4 g.), was recrystallized from ethanol, m.p. 170–171°.

*Anal.* Calcd. for  $C_{28}H_{28}O_3$ : C, 82.44; H, 6.20. Found: C, 82.02; H, 6.21.

A solution of 0.4 g. of the ester in 15 ml. of acetic anhydride was heated under reflux for 12 hr.; 0.3 g. of starting material was recovered.

*Attempted hydrogenolysis of 2-benzhydryl-3-hydroxy-3,3-diphenylpropionic acid.* The acid in absolute ethanol was treated with hydrogen gas with Raney nickel as a catalyst at a pressure of 50 atm. and 100° for 4 hr. The product, a colorless oil, could not be induced to crystallize. Its infrared spectrum showed a weak carbonyl band. It was concluded that fragmentation of the acid had occurred.

To a solution of the acid (0.2 g., 0.0005 mole) in 35 ml. of ethanol was added 10% palladium-on-charcoal as a catalyst. The acid failed to take up hydrogen over a period of 8 hr. and was recovered quantitatively. Hydrogenolysis also failed to occur with platinum oxide as a catalyst and at a pressure of 4 atm. of hydrogen.

URBANA, ILL.

(10) F. Arndt, *Org. Syntheses*, Coll. Vol. II, 165 (1943).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

## Reactions of trans- $\alpha$ -Phenylchalcone Oxides with Phenylmagnesium Bromide and Phenyllithium<sup>1</sup>

SISTER ST. FRANCIS DILGEN, C.S.J.,<sup>2</sup> AND DOUGLAS J. HENNESSY

Received October 27, 1961

The reactions of phenylmagnesium bromide and phenyllithium with trans- $\alpha$ -phenylchalcone oxide and two related trans- $\alpha,\beta$ -epoxyketones have been investigated. The phenyl substituent in the  $\alpha$ -position of the chalcone oxide bestowed an added stability on the primary addition products and permitted the isolation of the  $\alpha,\beta$ -epoxy alcohols when excess organometallic reagent was used at room temperature. When the  $\alpha,\beta$ -epoxy alcohols were forced to cleave under the influence of acid or organometallic reagent, the manner of cleavage depended upon the substitution in the molecule and on the reagent used.

Previously studied Grignard reactions of  $\alpha,\beta$ -epoxy ketones had generally been observed to yield epoxy alcoholates which readily underwent cleavage.<sup>3</sup> Since the observed cleavage took place between the oxirane ring and the alcoholic side

chain as shown in Fig. 1, path A, it was decided to investigate the effect of an  $\alpha$ -phenyl substituent on the course of the reaction. One equivalent of phenylmagnesium bromide reacted with trans- $\alpha,\beta$ -diphenylacrylophenone oxide (I) at room temperature to form an ether-insoluble complex

(1) Presented at the national meetings of the American Chemical Society in Miami in April 1957 and in New York in September 1957.

(2) Taken from the thesis presented to Fordham University in partial fulfillment for the Ph.D. degree by S. S. F. Dilgen, 1959.

(3) (a) N. G. Gaylord and E. I. Becker, *Chem. Revs.* **49**, 413 (1951). (b) E. P. Kohler and C. L. Bickel, *J. Am. Chem. Soc.*, **57**, 1099 (1935). (c) E. P. Kohler, N. K. Richtmyer, and W. F. Hester, *J. Am. Chem. Soc.*, **53**, 205 (1931). (d) C. L. Bickel, *J. Am. Chem. Soc.*, **59**, 325 (1937).