ketone (1667 cm.⁻¹), a monosubstituted phenyl derivative (692, 755 cm.⁻¹), and a duryl group (870 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 $C_{31}H_{34}O_2$ compound precipitated as colorless crystals, m.p. 206.5-208°, dec. An analytical sample melted at 210-210.5°.

Anal. Caled. for $C_{31}H_{34}O_2$: 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 ($C_{31}H_{34}$ O₂) 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 sample⁹ 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.

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

Condensation of Benzalacetophenone with Phenylmagnesium Bromide. 2-Benzhydryl-2-hydroxy-3,3-diphenylpropionic Acid¹

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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 *diaddition* product, was obtained accompanied by the 1,4-addition product, β , β -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.³

$$C_{6}H_{5}CH = CHCOC_{6}H_{5} \xrightarrow{1. C_{6}H_{6}MgBr} \xrightarrow{2. H_{4}O} OH$$

$$(C_{6}H_{5})_{2}CHCH_{2}C(C_{6}H_{5})_{2} \longrightarrow (C_{6}H_{5})_{2}CHCH = C(C_{6}H_{5})_{2}$$

$$I$$

$$I$$

$$I$$

$$I$$

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

Q	OH
$(C_6H_5)_2CHCHCC_6H_5$	$(C_6H_5)_2CHCHC(C_6H_5)_2$
$\rm CO_2H$	$\mathrm{CO}_{2}\mathrm{H}$
III	\mathbf{IV}

When a solution of the acid IV in ethanol was treated with hydrochloric acid, dehydration took place accompanied by decarboxylation, and 1,1,3,3tetraphenylpropene (II) was isolated as the product. The formation of this hydrocarbon indicated that the acid IV probably was a β -hydroxy acid; such acids are known to undergo this type of reaction.⁴ 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).

The structure of 2-benzhydryl-3-hydroxy-3,3diphenylpropionic acid was confirmed by synthesis. Benzhydrylbenzoylegetia paid propared by the

Benzhydrylbenzoylacetic acid, prepared by the method of Kohler and Tishler,⁵ was treated with phenylmagnesium bromide; the 2-benzhydryl-3hydroxy-3,3-diphenylpropionic acid that was formed proved to be identical with that made from benzalacetophenone directly.

The formation of the carbinol I from the unsaturated ketone must involve the addition of two molecules of phenylmagnesium bromide. The first molecule of reagent is known to react in the 1,4manner to give the corresponding bromomagnesium enolate. To produce the carbinol, the enolate would have to react as the isomeric keto Grignard reagent.

 $(C_{6}H_{\delta})_{2}CHCH \longrightarrow \bigcup_{\substack{i \\ C_{6}H_{\delta}}} (C_{6}H_{\delta})_{2}CHCHCOC_{6}H_{\delta} \longrightarrow I$

An alternative explanation, suggested by Lyle and Troscianicc,⁶ is that the addition of the second molecule of Grignard reagent occurs during the workup and involves the ketone formed by hydrolysis of the enolate followed by ketonization of the resulting enol. The course of this reaction is being studied further.

EXPERIMENTAL⁷

Addition of phenylmagnesium bromide to benzalacetophenone. A phenylmagnesium bromide solution was prepared by treating 45 g. of magnesium with 213 g. of bromobenzene in 750 ml. of anhydrous ether. A crystal of iodine was used to start the reaction. The addition of bromobenzene to the reaction mixture was completed in 1 hr., and the solution was heated under reflux for an additional 30 min. The Grignard solution was passed through glass wool to remove the excess magnesium. A solution of 20 g. (0.096 mole) of benzalacetophenone in 200 ml. of benzene was added to the Grignard solution in the course of 40 min. An additional 150 ml. of benzene was added, and the solution allowed to evaporate at its boiling point. After the temperature of the boiling solution reached 78°, the solution was heated under reflux with efficient stirring for 17 hr. The reaction mixture, the volume of which was 600 ml., was then decomposed with ice-cold saturated ammonium chloride solution. The organic layer was washed and dried and the solvent distilled. Removal of the biphenyl by distillation under reduced pressure left a viscous brown oil that weighed 30 g. A 5-g. portion of the oil was heated under reflux with 100 ml. of petroleum ether (b.p. 80-100°) for 4 hr. The solution was filtered, and enough of the solvent allowed to evaporate at room temperature to bring the volume to 40 ml.; colorless crystals weighing 3.5 g. (60%) separated. After recrystallization from petroleum ether, the needle-like crystals melted at 95-96°. The product showed a 10° depression in melting point when mixed with an authentic sample of β , β -diphenylpropiophenone. Its melting point was also depressed by an authentic sample of 1,1,3-triphenyl-1-propanol. The melting point reported in the literature for 1,1,3,3-tetraphenyl-1propanol is 95-96°.³

Anal.⁸ Calcd. for $C_{27}H_{24}O$: C, 88.97; H, 6.64: Found: C, 88.98; H, 6.74.

The infrared spectrum,⁹ determined in chloroform solution, exhibits bands attributable to a hydroxyl group (3525 cm.⁻¹), a methylene group (1465 cm.⁻¹), and a tertiary benzyl-type alcohol group 1115 cm.⁻¹). Absorption assignable to a carbonyl function or an olefinic double bond is absent.

The 40 ml. of mother liquor yielded 0.3 g. of a product that melted at 91-93° after recrystallization from petroleum ether. A mixed melting point determination with β , β -diphenylpropiophenone showed no depression.

Dehydration of 1,1,3,3-tetraphenylpropanol was carried out according to the method of Vorländer and Siebert.³ From a 5-g. portion of the propanol was obtained 3.2 g. of pure 1,1,3,3-tetraphenylpropene, m.p. 125-126°. This value agrees with the melting point reported in the literature.³ The infrared spectrum, measured in chloroform solution, supports the propene structure.

Anal. Calcd. for C₂₇H₂₂: C, 93.60; H, 6.40. Found: C, 93.42; H, 6.36.

1,1,3-Triphenyl 3-p-chlorophenylpropene. p-Chlorobenzal-acetophenone (5 g., 0.021 mole) in 50 ml. of benzene was added to an ether solution of 0.33 mole of phenylmagnesium bromide. An additional 60 ml. of benzene was added to the reaction mixture. The solution was heated without a cooling condenser until the temperature of the mixture had reached 78°, then under reflux for 18 hr. Decomposition of the reaction mixture was carried out with cold saturated ammonium chloride solution. The organic layer was washed with water, and the solvent was distilled under reduced pressure. The residue consisted of 9.6 g. of an oil; a 2-g. portion of it was dissolved in 15 ml. of acetic anhydride, and the resulting solution was heated under reflux for 8 hr. After distillation of the solvent under reduced pressure, the residual oil was chromatographed on acid-washed alumina. With cyclohexane-ether (16:1) as eluent, the collected fractions gave an oil after distillation of the solvent. Crystallization from ethanol gave the olefin as colorless solid, m.p. 93-94°. The infrared spectrum revealed the absence of ketone and alcohol groups; a band at 840 cm. $^{-1}$ is indicative of a trisubstituted double bond. The yield of olefin was 0.6 g. (35%).

Anal. Calcd. for $C_{27}\dot{H}_{21}Cl$: C, 85.14; H, 5.56. Found: C, 85.44; H, 5.69.

1,1,3-Triphenyl-3-p-chlorophenylpropene from β -p-chlorophenyl- β -phenylpropiophenone. β -p - Chlorophenyl- β -phenylpropiophenone (1 g., 0.004 mole) in 15 ml. of ether was added to a solution of 0.01-mole of phenylmagnesium bromide. The reaction mixture was heated under reflux for 1 hr. and decomposed with cold saturated ammonium chloride solution. The organic layer was washed with water, dried, and concentrated by distillation. The residual oil was dissolved in 15 ml. of acetic anhydride and heated under reflux for 8 hr. The solvent was then distilled under reduced pressure, and the product crystallized from ethanol, m.p. 93–94°, yield 1.0 g. It did not show a depression in melting point when mixed with a sample of the propene previously described.

2-Benzhydryl-3-hydroxy-3,3-diphenylpropionic acid. A solution of 5 g. (0.024 mole) of benzalacetophenone in 50 ml. of benzene was added to a solution of 3.4 moles of phenylmagnesium bromide. An additional 60 ml. of benzene was then added, and heating without a cooling condenser was carried out until the temperature of the mixture had reached

⁽⁵⁾ E. P. Kohler and M. Tishler, J. Am. Chem. Soc., 54, 1594 (1932).

⁽⁶⁾ R. E. Lyle and H. J. Troscianiec, J. Org. Chem., 24, 333 (1959).

⁽⁷⁾ All melting points are uncorrected.

⁽⁸⁾ The microanalyses were carried out by Mr. J. Nemeth, Mrs. R. Maria Benassi, Mr. Lucy Chang, Mrs. Esther Fett, Mrs. Ruby Ju, Mr. Rollo Nesset, Miss Claire Higham, and Miss Jane Liu.

⁽⁹⁾ The infrared spectra were determined by Mr. James Brader, Mrs. Louise Griffing, Mrs. Beverly Thomas, Mr. Paul McMahon, Mrs. Betty Verkade, and Miss Clair Leubka.

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 β , β -diphenylpropiophenone 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. Caled. for C₂₈H₂₄O₃: C, 82.33; H, 5.92. Found:

C, 82.51; H, 6.17. The acid was made also from β,β -diphenyl- α -bromopropiophenone by way of benzhydrylbenzoylacetic 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 benzhydrylbenzoylacetic 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 α -benzhydrylbenzoylacetic 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 $\beta_{\beta}\beta$ -diphenylpropiophenone 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. $124-126^{\circ}$. 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.¹⁰ 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. Caled. for C29H26O3: 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-3,3diphenylpropionic 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.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

Reactions of *trans-α*-Phenylchalcone Oxides with Phenylmagnesium Bromide and Phenyllithium¹

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The reactions of phenylmagnesium bromide and phenyllithium with trans- α -phenylchalcone oxide and two related trans- α , β -epoxyketones have been investigated. The phenyl substituent in the α - position of the chalcone oxide bestowed an added stability on the primary addition products and permitted the isolation of the α , β -epoxy alcohols when excess organometallic reagent was used at room temperature. When the α , β -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 α,β epoxy ketones had generally been observed to yield epoxy alcoholates which readily underwent cleavage.³ 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 α -phenyl substituent on the course of the reaction. One equivalent of phenylmagnesium bromide reacted with *trans*- α,β -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.

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