

## Experimental

### I. Addition of the Magnesium Derivative of $\beta,\beta$ -Diphenyl Propiophenone to Unsaturated Ketones

Preliminary experiments showed that in an atmosphere of nitrogen it is possible to convert a mole of  $\alpha$ -bromo- $\beta,\beta$ -diphenyl propiophenone completely into the magnesium derivative represented by (I) by means of a solution of phenylmagnesium bromide prepared from 1.1 atoms of magnesium. These proportions were therefore used in the following experiments.

**Addition to Benzal Acetophenone,  $\beta$ -Phenyl- $\gamma$ -benzoyl- $\gamma$ -benzhydryl Butyrophe- none. III.**—Fourteen and six-tenths grams of the bromo compound was added to a solution of phenylmagnesium bromide prepared from 1.06 g. of magnesium. Although sparingly soluble in ether, the bromo compound dissolved rapidly in the reagent. The solution was boiled for an hour, then treated with 8.33 g. of the unsaturated ketone. It immediately developed a deep orange color and it soon began to deposit a crystalline yellow magnesium derivative (II). It was stirred at the ordinary temperature for forty-five minutes and then filtered. The filtrate and half of the solid were treated separately with iced acid in the usual manner, and the rest of the solid with ammonia and ammonium chloride. All three portions gave the same product—a compound which separated from acetone and alcohol in small prismatic crystals and which melted at  $180^\circ$ .

*Anal.* Calcd. for  $C_{38}H_{30}O_2$ : M, 492; C, 87.5; H, 6.1. Found: M, 468; C, 87.7; H, 6.3.

**The Mono-oxime, IV.**—To a solution of 10 g. of the diketone in 1000 cc. of boiling alcohol were added 8.5 g. of hydroxylamine hydrochloride and 18 g. of potassium hydroxide. The solution was boiled for three hours, then distilled to small volume and diluted with water. The product was recrystallized from alcohol.

*Anal.* Calcd. for  $C_{28}H_{31}O_2N$ : C, 84.9; H, 6.1. Found: C, 85.4; H, 6.3.

The oxime is readily soluble in ether, moderately soluble in boiling alcohol. It separates from alcohol in stout needles or long prisms and it melts at  $165^\circ$ . In order to confirm its relation to the diketone, an alcoholic solution containing a small quantity of the oxime and a little concentrated hydrochloric acid was digested on a steam-bath and then diluted with water. The diketone was the only product.

**Beckmann Rearrangement of the Oxime,  $\beta$ -Phenyl- $\gamma$ -benzoyl- $\gamma$ -benzhydryl-butyric Anilide. V.**—To a solution of 5.5 g. of the oxime in 300 cc. of absolute ether 5.5 g. of phosphorus pentachloride was added in small portions. The mixture was boiled for twenty minutes, then concentrated to 150 cc., and gradually poured into ice water. The resulting gummy precipitate became granular when the ether was evaporated and the residue was digested on a steam-bath. The solid was recrystallized from alcohol.

*Anal.* Calcd. for  $C_{38}H_{31}O_2N$ : C, 84.9; H, 6.1. Found: C, 85.0; H, 6.4.

The anilide is sparingly soluble in ether, moderately soluble in boiling alcohol. It crystallizes in thin needles and it melts at  $198^\circ$ . The yield was excellent.

**Hydrolysis of the Anilide,  $\beta$ -Phenyl- $\gamma$ -benzoyl- $\gamma$ -benzhydryl-butyric Acid. VI.**—The anilide is hydrolyzed with difficulty. An attempt to hydrolyze it by prolonged boiling with alcoholic potassium hydroxide failed completely, all of the anilide being recovered. It can be hydrolyzed by protracted heating to  $180^\circ$  with concd. hydrochloric acid, but owing to cleavage and other reactions, the yield is small—about 35%. It was finally hydrolyzed more successfully by heating it for eight hours to  $180^\circ$  with a solution of concd. hydrochloric acid in glacial acetic acid. The yield of acid was 60%. It crystallized from ether and petroleum ether in long slender needles and melted at  $156^\circ$ .

*Anal.* Calcd. for  $C_{30}H_{28}O_3$ : C, 83.0; H, 6.1. Found: C, 83.0; H, 6.3.

**Bromination of the Acid,  $\beta$ -Phenyl- $\gamma$ -bromo- $\gamma$ -benzoyl-butyric Acid, VII.**—Bromine

was added, little by little, to a solution of the acid in chloroform until the color persisted. The solution was allowed to evaporate spontaneously; it gradually deposited a crystalline bromo acid and left an oily residue. The oil was removed with ether and petroleum ether, and distilled with steam. The distillate contained a precipitate which, after crystallization from ether, melted at 66° and which was identified as diphenylcarbinol by comparison with a sample on hand. One of the bromination products, therefore, was diphenylmethyl bromide.

The bromo acid was recrystallized from chloroform and petroleum ether. It separated in small prisms and it melted at 166°.

*Anal.* Calcd. for  $C_{17}H_{15}O_3Br$ : C, 58.8; H, 4.4; Br, 22.7. Found: C, 58.5; H, 4.5; Br, 22.4.

**$\beta$ -Phenyl- $\gamma$ -benzoyl-butyro Lactone, VIII.**—The lactone gradually separates as a crystalline precipitate when a clear solution of the bromo acid in the minimum quantity of dilute sodium carbonate is left to itself; but it is more easily obtained by warming a moist ethereal solution of the hydroxy acid with a little hydrogen chloride. It was purified by crystallization from ether and petroleum ether from which it separates in small cubes melting at 120°.

*Anal.* Calcd. for  $C_{17}H_{14}O_3$ : C, 76.7; H, 5.3. Found: C, 76.7; H, 5.4.

**$\beta$ -Phenyl- $\gamma$ -hydroxy- $\gamma$ -benzoyl-butyric Acid,  $C_6H_5COCHOHCH(C_6H_5)CH_2COOH$ , IX.**—The hydroxy acid is very readily obtained by dissolving either the lactone or the bromo acid in excess of base and acidifying the solution. It was recrystallized from ether and petroleum ether from which it separated in colorless needles melting at 146°.

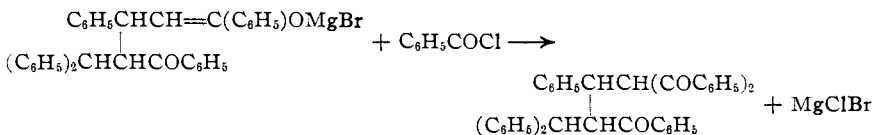
*Anal.* Calcd. for  $C_{17}H_{16}O_4$ : C, 71.8; H, 5.6. Found: C, 71.6; H, 5.7.

**Bromination of the Diketone.**—Bromine was added in small quantities to a solution of 0.5 g. of the diketone in 20 cc. of chloroform until the color persisted. The solution was warmed for an hour, then concentrated and diluted with ether. As was to be expected, the product was a mixture of mono and dibromo compounds, but by repeated recrystallization from methyl alcohol it was possible to isolate a monobromo compound which melted at 132° and which was identified as  $\alpha, \gamma$ -dibenzoyl- $\beta$ -phenyl- $\gamma$ -bromopropane, by comparison with a sample on hand. The yield was about 33%.

**Action of Benzoyl Chloride on the Secondary Magnesium Derivative.**—Although this magnesium derivative (II) does not combine either with more unsaturated ketone or with benzaldehyde, it still reacts with benzoyl chloride. An ethereal solution of 14.6 g. of  $\alpha$ -bromo- $\beta, \beta$ -diphenyl propiophenone was added to a solution of phenylmagnesium bromide prepared from 1.06 g. of magnesium. After this solution had been boiled for twenty minutes, it was treated with 8.33 g. of benzal acetophenone and boiled for four hours during which the usual yellow magnesium derivative was deposited. Finally 7 g. of benzoyl chloride was added and the mixture was boiled again until the yellow magnesium derivative was completely replaced by a colorless crystalline precipitate. The excess of benzoyl chloride was removed with sodium carbonate and the organic product purified by recrystallization from benzene. It separated in silky needles and melted at 180°. The yield was 17.5 g.

*Anal.* Calcd. for  $C_{48}H_{34}O_3$ : C, 86.4; H, 5.7. Found: C, 86.5; H, 6.0.

The composition shows that the reaction introduces an additional benzoyl group. In all probability the substance is a triketone formed in accordance with the equation



Thus it was not hydrolyzed even when it was boiled with a solution of potassium hydroxide in methyl alcohol which rapidly hydrolyzed all the benzoates encountered in this work in the cold. It therefore is not a benzoate but thus far its structure has not been established with certainty.

**Addition to Benzalacetone,  $\alpha$ -Benzhydryl- $\beta$ -phenyl- $\gamma$ -acetyl Butyrophenone,  $\text{CH}_3\text{COCH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CH}[\text{CH}(\text{C}_6\text{H}_5)_2]\text{COC}_6\text{H}_5$ .**—The reaction was carried out in the same manner as with benzalacetophenone and the substances were used in the same proportions. The product was an oily mixture from which it was difficult to separate a definite compound, and the amount of solid ultimately isolated was small. The solid crystallized from ether-petroleum ether in transparent prisms and melted at  $153^\circ$ .

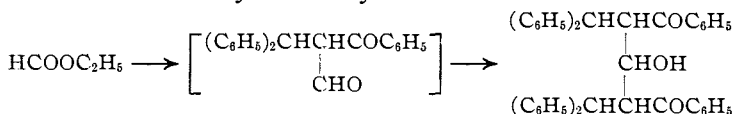
*Anal.* Calcd. for  $\text{C}_{31}\text{H}_{28}\text{O}_2$ : C, 86.1; H, 6.5. Found: C, 85.9; H, 6.7.

## II. Reaction of the Magnesium Derivative of Diphenyl Propiophenone with Aldehydes and Esters

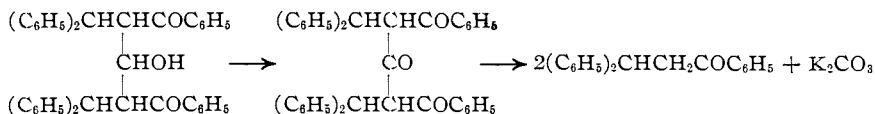
As indicated in the introduction, the magnesium derivative reacts with aldehydes but not with ketones; with ethyl formate but not with more complex esters. The structure of the products of these reactions was established with comparative ease. The product from benzaldehyde reacted with two moles of methylmagnesium iodide and liberated one mole of methane, showing that it contained both an hydroxyl and a carbonyl group. In all probability, therefore, it had been formed by the addition of the magnesium derivative to the carbonyl group of the aldehyde—a fact which was definitely established by oxidizing the substance to benzhydryl dibenzoyl methane



The composition of the product from ethyl formate showed that it had been formed from two molecules of the magnesium derivative and one of the ester. It was *a priori* probable, therefore, that the reaction had followed the same course as with benzaldehyde, the ester being in effect and the intermediate in reality an aldehyde



By cautious treatment with chromic acid it was possible to oxidize the product to a triketone, which alkalis cleaved quantitatively to carbonate and two molecules of diphenyl propiophenone



**Addition to Benzaldehyde.  $\alpha$ -Phenyl- $\beta$ -benzoyl- $\gamma,\gamma$ -diphenyl Propanol. XI.**—A solution of 4 g. of benzaldehyde in an equal volume of ether was added gradually to a solution of the magnesium derivative which had been prepared in the usual manner from 14.6 g. of the bromo compound. The mixture was boiled for four hours during which it gradually turned to a thick paste. By decomposition with iced acid and the usual

manipulations this paste was converted into a solid. The solid was purified by crystallization from acetone and methyl alcohol. It separated in needles and it melted at 133°. The yield was 77%.

*Anal.* Calcd. for  $C_{23}H_{22}O_2$ : C, 85.7; H, 6.1. Found: C, 85.5; H, 6.2.

**Oxidation.**—A solution of 0.75 g. of chromic acid in the minimum quantity of water was added gradually to a warm solution of one gram of the alcohol in 35 cc. of glacial acetic acid. The solution was warmed on a steam-bath until the color changed to green, then allowed to cool. It deposited 0.68 g. of fine needles which melted at 225°, and were identified as benzhydryl dibenzoyl methane by comparison with a sample on hand.

**Reaction with Ethyl Formate,  $\alpha,\gamma$ -Dibenzoyl- $\alpha,\gamma$ -dibenzhydryl- $\beta$ -hydroxy Propane.** XII.—One and one-half grams of ethyl formate was added to a solution of the magnesium derivative which had been prepared from 14.6 g. of the bromo compound. A white precipitate formed immediately but the mixture was boiled for forty-five minutes before it was decomposed with ice and acid in the usual manner. The product was recrystallized from benzene from which it separated in thin needles which melted at 202°. The yield was quantitative.

*Anal.* Calcd. for  $C_{48}H_{46}O_3$ : C, 86.0; H, 6.0. Found: C, 85.9; H, 6.0.

**Oxidation,  $\alpha,\gamma$ -Dibenzoyl- $\alpha,\gamma$ -dibenzhydryl Acetone.**—A solution of 0.12 g. of chromic acid in acetic acid was added to a solution of one gram of the hydroxyl compound in 150 cc. of hot glacial acetic acid. The color changed immediately and when the solution was diluted with a little water and cooled it deposited 0.75 g. of the triketone. The substance was purified by recrystallization from glacial acetic acid from which it separated in needles melting at 232°.

*Anal.* Calcd. for  $C_{48}H_{44}O_3$ : C, 86.0; H, 5.7. Found: C, 86.0; H, 5.7.

**Cleavage of the Triketone.**—A solution of 0.4 g. of the oxidation product in 10% alcoholic potassium hydroxide was boiled for nine hours, then diluted with water and extracted with ether. The ethereal extract, on evaporation, left pure  $\beta,\beta$ -diphenyl propiophenone.

### III. Experiments with the Magnesium Derivative of $\alpha,\beta,\beta$ -Triphenyl Propiophenone

The magnesium derivative was prepared in ethereal solution by the action of phenylmagnesium bromide on the alpha bromo derivative of the ketone or on benzal desoxybenzoin. Attempts to add it to benzal acetophenone, benzaldehyde and formic ester were unsuccessful. In each case, after prolonged boiling, hydrolysis resulted only in the bromine-free ketone.

**Reaction with Benzoyl Chloride,  $\alpha,\beta,\gamma,\gamma$ -Tetraphenylpropenyl Benzoate, XVI.**—An ethereal solution of 8.8 g. of the bromo compound was added to a solution of phenylmagnesium bromide prepared from 0.52 g. of magnesium. The mixture was boiled for forty-five minutes, then treated with 3.0 g. of benzoyl chloride, boiled for another hour and hydrolyzed with iced acid. The product was crystallized from ether and methyl alcohol. It separated in cubical crystals and it melted at 110°. It is very readily soluble in ether, sparingly soluble in methyl alcohol. The yield was 7.2 g.

*Anal.* Calcd. for  $C_{34}H_{28}O_2$ : M, 466; C, 87.5; H, 5.5. Found: M, 447; C, 87.5; H, 5.5.

In a subsequent experiment 9.5 g. of benzal desoxybenzoin was added to a solution of phenylmagnesium bromide prepared from 0.8 g. of magnesium. The mixture was boiled for twenty-five minutes, then treated with 5.7 g. of benzoyl chloride and boiled for two hours. In this case the usual manipulation resulted in a mixture composed of the benzoate melting at 110° and a stereoisomeric benzoate melting at 131°. The substance

was purified by recrystallization from methyl alcohol, in which it is sparingly soluble and from which it separated in needles. The isomers were formed in approximately equal amounts, the yield of the higher melting compound being 7.5 g.

*Anal.* Calcd. for  $C_{28}H_{26}O_2$ : C, 87.5; H, 5.5. Found: C, 87.6; H, 5.8.

**Hydrolysis of the Benzoates.**—Half a gram of each benzoate was dissolved in the minimum quantity of boiling absolute methyl alcohol. To each solution enough methyl alcoholic potassium hydroxide was added to make the concentration of the base 0.2%. The solutions were then set aside without further heating. Triphenyl propiophenone began to crystallize as the solutions became cool. In a few hours both solutions were allowed to evaporate to complete dryness in a current of air. From the residue, water extracted sodium benzoate, and left pure ketone. The yield was quantitative.

***p*-Bromodesoxybenzoin. XVII.**—To a solution of 77 g. of phenyl acetyl chloride in 150 cc. of bromobenzene was added, in small portions and with constant stirring, 65 g. of powdered aluminum chloride. The mixture was stirred for a day at the ordinary temperature, then left to itself for twenty-four hours before it was decomposed with ice and concentrated hydrochloric acid. Distillation with steam removed the excess of bromobenzene and left an orange colored paste which showed no tendency to solidify and which therefore was distilled under diminished pressure. The first fraction, boiling at 160–200° (12 mm.), solidified on cooling. Recrystallization of the solid from methyl alcohol gave 58 g. of a product which crystallized in needles and melted at 115°.

*Anal.* Calcd. for  $C_{14}H_{11}OBr$ : C, 61.1; H, 4.0. Found: C, 61.2; H, 4.1.

**$\alpha,\beta$ -Diphenyl- $\beta$ -chloro *p*-Bromopropiophenone. XVIII.**—A solution of 30 g. of *p*-bromodesoxybenzoin in 60 g. of benzaldehyde was saturated with dry hydrogen chloride, then kept at 0° for ten hours in a slow current of the gas. The resulting solid was collected on a filter, washed with ether and petroleum ether and recrystallized from alcohol. It separated in needles which melted at 171°.

*Anal.* Calcd. for  $C_{21}H_{16}OClBr$ : C, 63.1; H, 4.0. Found: C, 63.1; H, 4.2.

**Benzal *p*-Bromodesoxybenzoin, XIX.**—A solution of 30 g. of the chloro compound in 500 cc. of methyl alcohol containing one equivalent of potassium acetate and slightly less than one equivalent of sodium carbonate was boiled for four hours. Most of the solvent was then removed by distillation. The residue, on cautious dilution with water, deposited a crystalline solid which crystallized from ether in large prisms, and which melted at 105°.

*Anal.* Calcd. for  $C_{21}H_{16}OBr$ : C, 69.4; H, 4.1. Found: C, 69.5; H, 4.3.

**$\alpha$ -(*p*-Bromophenyl)- $\beta$ -benzhydryl- $\beta$ -phenyl-ethenyl Benzoate. XXIII.**—An ethereal solution of benzal *p*-bromo desoxybenzoin was added to a solution of phenylmagnesium bromide prepared from 1.2 g. of magnesium. The mixture was boiled for twenty minutes, then treated with 7.5 g. of benzoyl chloride and boiled for two hours more. The usual decomposition with iced acid gave an oil which contained benzoyl chloride. An ethereal solution of the oil was freed from benzoyl chloride by shaking with sodium carbonate, then dried, concentrated and diluted with petroleum ether. It deposited a solid which crystallized in small lustrous prisms and melted at 144°.

*Anal.* Calcd. for  $C_{23}H_{20}O_2Br$ : C, 74.8; H, 4.6. Found: C, 74.7; H, 4.8.

**Hydrolysis,  $\alpha,\beta,\beta$ -Triphenyl-*p*-bromo Propiophenone ( $C_6H_5$ )<sub>2</sub>CHCH( $C_6H_5$ )COC- $H_4Br$ .**—The hydrolysis was carried out in exactly the same manner as that of the bromine-free benzoates. The crude product melted at 200° and the melting point was not changed by recrystallization from acetone and methyl alcohol from which the bromo ketone crystallized in large lustrous needles. The aqueous extract of the residue, that was left after the evaporation of the mother liquors, contained only sodium benzoate.

*Anal.* Calcd. for  $C_{27}H_{21}OBr$ : C, 73.5; H, 4.8. Found: C, 73.4; H, 4.9.

$\alpha,\beta$ -Diphenyl- $\beta$ -benzhydryl-ethenyl *p*-Bromobenzoate. XXII.—To a solution of phenylmagnesium bromide from 0.8 g. of magnesium was added 8.4 g. of finely powdered benzal desoxybenzoin. The mixture was boiled for twenty minutes, then treated with 7.5 g. of freshly distilled *p*-bromobenzoyl chloride and boiled again for two hours. The usual manipulations gave a product which was sparingly soluble in ether and in alcohol, which crystallized in prisms, and which melted at 183°.

*Anal.* Calcd. for  $C_{33}H_{28}O_2Br$ : C, 74.8; H, 4.6. Found: C, 74.7; H, 4.7.

**Hydrolysis.**—The ester on hydrolysis with dilute methyl alcoholic potassium hydroxide gave but two products: triphenyl propiophenone and *p*-bromobenzoic acid.

### Summary

1. The magnesium derivatives which are formed by the addition of Grignard reagents to those  $\alpha,\beta$ -unsaturated ketones which have no substituents in the alpha position behave like the enolates of  $\beta$ -ketonic esters; like these enolates they combine with unsaturated ketones and with other substances that have sufficiently active carbonyl groups. The reaction with acid chlorides results in the formation of C-acyl derivatives.

2. The magnesium derivatives which are formed by adding Grignard reagents to  $\alpha,\beta$ -unsaturated ketones which have hydrocarbon residues in the alpha position, combine neither with unsaturated ketones nor with aldehydes; they therefore do not form secondary products. The reaction between these magnesium derivatives and acid chlorides results in the formation of O-acyl derivatives.

CONVERSE MEMORIAL LABORATORY  
CAMBRIDGE, MASSACHUSETTS

RECEIVED JULY 26, 1932  
PUBLISHED MARCH 7, 1933

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

## Furan Reactions. IV. Furoic Acid from Furfural

BY CHARLES D. HURD, J. W. GARRETT<sup>1</sup> AND E. N. OSBORNE<sup>1</sup>

In the Cannizzaro reaction with furfural, mineral acids cannot be used to neutralize the excess of alkali without resinifying the furfuryl alcohol which is formed. Hence, it is customary<sup>2</sup> to extract the latter with ether before acidification. In the method proposed, the excess of alkali is neutralized with furoic acid and the furfuryl alcohol separated directly, thus making the method suitable for large scale use. Also, the excess of alkali may be omitted altogether with yields only slightly lower.

The direct oxidation of furfural to furoic acid by means of potassium dichromate and sulfuric acid has also been studied and a satisfactory method developed. The manganous salt of furoic acid was synthesized. It was found to crystallize with three molecules of water.

(1) Holders of Quaker Oats Fellowships, administered through the Miner Laboratories, Chicago.  
(2) Wilson, "Organic Syntheses," John Wiley and Sons, New York, 1926, Vol. VI, p. 44.