THE CLEAVAGE OF BETA DIKETONES. I. CLEAVAGE BY ORGANIC MAGNESIUM COMPOUNDS

BY E. P. KOHLER AND J. L. E. ERICKSON

In a recent communication from this Laboratory,[1] it was reported that organic magnesium compounds effect a very characteristic cleavage of α-oxido ketones. We have observed a somewhat similar cleavage of β-diketones. In a study of the relative activity of the three carbonyl groups of diphenylpropane trione, we added this substance to phenyl magnesium bromide in the usual manner and obtained benzoin and triphenyl carbinol. Manifestly, these products are due to cleavage, and from the formation of triphenyl carbinol it is evident that this cleavage is anterior to the final decomposition of the magnesium derivatives with acids.

From general considerations as well as from the results published by Neufville and v. Pechmann,[2] it appears probable that the central carbonyl group in the triketone is much the most active of the three. If this is really the case, then the primary reaction between the triketone and phenyl magnesium bromide would be expected to yield phenyl dibenzoyl carbinol, a very interesting disubstitution product of a β-diketone. In the hope of discovering some means of confining the process to this first stage, we decided to make a more careful examination of the action of organic magnesium compounds on other β-diketones.

Surprisingly few β-diketones have heretofore been treated with Grignard reagents. Zelinsky[3] added acetylacetone to methyl magnesium iodide and observed a vigorous reaction, but he obtained only a very small quantity of a product, of which he states, merely, that it boiled at 101–102° under 15 mm., and that its composition corresponded approximately to $C_7H_{16}O_2$. Zerewitinoff[4] announced later that the diketone liberates one mole of methane from a solution of methyl magnesium iodide in isoamyl ether; he made no attempt to isolate any products.

More definite results were reported by Smedley,[5] who added dimethyl dibenzoylmethane to methyl magnesium iodide. She concluded that the reagent combined with each of the carbonyl groups, and that the final product was the ditertiary alcohol which would be expected as the result of such a process—$C_6H_5(CH_3)COHC(CH_3)_2C(OH)(CH_3)C_6H_5$. There is no evidence in support of these conclusions.

The only other open chained β-diketone that has been treated with a

[1] Kohler, Richtmyer and Hester, THIS JOURNAL, 53, 205 (1931).

[2] Neufville and v. Pechmann, Ber., 23, 3379 (1890).

[3] Zelinsky, ibid., 35, 2138 (1902).

[4] Zerewitinoff, ibid., 41, 2243 (1908).

[5] Smedley, J. Chem. Soc., 97, 1493 (1910).

Grignard reagent is dibenzoyl methane. Vorländer, Osterburg and Meye[6] added this diketone to phenyl magnesium bromide and proved, conclusively, that when the resulting magnesium compound was acidified, the product was β-hydroxy-β,β-diphenyl propiophenone. They, therefore, wrote the equation

$$C_6H_5COCH_2COC_6H_5 + C_6H_5MgBr \longrightarrow (C_6H_5)_2C(OMgX)CH_2COC_6H_5$$
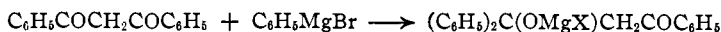
In addition to these open chained compounds one cyclic β-diketone of an unusual type has been examined. Wedekind and Miller[7] added tetramethyl cyclobutanedione to an excess of ethyl magnesium bromide and obtained, in almost the calculated quantity, the corresponding ditertiary alcohol

$$(CH_3)_2C-CO \qquad\qquad (CH_3)_2C-C(C_2H_5)OH$$
$$OC-C(CH_3)_2 \qquad\qquad HO(C_2H_5)C-C(CH_3)_2$$

If one were to judge from these meager reports one would have to conclude that the reaction between β-diketones and organic magnesium compounds is relatively simple and uniform—far more uniform than would be expected from the varied results that have been obtained from β-ketonic esters. In reality it is neither simple nor uniform, as may be seen from the following list of diketones and the final products which we obtained from them.
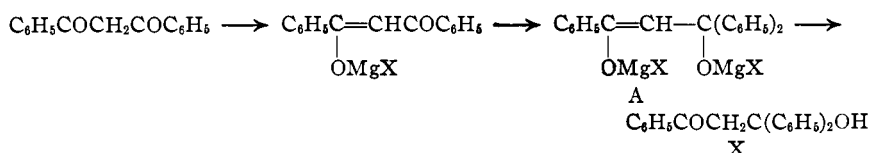
I	$C_6H_5COCH_2COC_6H_5$	$(C_6H_5)_2C(OH)CH_2COC_6H_5$
II	$CH_3COCH_2COCH_3{}^a$	$(CH_3)_2C(OH)CH_2COCH_3$
III	$C_6H_5COCH(C_6H_5)COC_6H_5$	$C_6H_5COCH_2C_6H_5 + (C_6H_5)_3COH$
IV	$C_6H_5COCH(CH_3)COC_6H_5$	$C_6H_5COCH_2CH_3 + (C_6H_5)_3COH$
V	$CH_3COC(CH_3)_2COCH_3$	$CH_3COCH(CH_3)_2 + (C_6H_5)_2(CH_3)COH$
Va	$CH_3COC(CH_3)_2COCH_3{}^b$	$CH_3COCH(CH_3)_2 + CH_3COC_6H_2(CH_3)_3$
VI	$C_6H_5COC(CH_3)_2COC_6H_5$	$C_6H_5COCH(CH_3)_2 + (C_6H_5)_3COH$
VII	$C_6H_5COCHBrCOC_6H_5$	$C_6H_5COCH_2COC_6H_5$
VIII	$C_6H_5COCBr_2COC_6H_5$	$(C_6H_5)_2COHCHBrCOC_6H_5$
IX	$C_6H_5COCOCOC_6H_5$	$C_6H_5COCHOHC_6H_5 + (C_6H_5)_3COH$

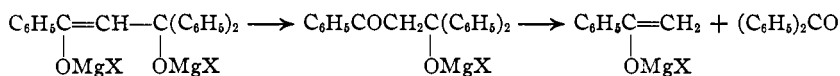   [a] With methyl magnesium iodide.   [b] With mesityl magnesium iodide.

An examination of this list shows that relatively normal products are obtained from those compounds only which are largely or entirely enolic. Even in the case of these substances the reaction is not quite as simple as it was formulated by Vorländer and his collaborators, because quantitative determinations show that they react with two moles of reagent and liberate a mole of gas. When they are added to but one equivalent of reagent, half of the material is recovered unchanged, and when, inversely, one equivalent of reagent is added to the substance, all of the latter is recovered. The reaction with phenyl magnesium bromide must therefore be represented as follows

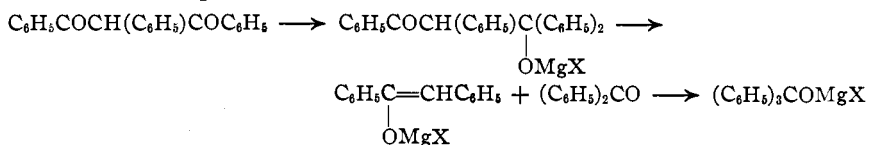   [6] Vorländer, Osterburg and Meye, *Ber.*, **56**, 1136 (1923).
    [7] Wedekind and Miller, *ibid.*, **44**, 3285 (1911).

$$C_6H_5COCH_2COC_6H_5 \longrightarrow \underset{\underset{OMgX}{|}}{C_6H_5C}{=}CHCOC_6H_5 \longrightarrow \underset{\underset{OMgX}{|} \quad \underset{OMgX}{|}}{C_6H_5C}{=}CH{-}C(C_6H_5)_2 \longrightarrow$$

$$A$$

$$C_6H_5COCH_2C(C_6H_5)_2OH$$

$$X$$

In the case of these highly enolized β-diketones the outcome is quite definite; it is not possible to add more than one equivalent of the reagent, and no cleavage occurs anterior to the decomposition of the resulting magnesium derivatives with acids. It is necessary, however, to exercise great care in acidifying these magnesium derivatives, because they can pass into intermediate monomagnesium compounds that undergo cleavage with ease

$$\underset{\underset{OMgX}{|} \quad \underset{OMgX}{|}}{C_6H_5C}{=}CH{-}C(C_6H_5)_2 \longrightarrow \underset{\underset{OMgX}{|}}{C_6H_5COCH_2C}(C_6H_5)_2 \longrightarrow \underset{\underset{OMgX}{|}}{C_6H_5C}{=}CH_2 + (C_6H_5)_2CO$$

The situation is quite different in the case of the mono- and disubstitution products of these simple diketones. The monosubstitution products are too little enolized or too feebly acidic to form copper derivatives with copper acetate; they liberate only traces of gas from methyl magnesium iodide; they nevertheless consume two equivalents of the reagent.[8] Here the first step is the addition of the reagent to one of the carbonyl groups. The resulting magnesium derivative is unstable and it decomposes in a manner that is essentially the same as that of the magnesium compounds which are formed from α-oxido ketones. The entire process, then, must be represented as follows

$$C_6H_5COCH(C_6H_5)COC_6H_5 \longrightarrow \underset{\underset{OMgX}{|}}{C_6H_5COCH(C_6H_5)C}(C_6H_5)_2 \longrightarrow$$

$$\underset{\underset{OMgX}{|}}{C_6H_5C}{=}CHC_6H_5 + (C_6H_5)_2CO \longrightarrow (C_6H_5)_3COMgX$$

The extent of this kind of cleavage, and the ease with which it takes place, naturally vary with the stability of the first magnesium derivative. From the products which have been obtained with dialkyl acetacetic esters,[9] it is reasonable to infer that cleavage is less likely to occur with alkyl than with phenyl magnesium halides, and our experiments with β-hydroxy-β,β-diphenyl propiophenone show that it also takes place less readily with compounds that have less highly branched chains. These experiments with the hydroxy ketone are of special interest because in contrast with the dibenzoyl methane from which it is obtained, it can form the type of magnesium derivative that may cleave
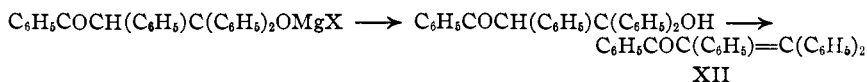
$$C_6H_5COCH_2C{-}(C_6H_5)_2OH \longrightarrow C_6H_5COCH_2C(C_6H_5)_2OMgX$$

$$B$$

[8] Kohler, Stone and Fuson, THIS JOURNAL, **49**, 3181 (1927).

[9] Slavjanoff, *J. Russ. Phys.-Chem. Soc.*, 39, 140 (1907).

According to Vorländer and Meye,[10] the hydroxy ketone does not react with phenyl magnesium bromide; but they must have been deceived by the similarity in the melting points of the hydroxy ketone and that of one of the products of the reaction. In reality the substances react with great ease. One of the products is triphenyl carbinol, which shows that the magnesium compound B undergoes the usual cleavage; but in addition to this there is formed an equal quantity of the dihydroxyl compound, $(C_6H_5)_2$-$COHCH_2COH(C_6H_5)_2$ (XI).

At times it is possible to avoid cleavage almost entirely by operating at a sufficiently low temperature. Thus by proceeding in the reverse of the usual manner, adding phenyl magnesium bromide cautiously to phenyl dibenzoyl methane while the temperature was kept below $-10°$ and acidifying without delay, it was possible to secure a fair yield of tetraphenyl propenone—the dehydration product of the corresponding tertiary alcohol.

$$C_6H_5COCH(C_6H_5)C(C_6H_5)_2OMgX \longrightarrow C_6H_5COCH(C_6H_5)C(C_6H_5)_2OH \longrightarrow$$
$$C_6H_5COC(C_6H_5)\!\!=\!\!C(C_6H_5)_2$$
$$XII$$

As would be expected from the foregoing analysis, β-diketones which have two substituents in the methylene group behave precisely like those which have but one. Smedley's conclusions are not in agreement with this view, but we are convinced that she was misled by her results. She subjected her product to distillation under diminished pressure and analyzed a fraction boiling at 120–125° under 55 mm. This is manifestly far too low a boiling point for the ditertiary alcohol $C_6H_5(CH_3)COHC(CH_3)_2$-$C(OH)(CH_3)C_6H_5$. According to our interpretation, this reaction would be expected to yield the cleavage products dimethyl acetophenone and phenyl methyl carbinol. Since these substances have approximately the boiling point given by Smedley, it seems likely that she analyzed a mixture that happened to have the same composition as the ditertiary alcohol. We treated the same diketone with phenyl magnesium bromide and obtained only cleavage products.

The bromine substitution products are exceptions. They undergo the peculiar reaction of α bromo ketones which was reported many years ago by Kohler and Johnstin,[11] and which has since been observed by others.[12] The mechanism of this reaction will be considered in a later paper.
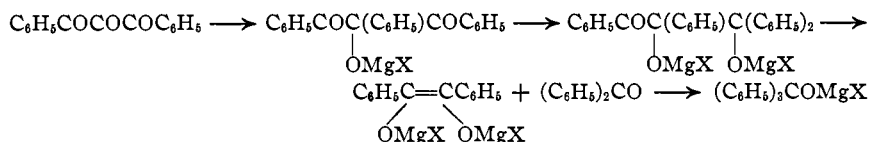
In the light of the foregoing results it is not difficult to follow the course of the reaction between phenylmagnesium bromide and diphenyl propanetrione. The most active carbonyl group combines with a molecule of the
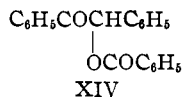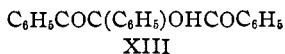
[10] Ref. 6, p. 1138.

[11] Kohler and Johnstin, *Am. Chem. J.*, **33**, 35 (1905).

[12] Umnova, *J. Russ. Phys.-Chem. Soc.*, **45**, 881 (1913); Löwenbein and Schuster, *Ann.*, **481**, 106 (1930); Fisher, Oakwood and Fuson, THIS JOURNAL, **52**, 5037 (1930).

reagent and the addition product behaves like any other disubstituted β-diketone

$$C_6H_5COCOCOC_6H_5 \longrightarrow \underset{\underset{OMgX}{|}}{C_6H_5COC(C_6H_5)COC_6H_5} \longrightarrow \underset{\underset{OMgX\ \ \ OMgX}{|\ \ \ \ \ \ |}}{C_6H_5COC(C_6H_5)C(C_6H_5)_2} \longrightarrow$$

$$\underset{\underset{OMgX\ \ OMgX}{\diagup\ \ \ \diagdown}}{C_6H_5C{=}CC_6H_5} + (C_6H_5)_2CO \longrightarrow (C_6H_5)_3COMgX$$

In a preliminary attempt to isolate the carbinol corresponding to the intermediate magnesium compound the reagent was added to the triketone at a low temperature and the resulting magnesium derivative was decomposed immediately. The product was a crystalline solid which had the composition of phenyl dibenzoyl carbinol XIII, but which proved to be the benzoate of benzoin XIV.

$$\begin{array}{cc} C_6H_5COC(C_6H_5)OHCOC_6H_5 & \underset{\underset{OCOC_6H_5}{|}}{C_6H_5COCHC_6H_5} \\ \text{XIII} & \text{XIV} \end{array}$$

Experimental Part

Since many of the diketones on the list were examined by the same general procedure, it is not necessary to describe the experiments with each of these substances in detail. Experimental details will be given, therefore, only in those cases in which a special procedure was adopted or in which the reaction resulted in the formation of compounds which were not known heretofore.

The general method of procedure was to add either the diketone itself or its ethereal solution to a large excess of the Grignard reagent, warm for a few minutes to complete the reaction, decompose the magnesium derivatives either with ice and dilute acid or ice and ammonium chloride, and separate the products by whatever method seemed best.

Dibenzoyl Methane, I.—Since Vorländer and Meye's equation[6] accounts neither for the gas evolved when the diketone reacts with methyl magnesium iodide, nor for the fact that, unlike its alkyl substitution products, it is not cleaved by Grignard reagents, it was necessary to reëxamine the behavior of this substance toward Grignard reagents. The true course of the reaction was established by means of three experiments with phenyl magnesium bromide.

In the first experiment the reagent was added gradually to a slight excess of the diketone, the mixture was boiled for an hour, then decomposed with iced acid in the usual manner. Of the 10 g. of diketone used all but 0.35 g. was recovered. After removing the last of the diketone in the form of its copper derivative, there remained a few drops of oil, but no triphenyl carbinol could be detected in this residue. The first step in the reaction, therefore, is the formation of the magnesium bromide derivative of the enol, and even prolonged boiling does not result in cleavage at this stage.

In the second experiment the operation was reversed, the diketone being added to an excess of reagent. On prolonged boiling this mixture gradually deposited a gray crystalline magnesium derivative. This was collected, washed with ether, and decomposed with iced acid; it gave mainly β,β-diphenyl-β-hydroxy propiophenone (X), the sub-

stance previously obtained in the same manner by Vorländer and Meye. Some more of this hydroxyl compound was also obtained on acidifying the filtrate from the solid magnesium compound, making a total yield of 82%. The oily residue from the hydroxy ketone was composed of acetophenone—which was removed by oxidation—and benzophenone, which was separated by distillation with steam. These are decomposition products of the unstable hydroxy ketone. Since no triphenyl carbinol could be detected, there was no cleavage during the Grignard reaction.

In the last experiment 20 g. of the hydroxy ketone X was added to a solution of phenyl magnesium bromide which had been prepared from 7.0 g. of magnesium. The solid ketone was added at a rate that kept the liquid boiling gently and the mixture was boiled for fifteen minutes after all the solid had been added. The magnesium derivatives were decomposed with iced acid, and the ethereal layer washed and dried in the usual manner. After concentration, and dilution with petroleum ether, it first deposited several crops of triphenyl carbinol (9.2 g.) and then 7.4 g. of a different product melting at 121–123°.

The lower melting product was purified by recrystallization from ether and petroleum ether from which it separated in flat prisms.

Anal. Calcd. for $C_{27}H_{24}O_2$: C, 85.3; H, 6.3. Found: C, 85.9; H, 6.2.

In the machine the substance consumed approximately two moles of methyl magnesium iodide and liberated two moles of methane; it is therefore a dihydroxyl compound. A similar substance was obtained by Berberianu[13] by the action of phenyl magnesium bromide on β-hydroxy-β,β-diphenyl propionic ester. After recrystallization from alcohol our product, like Berberianu's, melts at 104°, loses alcohol at the melting point, then resolidifies and melts again at a higher temperature.

Oxidation.—To a solution of 1 g. of the substance in glacial acetic acid was added a solution of 1 g. of chromic acid in an equal weight of water. The mixture was warmed on a steam-bath for an hour, then diluted with water, neutralized and distilled with steam. From the distillate ether extracted 0.93 g. of pure benzophenone instead of 0.96 g. calculated on the assumption that the substance is tetraphenyl propanediol (XI).

Acetylacetone. II.—Our general procedure probably differed from that of Zelinsky[3] only in the care with which we acidified. We dribbled our magnesium compound into a mixture of ice and concentrated hydrochloric acid which was stirred vigorously and then maintained at a temperature of about −20°. The product was isolated by distillation under diminished pressure, and identified as diacetone alcohol by its boiling point, its composition and its conversion into mesityl oxide. The yield was 92%.

Phenyl Dibenzoyl Methane, III.—The products obtained by the usual procedure were desoxybenzoin and triphenyl carbinol. These substances were separated by crystallization from mixtures of ether and petroleum ether and identified by comparison with authentic samples. In an "inverse Grignard reaction" an ethereal solution of phenyl magnesium bromide prepared from 0.6 g. of magnesium was added gradually to a suspension of 3.0 g. of the diketone in ether which was kept at −10° by means of a freezing mixture. When the resulting solution was added to iced acid it deposited a very sparingly soluble crystalline solid. After washing with alcohol and ether, the solid melted sharply at 150°. It was identified as tetraphenyl propenone (XII) by comparison with a sample on hand. The yield was 67%.

Methyl Dibenzoylmethane, IV.—The ethereal solution of the products was concentrated, then gradually diluted with petroleum ether until it deposited nearly all of the triphenyl carbinol. The residue on distillation yielded an oil boiling at 210–215°. When this oil was treated with semicarbazide it formed the semicarbazone of propiophenone melting at 177–178°.

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[13] Berberianu, *Chem. Abstracts*, **8**, 1423 (1914).

Dimethyl Acetylacetone, V.—Combes' method of preparing dimethyl acetylacetone by heating the sodium derivative of acetylacetone with methyl iodide in a sealed tube to 130°[14] is not very satisfactory. Better yields and a purer product were obtained in the following manner. To a boiling solution of 20 g. of acetylacetone and 71 g. of methyl iodide in absolute methyl alcohol was added, slowly, a solution of sodium methylate containing 9.2 g. of sodium. The solution was stirred continuously during the addition of the methylate and boiled for half an hour after all had been added. Most of the methyl alcohol was then removed by distillation under diminished pressure, and enough water was added to the residue to dissolve the sodium iodide. The aqueous solution was thoroughly extracted with ether, the ethereal solution dried over calcium chloride and evaporated.

The residue was an oil which when it was distilled under diminished pressure boiled at 69° under 12 mm. and gave a distillate that immediately solidified, giving a mass of colorless crystals melting at 21°, and having an odor resembling that of camphor. The yield was 50%.

Action of Phenyl Magnesium Bromide.—The etheral solution of the product, which was obtained in the usual manner, was dried and evaporated until almost free from ether. The residue, on dilution with a small quantity of petroleum ether, deposited a crystalline solid which melted at 81°. When this was mixed with a sample of diphenyl methyl carbinol prepared by the action of phenyl magnesium bromide on acetophenone it caused no depression of the melting point. The yield was almost quantitative.

Action of Mesityl Magnesium Bromide.—In order to prove definitely that the cleavage of the diketones occurs at the same stage as that of the oxides, dimethyl acetyl-acetone was also treated with mesityl magnesium bromide. The product, isolated by fractional distillation under diminished pressure, was an oil which distilled at 110–111° under 10 mm.; yield, 6 g. from 10 g. of the diketone.

For the purpose of identification 2 cc. of a 10% solution of sodium methylate was added to a methyl alcoholic solution of 0.7 g. of the oil and 0.8 g. of m-nitrobenzaldehyde. The solution was boiled for a few minutes, then diluted with enough water to produce a slight turbidity and set aside. It deposited a golden-yellow solid which, after recrystallization, melted at 82°. For comparison a sample of m-nitro benzal acetomesitylene was prepared in the same manner from acetomesitylene. The two preparations, and a mixture of both, melted at the same temperature.

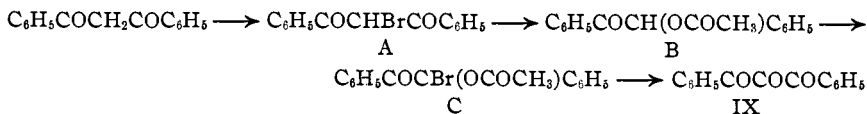*Anal.* Calcd. for $C_{18}H_{17}O_3N$: C, 73.2; H, 5.8. Found: C, 73.5; H, 6.0.

Dimethyl Dibenzoyl Methane, VI.—Since Smedley had reported that this diketone adds methyl magnesium iodide to form a product similar to that which is obtained from dibenzoyl methane itself, we carried out the reaction with phenyl magnesium bromide at −10°, and decomposed the resulting magnesium compounds with especial care. But when the concentrated ethereal solution of the products was cautiously diluted with petroleum ether, it deposited almost the calculated quantity of triphenyl carbinol. The mother liquor, on distillation, yielded an oil that boiled between 210–220°, and formed an oxime which melted at 59–60°—the melting point of the isobutyrophenone oxime.

Wieland and Bloch's[15] method for the preparation of diphenyl triketone, using di-benzoyl methane and nitrogen tetroxide was tried but abandoned in favor of the older method of Neufville and v. Pechmann,[16] which gave better yields and a purer product. This method involves the following steps

[14] Combes and Combes, *Bull. soc. chim.*, [3] 7, 783 (1892).

[15] Wieland and Bloch, *Ber.*, 37, 1524 (1904).

[16] Neufville and v. Pechmann, *ibid.*, 23, 3379 (1890).

$$C_6H_5COCH_2COC_6H_5 \longrightarrow C_6H_5COCHBrCOC_6H_5 \longrightarrow C_6H_5COCH(OCOCH_3)C_6H_5 \longrightarrow$$
$$ A B$$
$$C_6H_5COCBr(OCOCH_3)C_6H_5 \longrightarrow C_6H_5COCOCOC_6H_5$$
$$C IX$$

The bromination of dibenzoyl methane was conducted essentially as described by v. Pechmann. The yield was 236 g. of bromo compound from 224 g. of the diketone, equivalent to 78%. For the purpose of preparing the acetate, 106 g. of the bromo ketone was added to a solution of 49 g. of freshly fused potassium acetate in 400 cc. of glacial acetic acid. The mixture was boiled for forty-five minutes, after which time the transformation was found to be complete. To the clear liquid enough water to produce turbidity was added while the solution was stirred continually and allowed to cool. It first deposited an oil which in a short time solidified to a brown mass, then colorless needles which filled the liquid. The solid was collected, washed, and recrystallized from methyl alcohol. It was then obtained in snow white crystal melting at 94°. The yield was 78.5 g. or 79%.

Bromo Dibenzoyl Carbinol Acetate, C.—The bromination of the acetate was carried out in a manner similar to that of dibenzoyl methane. It is important to cool the solution well, to add the bromine very slowly, and to stir constantly to avoid local rise in temperature. To a solution of 77 g. of the acetate in 400 g. of chloroform was added in the course of three hours 44 g. of bromine. A stream of dry air was then passed through the solution to remove the hydrogen bromide as completely as possible.

The bromo compound may be isolated by allowing the solution to evaporate, washing the residue with alcohol and recrystallizing it from chloroform and petroleum ether; but for the purpose of making the triketone it was more convenient to operate directly with the chloroform solution as it is left after the bromination. This solution was concentrated, then transferred to a Claisen distilling flask and freed from chloroform by distillation. The flask was then heated at about 120° until the bromo acetate had decomposed and all of the acetyl bromide had distilled. The residue, which was almost pure triketone, was then distilled under diminished pressure. It was collected as a brown oil which promptly solidified to a golden-yellow crystalline mass.

The average yield of pure, redistilled triketone, boiling at 179–181° under 4 mm., was 50 g. from 77 g. of the acetate. The triketone may be recrystallized from boiling petroleum ether which has been distilled from phosphorus pentoxide. It separates in golden-yellow needles melting at 69–70°. As it is extremely hydroscopic and in the air rapidly becomes coated with the white hydrate, it must be kept in a vacuum desiccator or in sealed tubes.

Reaction with Phenyl Magnesium Bromide.—An ethereal solution of phenyl magnesium bromide was prepared in the usual manner from 11.8 g. of magnesium. Meanwhile diphenyl triketone was distilled into a cylindrical dropping funnel provided with a side tube by means of which it could be connected with the distilling flask while the apparatus was exhausted through the top of the funnel. After collecting 14.5 g. of the triketone in this receiver, ether was distilled into it from the Grignard solution. In this manner it was possible to secure a solution in perfectly dry ether and in an apparatus that was convenient for the next step in the operation.

From the modified dropping funnel the ethereal solution of the triketone was added to the solution of phenyl magnesium bromide in the course of half an hour. Each drop produced a slight yellow precipitate which immediately redissolved. The mixture was boiled for an hour, then cooled and decomposed with ice and ammonium chloride. The ethereal layer was dried and concentrated. It gradually deposited crystals which melted at 131° and which were identified as benzoin by analysis and by a mixed melting point.

The mother liquor was evaporated to small volume and diluted with petroleum ether—it deposited a second crop of crystals which after recrystallization melted at 159° and which were identified as triphenyl carbinol. The yield of pure triphenyl carbinol was 9.8 g. or 62%. The same products were obtained when the magnesium derivatives were decomposed with iced acid.

Action of One Mole of Phenyl Magnesium Bromide. Inverse Grignard Reaction.—A solution of phenyl magnesium containing 1.82 g. of magnesium was added, gradually, to an ethereal solution of 14.30 g. of diphenyl triketone which was stirred rapidly throughout the operation. As each drop was added an insoluble magnesium compound was precipitated as a yellow solid. The mixture was decomposed with ammoniacal ammonium chloride and the ethereal solution was washed and dried in the usual manner. It yielded a colorless crystalline compound which melted at 123–124°.

Anal. Calcd. for $C_{21}H_{16}O_3$: C, 79.7; H, 5.1. Found: C, 79.8; H, 5.1.

The substance has the composition of phenyl dibenzoyl carbinol but when it was treated with excess of phenyl magnesium bromide it yielded products that were quite different from those which had been obtained from the triketone. Thus 0.95 g. of the substance was added to an ethereal solution of the bromide made from 0.48 g. of magnesium. The mixture was boiled for fifteen minutes and then decomposed with iced acid. The ethereal layer deposited colorless needles which melted at 164° and which were ultimately identified as triphenyl ethylene glycol by analysis and by comparison with a sample of the glycol that was prepared from benzoin by the method of Acree.[17]

The formation of triphenyl ethylene glycol suggested that our product might be the benzoate of benzoin. This substance was therefore prepared by benzoylating benzoin and a comparison showed that the two products are identical. In order to ascertain whether the benzoate is formed during the Grignard reaction or is the result of a rearrangement of the carbinol by the base used in decomposing the magnesium derivative, the experiment was repeated, but this time the mixture was treated with ice and dilute hydrochloric acid. The result was an oil which after many fractional recrystallizations was separated into benzoic acid and the same benzoin benzoate.

Summary

1. β-Diketones that have no substituents in the methylene group react with two equivalents of phenyl magnesium bromide. The product is a dimagnesium compound which on hydrolysis yields a β-hydroxy ketone.

2. β-Diketones that have one or more substituents in the methylene group likewise react with two equivalents of phenyl magnesium bromide but the result in this case is a mixture of two magnesium compounds, because the process involves a cleavage which is similar to that of oxido ketones.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS

[17] Acree, *Ber.*, **37**, 2762 (1904).