of glacial acetic acid for one-half hour. Yellow needles of the reaction product began to separate from the boiling solution, and the precipitation was completed by the addition of water. The crude oxidation product was dissolved in dilute sodium hydroxide solution at the boiling point and the yellow solution was filtered from a dark sludge of suspended material. When refiltered through a pad of charcoal, the solution was nearly colorless, and on adding acid and boiling, the product separated as a pale yellow precipitate in a nearly pure condition; yield 0.5 g. The substance is insoluble in cold alkali. On crystallization from dioxane, in which it is readily soluble, the substance formed fan-shaped clusters of pale yellow needles, m. p. 280.5–281.5°.

Anal. Calcd. for $C_{16}H_8O_3$: C, 77.41; H, 3.25. Found: C, 77.71; H, 3.39.

The analysis and properties are those of phenanthrene-8,9-dicarboxylic anhydride, for which Pschorr[8] reports the corrected melting point 283–284°. No depression was observed in the melting point on admixture with a slightly less pure sample of the anhydride previously prepared in this Laboratory.[14]

1′,2′,3′,4′-Tetrahydro-4,10-ace-1,2-benzanthracene (X).—This hydrocarbon was recovered from the purified picrate, m. p. 131–132°, described above, by distribution between ammonia water and ether. The compound crystallizes well when an ethereal solution is diluted with methanol and concentrated to the point of saturation. The sample for analysis was distilled in vacuum and recrystallized, forming silky, colorless needles melting at 106–107°. The solutions are beautifully fluorescent.

Anal. Calcd. for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.69; H, 7.24. *Anal.* (picrate). Calcd. for $C_{20}H_{18}\cdot C_6H_3O_7N_3$: N, 8.62. Found: N, 8.78.

Dehydrogenation of the hydrocarbon with a large excess of selenium was conducted at 300–320° for twenty hours. The product was extracted with benzene, the solution was passed through a tower of alumina, and the recovered material on crystallization from methanol gave pale yellow needles melting at 135–137° and showing no depression when mixed with 4,10-ace-1,2-benzanthracene.

Summary

The synthesis of 4,10-ace-1,2-benzanthracene, an isomer of the carcinogenically active cholanthrene, has been accomplished by the use of the modified Elbs reaction. This pyrolytic reaction, applied in another case where both a five-membered and a six-membered ring are available for condensation, was found to proceed in both possible directions. Further evidence was found of the tendency of 1,9-trimethylene derivatives of anthracene to undergo transformation to phenanthrene derivatives in the course of the pyrolysis.

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CAMBRIDGE, MASSACHUSETTS
RECEIVED MARCH 17, 1937

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[14] Fieser and Peters, THIS JOURNAL, **54**, 4373 (1932).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY, HARVARD UNIVERSITY]

The Tautomerism of Certain Derivatives of Acetomesitylene

BY E. P. KOHLER AND R. B. THOMPSON

In a recent study of the structure of the magnesium derivatives of mono ketones[1] it was found that the derivative of benzhydryl acetomesitylene is an enolate and that the corresponding enol is sufficiently persistent in solution to be detectable as peroxide. This observation is important because at present the only reliable evidence that a substance obtained by adding a metallic derivative to an unsaturated ketone or ester is an enolate, is its conversion into an enol by a process which does not enolize the corresponding ketone or ester.

It was found, also, that in a series of related mono ketones the mode of acylation of the magnesium derivatives appeared to be associated with the relative persistence of the enolic modifications. At the time this observation was made it was not possible to study the behavior of these enolates in reactions involving alkylation because they failed to react with any of the alkylating agents that were available. Having found, in the meanwhile, that magnesium derivatives of this type react very readily with chloromethyl ether we have now compared the mode of alkylation of the enolates which differed most in the mode of acylation, namely, the magnesium derivatives of benzhydryl acetophenone and benzhydryl acetomesitylene. We have also compared the tautomerism of a number of other ketonic derivatives of mesitylene with that of the corresponding derivatives of benzene. The results are embodied in the present paper.

When the magnesium derivative of benzhydryl acetophenone reacts with chloromethyl ether the result is a mixture composed of 30% of the

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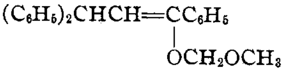
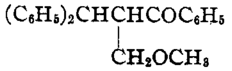
[1] Kohler, Tishler and Potter, THIS JOURNAL, **57**, 2517 (1935).

O-alkylation product I and 70% of the C-alkyl derivative II.



$$(C_6H_5)_2CHCH{=}\underset{OCH_2OCH_3}{\underset{|}{C}}C_6H_5$$

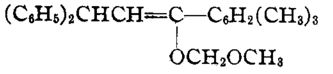
I



$$(C_6H_5)_2CH\underset{CH_2OCH_3}{\underset{|}{C}}HCOC_6H_5$$

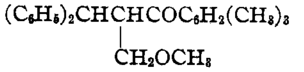
II

The magnesium derivative of benzhydryl acetomesitylene likewise yields both O- and C-alkyl derivatives but the relative amounts are almost completely reversed, at least 75% of the product being the O-alkyl derivative, III. In these two



$$(C_6H_5)_2CHCH{=}\underset{OCH_2OCH_3}{\underset{|}{C}}{-}C_6H_2(CH_3)_3$$

III

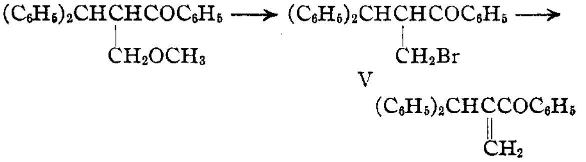


$$(C_6H_5)_2CH\underset{CH_2OCH_3}{\underset{|}{C}}HCOC_6H_2(CH_3)_3$$

IV

cases, therefore, alkylation and acylation follow the same course, both being associated in some manner with the persistence of the enolic form.

The O-alkylation products I and III are of little interest because their behavior is similar to that of all other acetals. The more interesting C-alkyl derivatives differ considerably in their chemical properties. Thus the benzene derivative II is insensitive both to bases and to dilute acids. In order to convert it into an unsaturated ketone it is necessary to replace the methoxyl group with bromine by prolonged heating with concentrated hydrobromic acid and then to eliminate hydrogen bromide from the bromo compound

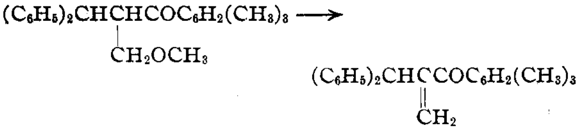


$$(C_6H_5)_2CH\underset{CH_2OCH_3}{\underset{|}{C}}HCOC_6H_5 \longrightarrow (C_6H_5)_2CH\underset{CH_2Br}{\underset{|}{C}}HCOC_6H_5 \longrightarrow (C_6H_5)_2CH\underset{CH_2}{\underset{\|}{C}}COC_6H_5$$

V

VI

In contrast both methyl alcoholic potassium hydroxide and acids convert the mesitylene derivative IV directly into the corresponding unsaturated ketone

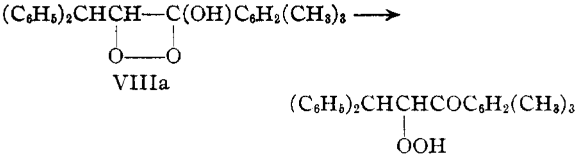


$$(C_6H_5)_2CH\underset{CH_2OCH_3}{\underset{|}{C}}HCOC_6H_2(CH_3)_3 \longrightarrow (C_6H_5)_2CH\underset{CH_2}{\underset{\|}{C}}COC_6H_2(CH_3)_3$$

VII

The properties of these C-alkylation products, like the behavior of the magnesium enolates toward acylating and alkylating agents, show that in ketones containing the group $-CHCOC_6H_2(CH_3)_3$ the mesitylene residue increases the activity of the α-hydrogen atoms, promotes enolization and enhances the stability of the enolic form. Although this form of benzhydryl acetomesitylene could not be isolated, we secured ample evidence of its presence and persistence in solutions obtained by acidifying its magnesium derivative. These solutions do not give a color reaction with ferric chloride—doubtless because the enol lacks the oxygen necessary for chelation[2]—but they decolorize bromine instantaneously and a titration by the Kurt Meyer method showed that they still contained about 90% of enol after several hours in a freezing mixture. They also absorb oxygen avidly, but when they are concentrated to the point of crystallization they deposit only the ketonic form which neither decolorizes bromine nor combines with oxygen.

As a result of autoxidation the enol is converted into a crystalline peroxide which differs, structurally, from all other substances of this type in that it has hydrogen in place of the usual hydrocarbon residue in the α position. In view of this peculiarity it is necessary to consider the possibility that the cyclic peroxide which would be expected may immediately undergo rearrangement to an open chained isomer



$$(C_6H_5)_2CH\underset{O}{\underset{|}{C}}H{-}\underset{O}{\underset{|}{C}}(OH)C_6H_2(CH_3)_3 \longrightarrow (C_6H_5)_2CH\underset{OOH}{\underset{|}{C}}HCOC_6H_2(CH_3)_3$$

VIIIa

VIIIb

In thermal stability and chemical activity the peroxide does not differ materially from known peroxides which are undoubtedly cyclic in structure. When it is heated it decomposes, with a flash, into mesitylene carbonic acid and diphenyl acetaldehyde. It readily loses one atom of oxygen to hydrogen iodide and to platinum and hydrogen, being reduced to a hydroxy ketone instead of to the usual oxanol. Like the peroxides of known structure, also, it is attacked by aqueous alkalies, but instead of being cleaved it is dehydrated to an α-diketone. All of these properties and products can be reconciled with either of the two formulas, but the peroxide is neutral while all known derivatives of hydrogen peroxide, including the naphthalene derivative discovered by Hock and Susemihl,[3] are distinctly acidic. It seems probable, therefore, that the substance is

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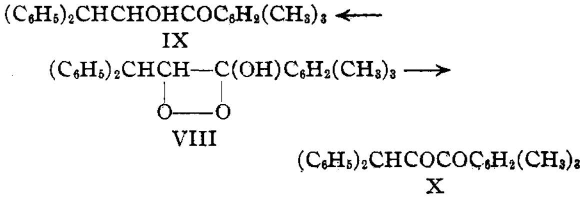
(2) Hantzsch, *Ann.*, **392**, 292 (1912).

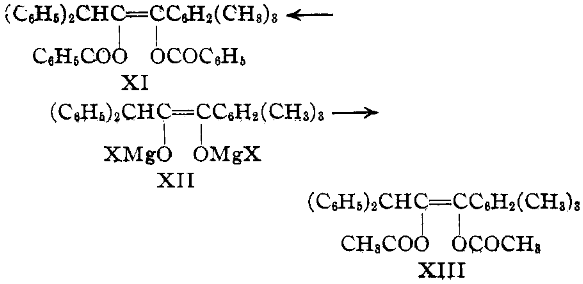
(3) Hock and Susemihl, *Ber.*, **66**, 61 (1933).

a cyclic peroxide, that the divergent reduction product is due to the instability of the oxanol[4] and that aqueous alkali rearranges the cyclic to the open chained form which is then dehydrated to the diketone



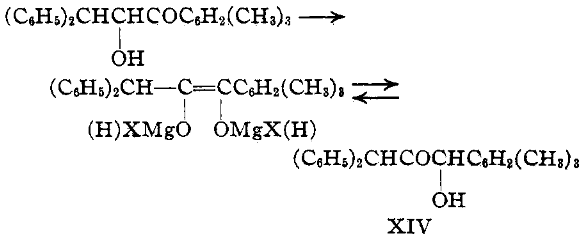
$$\underset{\text{IX}}{(C_6H_5)_2CHCHOHCOC_6H_2(CH_3)_3} \longleftarrow \underset{\text{VIII}}{(C_6H_5)_2CH\underset{\substack{|\\O}}{C}H\text{—}\underset{\substack{|\\ \text{—}O}}{C}(OH)C_6H_2(CH_3)_3} \longrightarrow \underset{\text{X}}{(C_6H_5)_2CHCOCOC_6H_2(CH_3)_3}$$

Although not perceptibly enolized in solution, the hydroxy ketone IX, like all other substances containing the group $CHCOC_6H_2(CH_3)_3$, is converted into an enolate by Grignard reagents. It liberates two moles of gas from methyl magnesium iodide and when the resulting magnesium compound is acylated the product is a di-ester



$$\underset{\text{XI}}{(C_6H_5)_2CH\underset{\substack{|\\C_6H_5COO}}{C}=\underset{\substack{|\\OCOC_6H_5}}{C}C_6H_2(CH_3)_3} \longleftarrow \underset{\text{XII}}{(C_6H_5)_2CH\underset{\substack{|\\XMgO}}{C}=\underset{\substack{|\\OMgX}}{C}C_6H_2(CH_3)_3} \longrightarrow \underset{\text{XIII}}{(C_6H_5)_2CH\underset{\substack{|\\CH_3COO}}{C}=\underset{\substack{|\\OCOCH_3}}{C}C_6H_2(CH_3)_3}$$

Evidently the magnesium derivative is a di-enolate which undergoes only O-acylation. The corresponding di-enol could not be isolated. Like the enol of benzhydryl acetomesitylene it is remarkably persistent in solution but when these solutions are concentrated they deposit only the isomeric hydroxy ketone



$$(C_6H_5)_2CH\underset{\substack{|\\OH}}{C}HCOC_6H_2(CH_3)_3 \longrightarrow (C_6H_5)_2CH\text{—}\underset{\substack{|\\(H)XMgO}}{C}=\underset{\substack{|\\OMgX(H)}}{C}C_6H_2(CH_3)_3 \rightleftarrows \underset{\text{XIV}}{(C_6H_5)_2CHCO\underset{\substack{|\\OH}}{C}HC_6H_2(CH_3)_3}$$

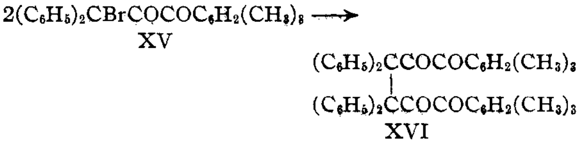
In this case, therefore, it is possible to follow, step by step, the isomerization of an hydroxy ketone by way of an intermediate di-enol. This same di-enol also serves as an intermediate in the interconversion of the hydroxy ketones and the α-diketone, X. It is an energetic reducing agent which decolorizes indophenol dyes as readily as do the well-known cyclic di-enols ascorbic acid and reductone. In contact with air it is oxidized rapidly to hydrogen peroxide and the α-diketone. The diketone, in turn, when it is reduced catalytically, yields colorless solutions that are indistinguishable from those which are obtained by acidifying the magnesium derivative of the di-enol. Here, clearly the di-enol is formed by 1,4-addition to the diketone.

In solution this diketone slowly enolizes, forming an equilibrium mixture which in alcohol is composed of approximately equal quantities of ketone and enol. As the system

$$\underset{\text{X (a)}}{(C_6H_5)_2CHCOCOC_6H_2(CH_3)_3} \rightleftarrows \underset{\text{X (b)}}{(C_6H_5)_2C=C(OH)COC_6H_2(CH_3)_3}$$

is uncommonly sluggish both the ketonic and the enolic forms can be isolated without much difficulty.

The ketonic form is stable in the air, but like other α-diketones it is oxidized by alkaline hydrogen peroxide, the products being diphenyl acetic and mesitylene carbonic acids. It forms exceedingly reactive halogen compounds that lose the halogen when they are shaken with metals, leaving residues which couple to a highly phenylated tetraketone



$$\underset{\text{XV}}{2(C_6H_5)_2CBrCOCOC_6H_2(CH_3)_3} \longrightarrow \underset{\text{XVI}}{\begin{array}{l}(C_6H_5)_2CCOCOC_6H_2(CH_3)_3\\ \quad\quad\;\;|\\(C_6H_5)_2CCOCOC_6H_2(CH_3)_3\end{array}}$$

The enolic form is comparatively stable in the solid state but in solution it is oxidized rapidly by free oxygen, being cleaved thereby to benzophenone and trimethylphenyl glyoxylic acid. It is also oxidized by such mild oxidizing agents as ferric chloride but the result is synthesis instead of cleavage, the product being the same tetraketone that is formed by the removal of bromine from the bromo ketone.

As a consequence of the sluggishness of the keto–enol system the diketone and its enol do not, as might be expected, give the same products when they are treated with Grignard reagents. Both substances liberate approximately one mole of gas from methylmagnesium iodide but while the ketone is reduced to the di-enolate XII, the enol is converted into a magnesium derivative which on acidification yields only β-phenyl benzalacetomesitylene. All attempts to establish the struc-

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(4) Madelung and Oberwegner, *Ann.*, **490**, 201 (1931).

ture of this magnesium derivative were unsuccessful but presumably it is an allenic compound

$$(C_6H_5)_2C{=}C(OH)COC_6H_2(CH_3)_3 \longrightarrow$$
$$(C_6H_5)_2C{=}C{=}C(OMgX)C_6H_2(CH_3)_3 \longrightarrow$$
$$(C_6H_5)_2C{=}CHCOC_6H_2(CH_3)_3$$

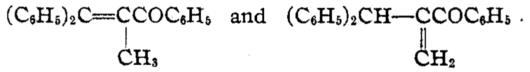
Having found that mesitylene derivatives can be employed for establishing the manner in which hydrogen adds to α-diketones, we undertook to utilize them also for ascertaining the mode of reduction of α,β-unsaturated ketones. To this end we reduced β-phenylbenzal acetomesitylene both catalytically and with zinc and acid. Some years ago Straus[5] inferred, from the nature of the products obtained from a series of unsaturated ketones, that in the catalytic reduction of these compounds 1,2- and 1,4-addition are competing reactions and that the outcome depends upon the same factors that control the mode of addition of Grignard reagents. Our experiments bring a measure of support to this inference. When phenylbenzal acetomesitylene was reduced with hydrogen and palladium on calcium carbonate the product was a mixture of approximately 88% of benzhydryl acetomesitylene and 12% of its enol. It is certain, therefore, that in this case at least 12% of the product is due to 1,4-addition of hydrogen but we were unable to determine whether the saturated ketone is due to 1,2-addition or to ketonization of the enol. In contrast the results obtained by reducing the unsaturated ketone with zinc and acid are quite conclusive; the reduction product yields the same amount of peroxide that is formed from the product obtained by adding phenylmagnesium bromide to benzalacetomesitylene. The reduction of α,β-unsaturated ketones with metal combinations, therefore, involves 1,4-addition to the conjugated system.

From the foregoing account it is evident that in every case in which it has been possible to establish the structure of a magnesium derivative resulting from the addition of a Grignard reagent to the conjugated system of an unsaturated ketone it has proved to be an enolate due to 1,4-addition. As the list now includes open chained and cyclic ketones, ketones with and without substituents in the α-position it is reasonable to assume a similar mode of addition to all systems of this type. It now seems clear, also, that the mode of alkylation and acylation of the enolates of mono ketones is associated in some manner with the stability of the corresponding enol, and it seems probable that the rate at which the enolic radical or ion is ketonized determines the relative amounts of C and O products that are formed.

Experimental Part

I. Alkylation

The two products obtained from each magnesium derivative were separable by crystallization. Facility of hydrolysis to the saturated ketones by acids was accepted as adequate proof of the O-alkyl derivatives. The formula of the C-alkyl derivative of benzhydryl acetophenone is based on the fact that the unsaturated ketone obtained by the indirect elimination of methyl alcohol is reducible to α-methyl-β,β-diphenyl propiophenone. For this unsaturated ketone, therefore, only two formulas are possible, namely



$$\underset{\displaystyle CH_3}{(C_6H_5)_2C{=}\underset{|}{C}COC_6H_5} \quad \text{and} \quad (C_6H_5)_2CH{-}\underset{\displaystyle CH_2}{\underset{\|}{C}}COC_6H_5\,.$$

As the substance reduces permanganate and forms a dibromide from which it is regenerated by potassium iodide the first of these formulas is excluded. And in the case of the mesitylene derivative the corresponding formula for the unsaturated ketone is excluded by the fact that it readily adds a mole of ethylmagnesium bromide.

Alkylation of Benzhydryl Acetophenone.—To an ethereal solution of phenylmagnesium bromide prepared from 2.5 g. of magnesium was added 10 g. of benzal acetophenone. The mixture was boiled for half an hour, treated with 8.5 g. of chloromethyl ether and boiled for two more hours. After cooling, the clear ethereal layer was decanted from the paste adhering to the walls of the vessel, treated with ammonia and ammonium chloride and distilled with steam. The distillate contained only diphenyl and benzyl methyl ether. The oily residue contained the acetal. By suitable treatment it was obtained as a solid which crystallized from methyl alcohol in plates and melted at 64–65°. The yield was 4.65 g. or 30%.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.6; H, 6.7. Found: C, 83.6; H, 6.8.

The paste, left after decanting the ethereal solution, contained the C-alkylation product II. It was likewise treated with ammonia–ammonium chloride. The ether was thus obtained as a solid which crystallized from methyl alcohol in prisms and melted at 131–132°. The yield was 11 g. or 70%.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.6; H, 6.7. Found: C, 83.3; H, 6.6.

α-Benzhydryl-β-bromo Propiophenone, V.—As the C-alkyl derivative was not affected by either dilute acids or bases it was heated in a sealed tube for ten hours with a large excess of 50% hydrobromic acid. The solid product

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(5) Straus and Grindel. *Ann.*, **439**, 276 (1924).

crystallized from alcohol in fine needles melting at 163°. The yield was 91%.

Anal. Calcd. for $C_{22}H_{19}OBr$: C, 69.7; H, 5.1. Found: C, 69.9; H, 5.2.

α-Benzhydrylvinyl Phenyl Ketone, VI.—The bromo compound was converted into the unsaturated ketone by dissolving it in boiling alcoholic potassium hydroxide. The ketone crystallized from alcohol in coarse needles melting at 115°.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.6; H, 6.1. Found: C, 88.9; H, 6.3.

Unlike vinyl phenyl ketone itself this benzhydryl derivative shows no tendency to polymerize or undergo autoxidation. It is, however, readily oxidized by permanganate and in the presence of platinum it is rapidly reduced to α-methyl-β,β-diphenyl propiophenone.

The dibromide of the ketone crystallized from alcohol in prisms melting at 105°. It lost its bromine and regenerated the unsaturated ketone when it was boiled with methyl alcoholic potassium iodide.

Anal. Calcd. for $C_{22}H_{18}OBr_2$: C, 57.6; H, 4.0. Found: C, 57.7; H, 4.1.

α-Methyl-β,β-diphenylvinyl Phenyl Ketone, $(C_6H_5)_2C{=}C(CH_3)COC_6H_5$.—This isomeric unsaturated ketone was obtained in small quantities when the C-alkyl derivative was boiled with concentrated sodium ethylate. It crystallized from alcohol in prisms melting at 114°. Unlike its isomer it does not reduce permanganate.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.6; H, 6.1. Found: C, 88.5; H, 6.1.

Alkylation of Benzhydryl Acetomesitylene.—A solution of the magnesium derivative was prepared by adding 5 g. of the ketone to ethyl magnesium bromide formed from 0.6 g. of magnesium in 100 cc. of ether and 50 cc. of benzene, and boiling for half an hour. To this solution was added 2 g. of chloromethyl ether. The mixture was boiled for two hours, then decomposed with ammonia and ammonium chloride. The ethereal layer, on evaporation, deposited a mixture which was separated by extraction with low-boiling petroleum ether. The extract deposited the acetal III. It crystallized from methyl alcohol in needles melting at 92°. The yield was 77–80%.

Anal. Calcd. for $C_{26}H_{28}O_2$: C, 83.0; H, 7.6. Found: C, 82.8; H, 7.4.

The residue left after extraction with petroleum ether was recrystallized from methyl alcohol. It separated in prisms melting at 155°. The yield of the ether IV was 18–20%.

Anal. Calcd. for $C_{26}H_{28}O_2$: C, 83.0; H, 7.6. Found: C, 83.2; H, 7.7.

α-Benzhydrylvinyl Mesityl Ketone, VII.—The ether was heated to 100° with 50% hydrobromic acid and boiled for one and one-half hours with methyl alcoholic potassium hydroxide. In both cases the product was the unsaturated ketone. The ketone crystallizes from methyl alcohol in prisms melting at 109–110°. The yield was 90%. Like the corresponding benzene derivative it combines with bromine and reduces permanganate.

Anal. Calcd. for $C_{25}H_{24}O$: C, 88.2; H, 7.1. Found: C, 87.9; H, 7.4.

II. Acylation

The magnesium enolate of benzhydryl acetomesitylene was obtained either by adding phenylmagnesium bromide to benzalacetomesitylene or by boiling the ethereal solutions of the saturated ketone itself with a slight excess of ethylmagnesium bromide. For the purpose of getting solutions of the enol the enolate was decomposed with iced acid in the presence of ether, the ether solution washed with ice-water and rapidly dried with sodium sulfate. A titration with bromine showed that a solution prepared in this manner contained 90–95% of enol.

The Peroxide, VIII.—For the purpose of preparing the peroxide the ethereal solution obtained by acidifying the enolate was diluted with three or four times its volume of petroleum ether and then washed with ice-water. A rapid current of oxygen was passed through the moist solution for several hours to complete the precipitation of peroxide which began in about an hour. The peroxide was purified by solution in ether and reprecipitation with petroleum ether. It crystallized in small needles melting, with decomposition, at 116–117°. The yield was 90%.

Reduction. α-Hydroxy-β,β-diphenylpropionyl Mesitylene, IX.—The peroxide was reduced both with hydrogen in the presence of platinum and by shaking it for several hours at the ordinary temperature with potassium iodide and glacial acetic acid. In both cases the product was the hydroxy ketone. The second method was found to be the more convenient. By recrystallization from hexane the hydroxy ketone was obtained in prisms melting at 76°. The yield was about 77%.

Anal. Calcd. for $C_{24}H_{24}O_2$: C, 83.7; H, 7.0. Found: C, 83.6; H, 7.1.

The acetate of the hydroxy ketone, prepared by acetylation with acetyl chloride, is convenient for identification because it is less soluble than the hydroxyl compound and crystallizes well from alcohol in prisms melting at 89°.

Anal. Calcd. for $C_{26}H_{26}O_3$: C, 80.8; H, 6.8. Found: C, 80.7; H, 7.0.

The benzoate, formed when the hydroxy ketone is treated with benzoyl chloride in pyridine, crystallizes from alcohol in prisms melting at 114–115°.

Anal. Calcd. for $C_{31}H_{28}O_3$: C, 83.0; H, 6.3. Found: C, 82.7; H, 6.5.

Isomerization, IX–XIV.—As the di-enol that is formed by adding excess of a Grignard reagent to the hydroxy ketone and acidifying the product, undergoes autoxidation much more rapidly than ketonization, the ordinary methods of manipulating organic magnesium derivatives yield only oxidation products. In order to secure a hydroxy ketone it was necessary, therefore, either to promote ketonization by addition of a base like piperidine or to prevent oxidation by addition of a reducing agent. The best results were obtained by the following procedure. An ethereal solution of 4 g. of the hydroxy ketone was added to a solution of ethylmagnesium bromide containing slightly more than two moles of reagent. The mixture was boiled for an hour then treated with excess of zinc dust and acidified by cautious addition of cold dilute acetic acid. The acidified solution was left to itself for a week in a securely corked flask before the product was isolated in the usual manner. The result was the isomeric hydroxy ketone. It crystallized from alcohol in prisms and melted at 77–78°. The yield was 90%.

Anal. Calcd. for $C_{24}H_{24}O_2$: C, 83.7; H, 7.0. Found: C, 83.6; H, 6.9.

The Dibenzoate, XI.—The hydroxy ketone was converted into a magnesium derivative as described in the preceding experiment, slightly more than two equivalents of benzoyl chloride was added to the resulting solution and the mixture was boiled for four hours. The result was a solid which crystallized from alcohol in prisms and melted at 157°. The yield was 80–85%.

Anal. Calcd. for $C_{38}H_{32}O_4$: C, 82.6; H, 5.8. Found: C, 82.4; H, 6.0.

The Diacetate.—As the compositions of the mono- and di-benzoates are too similar for differentiation by analysis, the diacetate was prepared in the same manner. It was obtained in two forms, the one melting at 127–128° and the other at 149°. Both forms crystallize well from alcohol.

Anal. Calcd. for $C_{28}H_{28}O_4$: C, 78.5; H, 6.6. Found: (128°) C, 78.4; H, 6.4. (149°) C, 78.7; H, 6.7.

Benzhydryl Trimethylphenyl Diketone, X.—When the solution, obtained by converting either of the isomeric α-hydroxy ketones into the magnesium derivative in the manner described in the preceding experiments and acidifying, is handled in the usual manner it absorbs oxygen from the air and the principal product is the α-diketone. In addition to the diketone there is formed a small quantity (3–4%) of a high-melting hydrocarbon (212°) which presumably is an indene derivative.

The diketone is obtained more readily, however, by oxidization of the α-hydroxy ketone. For this purpose a warm solution of the crude hydroxy ketone in glacial acetic acid is treated with a solution of slightly more than the calculated quantity of chromic acid in 95% acetic acid. The mixture is kept at 50° for half an hour, then poured into water. The diketone is extracted with ether and crystallized from alcohol. It separates in yellow cubes melting at 74–75°.

Anal. Calcd. for $C_{24}H_{22}O_2$: C, 84.2; H, 6.4. Found: C, 84.2; H, 6.7.

In the solid state the diketone appears to be completely stable. In solution it enolizes in part but in the absence of bases the process is exceedingly slow; the enolic form absorbs oxygen rapidly but no measurable quantity of oxygen was absorbed when an alcoholic solution of the diketone was shaken with oxygen for three and one-half hours. In the presence of a trace of piperidine or sodium methylate, however, it enolizes more rapidly and in the course of fifteen minutes forms an equilibrium mixture composed of nearly equal quantities of enol and ketone.[6]

Reduction of the Diketone.—When a yellow solution of the diketone in methyl alcohol was shaken with hydrogen and platinum it rapidly absorbed hydrogen and became colorless. A drop of piperidine was added to promote the ketonization and the solution was then set aside for thirty-six hours, before it was filtered and concentrated. The product was the higher-melting hydroxy ketone and the yield was 95%. The reduction was repeated, but the colorless solution was filtered immediately and the filtrate was allowed to evaporate in contact with air. It turned yellow and deposited the α-diketone in a yield of 95%. The solution which had been oxidized in the air also contained a considerable quantity of hydrogen peroxide. As the hydroxy ketone is insensitive to oxygen, the formation of the diketone is proof that the reduction product is the di-enol.

Reaction with Ethylmagnesium Bromide.—An ethereal solution of 3 g. of the diketone was added to a solution of ethylmagnesium bromide containing slightly more than two equivalents of the reagent. A small quantity of benzene was added to prevent precipitation of magnesium compounds, the mixture was boiled and then treated with acetyl chloride in slight excess. The product was the higher-melting diacetate of the di-enol—proving that organic magnesium compounds reduce the diketone to the magnesium derivative of the di-enol.

The Enolic Form of the Diketone, Xb.—The diketone was converted into the enol by dissolving it in a slight excess of 2% methyl alcoholic potassium hydroxide and pouring the red solution of the resulting enolate into excess of 2 *N* hydrochloric acid. It usually separated as an oil that soon solidified. The solid was washed with water and crystallized from methyl alcohol or low-boiling petroleum ether. It separated in pale yellow prisms melting at 117°. The yield was quantitative.

Anal. Calcd. for $C_{24}H_{22}O_2$: C, 84.2; H, 6.4. Found: C, 83.8; H, 6.6.

The Phenyl Urethan.—The enol can be identified by converting it into the phenyl urethan which is perfectly stable. It crystallizes well from ether and petroleum ether in pale yellow needles melting at 148°.

Anal. Calcd. for $C_{31}H_{27}O_3N$: C, 80.6; H, 5.9; N, 3.0. Found: C, 80.4; H, 6.2; N, 3.3.

Autoxidation.—In the absence of air the pure solid enol is fairly stable but all samples ultimately liquefy. Its solutions slowly absorb oxygen, the enol being oxidized to benzophenone, mesityl glyoxalic acid and mesitylene carbonic acid. When it is acylated it forms only O-acyl derivatives, the structure of the acylation products being definitely established by the fact that when they were reduced with zinc and acetic acid they formed the corresponding acyl derivatives of α-hydroxy benzhydryl acetomesitylene.

The acetate, formed by heating the enol with acetyl chloride on a steam-bath for ten hours, crystallized from petroleum ether in pale yellow prisms melting at 86–87°.

Anal. Calcd. for $C_{26}H_{24}O_3$: C, 81.2; H, 6.3. Found: C, 81.3; H, 6.4.

The benzoate, formed by benzoylation in pyridine, crystallizes from alcohol in pale yellow prisms melting at 124°. The yield was 90%.

Anal. Calcd. for $C_{31}H_{26}O_3$: C, 83.4; H, 5.9. Found: C, 83.3; H, 5.9.

Halogenation.—The halides that are formed by the addition of chlorine or bromine to the enol immediately lose halogen acid and form the halogen substitution products of the α-diketone. As the action of free chlorine involves

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(6) The statement of Kohler and Weiner [This Journal, **56**, 434 (1934)] that benzhydryl phenyl diketone does not enolize is incorrect. A sample, equilibrated in methyl alcohol with a trace of piperidine, was titrated with bromine by H. E. Schroeder who found 15.5% enol.

substitution in the mesitylene group, the pure chloro compound is most readily made by employing a calculated quantity of sulfuryl chloride. The pure bromo compound can be made by operating with free bromine in chloroform at low temperatures. These halogen compounds are interesting because they are as reactive as the halogen derivatives of triaryl methanes. The constants of the chloro and bromo compounds as well as those of the corresponding ethers are shown in the following table.

	Calcd.		Found			M. p.,
	C	H	C	H	Form	°C.
$C_{24}H_{21}O_2 \cdot Cl$	76.5	5.6	76.4	5.9	Yellow plates	134
$C_{24}H_{21}O_2 \cdot Br$	68.4	5.0	68.1	5.4	Yellow plates	152
$C_{24}H_{21}O_2 \cdot OC_2H_5$	80.8	6.8	80.8	7.1	Prisms	121
$C_{24}H_{21}O_2 \cdot OCH_3$	80.6	6.5	80.6	6.8	Prisms	68

Coupling. The Tetraketone, XVI.—The enolic form of the α-diketone develops a brown color in alcoholic solutions of ferric chloride but the color soon fades. When the reaction was carried out with larger quantities the product was a sparingly soluble compound which crystallized from ether–petroleum ether in deep yellow prisms and which melted at 194°. The structure of this product was established by a synthesis from the bromo compound of the diketone. For this purpose a solution of 3 g. of the bromo compound in 50 cc. of dry benzene was shaken for twelve hours with 20 g. of mercury. The result was the same compound that had been obtained from the enol. The yield was 80–85%.

Anal. Calcd. for $C_{48}H_{42}O_4$: C, 84.4; H, 6.2; mol. wt., 682. Found: C, 84.1; H, 6.6; mol. wt., 685.

Catalytic Reduction of β-Phenylbenzal Acetomesitylene.—Preliminary experiments showed that the unsaturated ketone is reduced more rapidly by palladium on calcium carbonate than by platinum and hydrogen. Accordingly solutions of 4 g. of the ketone in ethyl acetate and in ether were shaken with hydrogen in the presence of 2 g. of the palladium catalyst until the calculated volume of hydrogen had been absorbed. The rate was the same in both solvents, the time required being an hour and three quarters. The suspensions were filtered, the filtrate was diluted with five times its volume of petroleum ether and saturated with oxygen. As the principal product was the saturated ketone, it was impossible to isolate pure peroxide but a crude estimate based on oxidation of acidified potassium iodide and on conversion to the enol of the diketone indicated that the mixture contained 10–12% of peroxide.

Reduction with Zinc and Acetic Acid.—A solution of 3 g. of the unsaturated ketone in 20 cc. of glacial acetic acid, 20 cc. of ether and 0.5 cc. of water was cooled in a freezing mixture and treated in the course of three minutes with 2.5 g. of zinc dust. The mixture was shaken in the freezing mixture for another three minutes, then poured in a mixture of 10 cc. of ether and 40 cc. of petroleum ether and washed rapidly with ice water until free from zinc and from most of the acetic acid. From the resulting ether–petroleum ether solution oxygen precipitated 3 g. of peroxide—a yield of 90%.

Summary

The paper presents evidence that the system $C{=}C(OH)C_6H_2(CH_3)_3$ is unusually persistent in solution. By utilizing this peculiarity it was possible to prove that the catalytic reduction of α-diketones proceeds by 1,4-addition to the oxygen atoms, that the reduction of α,β-unsaturated ketones with palladium on calcium carbonate and hydrogen proceeds at least in part by 1,4-addition to the conjugated system and that the reduction of α,β-unsaturated ketones by zinc and acid proceeds whol y by 1,4-addition.

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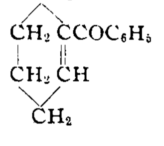
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Application of the Principle of Vinylogy to Unsaturated Ketones

BY R. E. CHRIST[1] AND REYNOLD C. FUSON

A methyl group, separated from a carbonyl group by one vinylene unit, exhibits properties that are similar to those which it possesses when it is attached directly to the carbonyl group.[2] The present paper is an extension of this principle to ketones in which the vinylene group forms a part of a six-membered ring.

Tetrahydrobenzophenone (I) was prepared from benzoyl chloride and cyclohexene by use of the Friedel–Crafts synthesis. This compound was of particular interest, inasmuch as it offered the possibility of testing whether the activating influence of a carbonyl group outside the ring could be exerted on a methylene group which was a member of the ring. The ketone was found to react with benzaldehyde in an alcoholic solution, sodium ethoxide being used as a condensing agent. The product isolated was the expected ketone (II).



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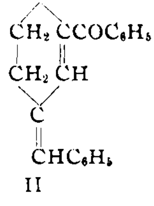

II

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(1) Du Pont Post-doctorate Fellow.

(2) Fuson, Christ and Whitman, THIS JOURNAL, **58**, 2450 (1936).