The free acid is only slightly soluble in boiling water, 0.1 g. dissolving in 300 cc., and almost insoluble in cold water and alcohol. It separates from its aqueous solutions in the form of soft white needles appearing in the form of rosets.

Anal. IV. Calcd. for $C_{11}H_{13}O_4N$: N, 6.28. Found: N, 6.03, 6.04.

The free acid is soluble in about 50 parts of boiling water from which it separates in hard elongated white plates which grow in rosets. It shows no tendency to form supersaturated aqueous solutions and is insoluble in alcohol.

Summary

Free tyrosine-N-acetic acid, its hydrochloride, the hydrochloride of its dimethyl ester and certain of its metallic derivatives have been prepared and described.

A new general method for the synthesis of α-imino dibasic acids has been outlined. Investigations will be continued on the derivatives of the four acids referred to in this paper and on the intermediate hydantoins involved in their synthesis.
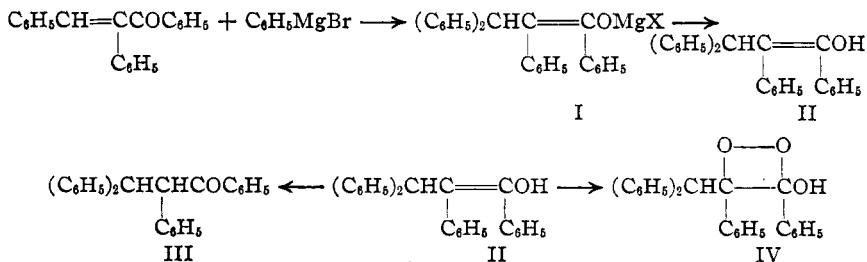
SOUTH HADLEY, MASSACHUSETTS

THE REACTION BETWEEN ALPHA, BETA-UNSATURATED KETONES AND ORGANIC MAGNESIUM COMPOUNDS. THE STRUCTURE OF THE ADDITION PRODUCTS

BY E. P. KOHLER AND W. E. MYDANS

Many α,β-unsaturated ketones combine with Grignard reagents and other metallic compounds to form metallic derivatives which on hydrolysis yield saturated ketones. In some cases, notably those in which there are substituents in the alpha position, it is known that the saturated ketones are secondary products, and that the primary products of hydrolysis are enols which are capable of combining with oxygen to form peroxides. In these cases it is reasonable to infer that the metallic derivatives are enolates which are formed by 1,4-addition to the conjugated system

$$C_6H_5CH{=}CCOC_6H_5 + C_6H_5MgBr \longrightarrow (C_6H_5)_2CHC{=\!=\!=}COMgX \longrightarrow$$

with pendant C_6H_5 groups. Structures labeled I and II are shown:

$$(C_6H_5)_2CHC{=\!=\!=}COH \quad \text{(II)}$$
with C_6H_5 C_6H_5 substituents

$$(C_6H_5)_2CHCHCOC_6H_5 \longleftarrow (C_6H_5)_2CHC{=\!=\!=}COH \longrightarrow (C_6H_5)_2CHC{-\!-\!-}COH$$
$$\overset{|}{C_6H_5} \qquad\qquad \overset{|}{C_6H_5}\ \overset{|}{C_6H_5} \qquad\qquad \overset{O-\!-\!-O}{\ }\ \overset{|}{C_6H_5}\ \overset{|}{C_6H_5}$$
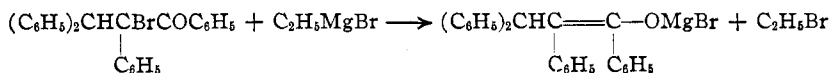$$\text{III} \qquad\qquad\qquad \text{II} \qquad\qquad\qquad \text{IV}$$

Owing to the rapidity with which most enols of mono ketones undergo rearrangement, this method of arriving at the structure of the metallic

derivatives is seldom applicable; in most cases the structure of the addition products, and consequently the mode of addition, has to be based on analogy or inferred from the course of metathetical reactions—both equally likely to lead to conclusions that are illusory. For securing evidence that is more reliable but two ways appear to be open, namely, proof of the presence of an ethylenic linkage or proof of the presence of a carbonyl group. We decided to explore the first of these possible ways.

To this end we planned to treat the addition products with oxygen. It is well known that many metallic enolates and all Grignard reagents undergo spontaneous oxidation. In both cases, doubtless the primary product is a peroxide, but the final result usually is oxidative cleavage. In the case under consideration the alternative peroxides, being very different in character, would be expected to give cleavage products that are distinctive

$$\begin{array}{cc} \text{RCHCOR} & \text{O——O} \\ | & | \quad | \\ \text{O—OMgX} & \text{RCH—C(R)OMgX} \end{array}$$
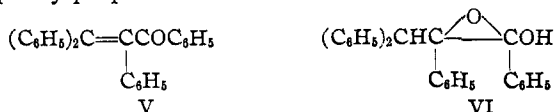
In order to keep as close to the known as possible we selected as the first magnesium compound to study the addition product represented by I. Ethereal solutions of this compound can be obtained both by the reaction indicated in the equation, and also by the action of ethylmagnesium bromide on alpha bromo-α,β,β-triphenylpropiophenone.

$$(C_6H_5)_2CHCBrCOC_6H_5 + C_2H_5MgBr \longrightarrow (C_6H_5)_2CHC\!\!=\!\!C\!-\!OMgBr + C_2H_5Br$$
$$\qquad\quad | \qquad\qquad\qquad\qquad\qquad\qquad\quad |\quad |$$
$$\qquad\quad C_6H_5 \qquad\qquad\qquad\qquad\qquad\qquad C_6H_5\ C_6H_5$$

When oxygen was passed into these solutions they immediately became yellow in color, then gradually changed into brown viscous liquids which, when freed from magnesium by treatment with acid or ammonium chloride, yielded a product that crystallized well and melted sharply.
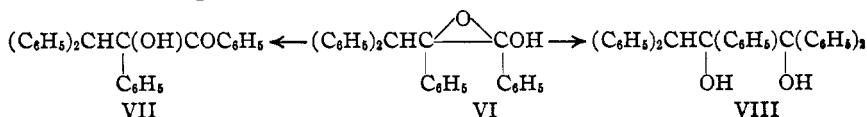
This substance proved to be composed of two compounds which cannot be separated by crystallization, namely, tetraphenylpropenone (V) and oxo tetraphenylpropanol VI

$$\begin{array}{cc} (C_6H_5)_2C\!\!=\!\!CCOC_6H_5 & (C_6H_5)_2CHC\overset{O}{\triangle}COH \\ | & |\qquad\ | \\ C_6H_5 & C_6H_5\quad C_6H_5 \\ \text{V} & \text{VI} \end{array}$$

The unsaturated ketone has been known for a long time but the oxanol is new and it is the first of its type. Our formula is based mainly on the following observations: (1) chromic acid oxidizes it to benzophenone and benzil, establishing the carbon chain and the position of the phenyl groups, (2) it rapidly liberates a mole of gas from methylmagnesium iodide, therefore contains one hydroxyl group, (3) among the products that are formed when it is heated is an isomer which was described in an earlier paper and there formulated as an alpha hydroxy ketone VII;[1]
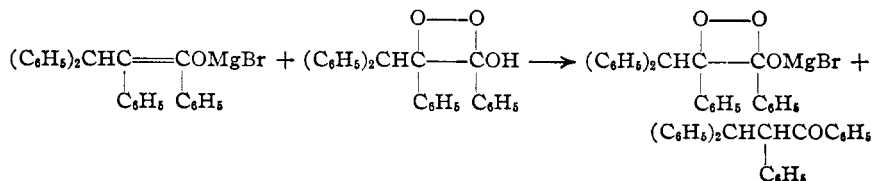
[1] Kohler, Richtmyer and Hester, THIS JOURNAL, 53, 205 (1931).

when it is heated with alkalies this isomer is formed quantitatively, and (4) phenylmagnesium bromide converts it in part into this same isomer and in part into a glycol of which the structure is certain (VIII). Assuming the formulas of the earlier paper to be correct, these transformations must be represented as follows

$$(C_6H_5)_2CHC(OH)COC_6H_5 \longleftarrow (C_6H_5)_2CHC\overset{O}{\overset{\diagup\diagdown}{}}COH \longrightarrow (C_6H_5)_2CHC(C_6H_5)C(C_6H_5)_2$$

$$\underset{\underset{VII}{C_6H_5}}{|} \qquad\qquad \underset{\underset{VI}{C_6H_5 \;\; C_6H_5}}{|\quad\;\;|} \qquad\qquad \underset{\underset{VIII}{OH \quad OH}}{|\quad\;\;|}$$
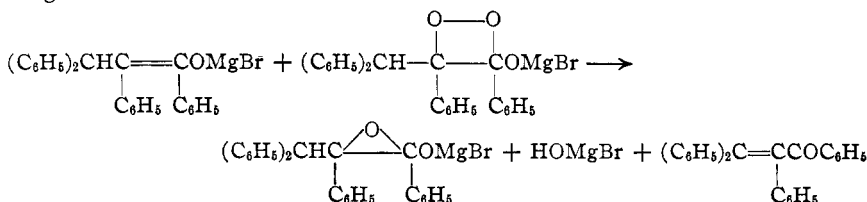
Since here for the first time an alpha hydroxy ketone and its cyclic isomer appear as two stable and independent compounds, there is, naturally, some difficulty in the allocation of the two possible formulas. The reasons for our choice are as follows. Since phenylmagnesium bromide converts both isomers into the glycol, at least one of them must be the oxanol VI; the other isomer might be either a stereoisomeric oxanol or an alpha hydroxy ketone. Of these two types of compounds the hydroxy ketone would be expected to be the more stable, both on general considerations and because most ethylene oxides are rearranged more or less readily into open-chained isomers. Ethylene oxides also generally combine with water when they are treated with bases—a process which would likewise transform an oxanol into an hydroxy ketone. For these reasons we regard our new compound as the oxanol and the isomer into which it passes on rearrangement as the hydroxy ketone but we realize that until derivatives of both isomers are available for comparison these formulas are open to revision.
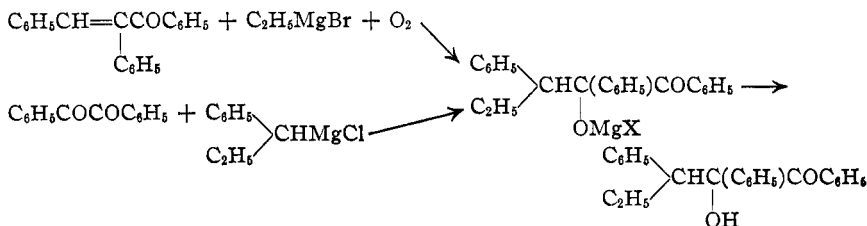
According to the foregoing account the autoxidation of the magnesium derivative appears to be much more involved than that of the enol which is formed from it by hydrolysis. It is possible, however, that the primary reaction is the same in both cases, the final products being due to the interaction of oxidized and unoxidized magnesium compounds. In order to test this possibility phenylmagnesium bromide was added to benzaldesoxybenzoin as before, but then the solution was treated with half a mole of the peroxide (IV) instead of with oxygen. The result was a mixture of magnesium derivatives which, on hydrolysis, yielded, along with some of the saturated ketone, the same crystalline product that had been obtained with oxygen. In this case, doubtless, the more acidic peroxide first reacts with one molecule of addition product to form a new magnesium derivative

$$(C_6H_5)_2CHC\!\!=\!\!COMgBr + (C_6H_5)_2CHC\overset{O—O}{\overset{|\quad\;|}{}}COH \longrightarrow (C_6H_5)_2CHC\overset{O—O}{\overset{|\quad\;|}{}}COMgBr +$$

$$\underset{C_6H_5 \;\; C_6H_5}{|\quad\;\;|} \qquad\qquad \underset{C_6H_5 \;\; C_6H_5}{|\quad\;\;|} \qquad\qquad \underset{C_6H_5 \;\; C_6H_5}{|\quad\;\;|}$$

$$(C_6H_5)_2CHCHCOC_6H_5$$
$$\underset{C_6H_5}{|}$$

The new magnesium derivative then oxidizes a second molecule of the addition product to the unsaturated ketone and is thus reduced to the magnesium derivative of the oxanol

$$(C_6H_5)_2CHC\!\!=\!\!COMgBr + (C_6H_5)_2CH-\overset{O——O}{\underset{\underset{C_6H_5}{|}}{C}}-\overset{}{\underset{\underset{C_6H_5}{|}}{C}}OMgBr \longrightarrow$$
$$\underset{\underset{C_6H_5}{|}\ \underset{C_6H_5}{|}}{}$$

$$(C_6H_5)_2CHC\overset{O}{\triangle}COMgBr + HOMgBr + (C_6H_5)_2C\!\!=\!\!CCOC_6H_5$$
$$\underset{\underset{C_6H_5}{|}\ \underset{C_6H_5}{|}}{}\qquad\qquad\qquad\underset{\underset{C_6H_5}{|}}{}$$

In the case under investigation the results confirmed the conclusions which had been reached in another manner, but they held little promise that in doubtful cases oxygen might be used with success for determining the structure of magnesium derivatives. We nevertheless examined one more case, starting with the same unsaturated ketone but employing ethyl instead of phenylmagnesium bromide. Here also a product was formed which had the composition and molecular weight of an oxanol but the same substance was synthesized by a method which would be expected to yield an hydroxy ketone and it could not be isomerized with alkalies. It therefore probably is not the oxanol but the isomeric alpha hydroxy ketone

$$C_6H_5CH\!\!=\!\!CCOC_6H_5 + C_2H_5MgBr + O_2 \searrow$$
$$\underset{\underset{C_6H_5}{|}}{}$$

$$\overset{C_6H_5\diagdown}{\underset{C_2H_5\diagup}{}}CHC(C_6H_5)COC_6H_5 \longrightarrow$$
$$\underset{\underset{OMgX}{|}}{}$$

$$C_6H_5COCOC_6H_5 + \overset{C_6H_5\diagdown}{\underset{C_2H_5\diagup}{}}CHMgCl \longrightarrow \overset{C_6H_5\diagdown}{\underset{C_2H_5\diagup}{}}$$

$$\overset{C_6H_5\diagdown}{\underset{C_2H_5\diagup}{}}CHC(C_6H_5)COC_6H_5$$
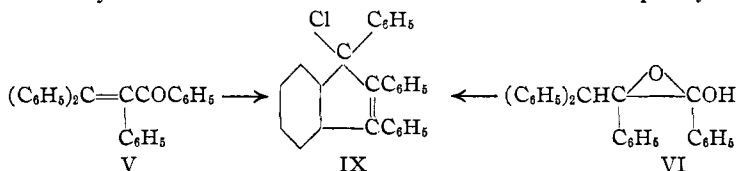$$\underset{\underset{OH}{|}}{}$$

Experimental Part

As was indicated in the introduction, the solutions of the magnesium derivative were made by two completely different reactions of which one required a slight excess of phenylmagnesium bromide, and the other an excess of ethylmagnesium bromide. The action of oxygen was examined in different solvents and at different temperatures, and the reaction was allowed to proceed for various intervals of time ranging from two to eighty hours. These comparative experiments need not be described in detail because, excepting that higher temperatures and prolonged action increased the quantity of oily by-products, changes in procedure had no effect on the result.
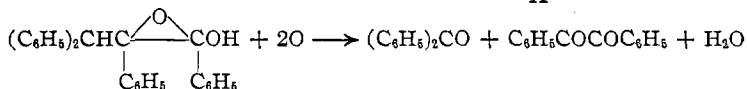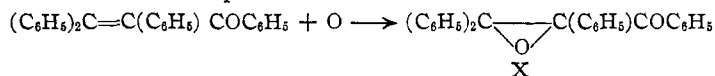
In all experiments the principal product was a substance which melts sharply at 162°. This substance is, doubtless, a definite compound containing the unsaturated ketone and the oxanol in equimolar quantities. The former melts at 154°, the latter at 159°; all mixtures prepared from these two compounds excepting those which contain less than 10% of

one of them melt higher than the components, the highest melting point attainable being 162°, which is reached when the components are mixed in equimolar quantities.
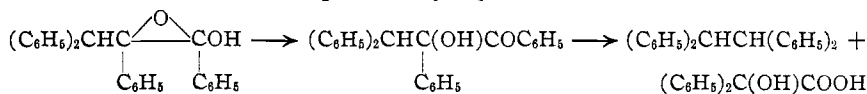
Inasmuch as this product cannot be separated by crystallization and contains as one component a new and entirely unexpected type of compound, it was necessary at the outset to subject it blindly to the action of a number of reagents in the hope of securing a clew to its character. In some reactions it behaves like a chemical individual because both components are converted into the same product as, for example, in the reaction with acetyl chloride which transforms both into chloro triphenyl indene

$$(C_6H_5)_2C{=}CCOC_6H_5 \longrightarrow \quad \longleftarrow (C_6H_5)_2CHC \overset{O}{\diagup}COH$$

$$\underset{V}{\overset{|}{C_6H_5}} \qquad\qquad \underset{IX}{} \qquad \underset{VI}{\overset{|}{C_6H_5}\ \overset{|}{C_6H_5}}$$
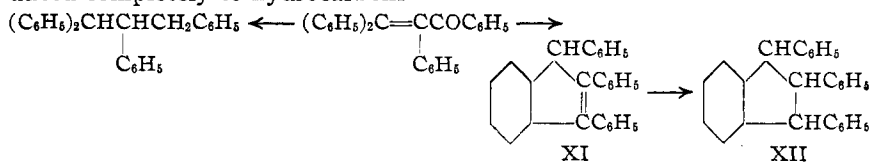
In other reactions both components participate but yield different products. Thus in glacial acetic acid chromic acid merely adds one atom of oxygen to the unsaturated ketone while under the same conditions it oxidizes the oxanol to benzophenone and benzil

$$(C_6H_5)_2C{=}C(C_6H_5)\ COC_6H_5 + O \longrightarrow (C_6H_5)_2C\underset{X}{\overset{\diagdown O \diagup}{\text{———}}}C(C_6H_5)COC_6H_5$$

$$(C_6H_5)_2CHC\overset{O}{\diagup}COH + 2O \longrightarrow (C_6H_5)_2CO + C_6H_5COCOC_6H_5 + H_2O$$
$$\underset{C_6H_5\ \ C_6H_5}{|\qquad |}$$

A few reagents, notably methyl alcoholic potassium hydroxide, transform the oxanol without affecting the ketone and leave a mixture from which the ketone can be separated by crystallization

$$(C_6H_5)_2CHC\overset{O}{\diagup}COH \longrightarrow (C_6H_5)_2CHC(OH)COC_6H_5 \longrightarrow (C_6H_5)_2CHCH(C_6H_5)_2 +$$
$$\underset{C_6H_5\ \ C_6H_5}{|\qquad |} \qquad\qquad \underset{C_6H_5}{|} \qquad\qquad (C_6H_5)_2C(OH)COOH$$

More frequently the unsaturated ketone is altered while the remarkably insensitive oxanol is left intact; thus hydrogen bromide in glacial acetic acid converts the former into a bromo indene under conditions under which it does not attack the latter. And, similarly, zinc in glacial acetic acid reduces only the ketone; even hydrogen iodide leaves the oxanol unchanged under conditions under which the unsaturated ketone is reduced completely to hydrocarbons

$$(C_6H_5)_2CHCHCH_2C_6H_5 \longleftarrow (C_6H_5)_2C{=}CCOC_6H_5 \longrightarrow$$
$$\underset{C_6H_5}{|} \qquad\qquad\qquad \underset{C_6H_5}{|}$$

XI XII

All these reactions in which the ketone alone is changed yield crystalline products from which the oxanol can be isolated by fractional crystallization but the separations are troublesome and wasteful. A more useful mixture of products was obtained with ethylmagnesium bromide, which combines with the unsaturated ketone and converts the oxanol into a magnesium derivative from which it is regenerated by acids; from the resulting mixture of products the oxanol can be separated without too great difficulty.

Most of the chemical properties of the ketone and the oxanol are inferred from the reactions of the crystalline mixture, but whenever there was any doubt with respect to the interpretation of the results, the reactions were subsequently repeated with each of the components. The procedure finally adopted for the preparation of the substance was as follows.

An ethereal solution of the magnesium derivative was prepared in the usual manner from 114 g. of benzaldesoxybenzoin and a solution of phenylmagnesium bromide containing 29 g. of magnesium. Into this solution which was chilled in a freezing mixture and stirred vigorously was passed a rapid stream of oxygen dried over phosphorus pentoxide. At the outset the gas was absorbed almost completely and a bright yellow color appeared immediately. The color gradually changed to green and finally to brown. After oxygen had been passed into the solution for three hours the viscous brown liquid was poured into iced hydrochloric acid. A crystalline solid separated in the ethereal layer. After allowing sufficient time for complete separation, the solid was collected on a filter, washed with ether and dried—yield 55 g. melting at 158–159°.

The ethereal filtrate, now almost black in color, was extracted with 10% aqueous sodium hydroxide until free from phenol; the extract by suitable manipulation yielded 14 g. of phenol, 0.7 g. of benzoic acid and a small quantity of tarry material. The ethereal layer on distillation with steam gave a distillate containing bromobenzene and diphenyl and left a residue which, after washing with ether to remove some colored resinous material, on drying melted at 154–158° and weighed 60 g. Recrystallization of the combined solids from acetone and ether gave 110 g. of pure product melting at 162°—a yield of 74.5%.

Analyses of many different samples gave values lying between 87.1 and 87.6% for carbon and 5.5 and 6.2% for hydrogen, the corresponding values for an equimolar compound of the ketone and the oxanol being 87.8 and 5.4%. The molecular weight was determined by both the freezing point and boiling point methods in a large variety of solvents and found not to vary more than 5% from a mean value of 363, instead of 369 calculated for an equimolar mixture. Assuming this molecular weight, one mole of substance liberated 0.9 mole of gas from methylmagnesium iodide.

The substance is sparingly soluble in all common solvents except boiling acetone and boiling chloroform. As would be expected, it is less soluble in all solvents than either of its components. Its solutions, like those of the unsaturated ketone, are yellow in color. •

Preparation with the Peroxide.—A solution of the magnesium derivative was made by adding 11.2 g. of α-bromo-α,β,β-triphenylpropiophenone to an ethereal solution of phenylmagnesium bromide, prepared from 0.66 g. of magnesium, and boiling the mixture for half an hour. This solution was cooled in a freezing mixture and treated with 5 g. of pure peroxide which was added in small quantities while the solution was stirred vigorously. The mixture was boiled for two and one-half hours. A pale yellow precipitate that formed at the outset increased as the reaction proceeded. After

having stood overnight the mixture was poured into iced acid, which precipitated 3.5 g. of solid.

The washed and dried solid was boiled with 75 cc. of dry ether for four hours for the purpose of extracting the saturated ketone. The residue—1.1 g.— after two recrystallizations from acetone, melted at 161°, and showed no depression in the melting point when mixed with the product obtained with oxygen. An analysis confirmed the identity of the two products.

Anal. Calcd.: C, 87.8; H, 5.4. Found: C, 87.4; H, 5.4.

Oxidation, Oxotetraphenylpropanone (X).—To a solution of 5 g. of the substance in 15 cc. of hot glacial acetic acid, 4.1 g. of chromic anhydride was added slowly. The solution was heated for two hours on a steam-bath, then poured on cracked ice. The resulting solution was extracted with ether. The ether extract, deep yellow in color, was freed from acetic acid, which also removed nearly a gram of benzoic acid, dried, concentrated, and diluted with petroleum ether. It deposited 0.77 g. of a product which after one recrystallization from alcohol melted at 157°.

Anal. Calcd. for $C_{27}H_{20}O_2$: C, 86.2; H, 5.3. Found: C, 86.4; H, 5.6.

Composition and melting point correspond to that of a substance which Japp and Klingemann[2] obtained by the action of chromic acid on the unsaturated ketone in cold acetic acid. We repeated their experiment and proved that our product was the same as theirs.

Addition of more petroleum ether to the filtrate from the oxido compound led to the separation of another crystalline compound which was identified as benzil and the mother liquors, on distillation with steam, yielded benzophenone.

Reaction with Acetyl Chloride.—1,2,3-Triphenyl-3-chloro Indene (IX).—Since the crystalline product contains an active hydrogen atom, an attempt was made to acetylate it with acetyl chloride. To this end 5 g. of the substance was boiled with acetyl chloride but all of it was recovered after thirty hours' boiling. A solution of 10 g. of the substance in excess of acetyl chloride was then sealed in a tube and heated in a steam-jacketed autoclave for fifteen hours. The orange colored solution was shaken with ice water and alcohol-free ether until it was free from acetyl chloride. The ethereal layer was washed with bicarbonate solution, dried, concentrated and mixed with low-boiling petroleum ether. It deposited a chloro compound which after recrystallization from benzene and petroleum ether melted at 115–116°.

Anal. Calcd. for $C_{27}H_{19}Cl$: C, 85.6; H, 5.1. Found: C, 85.7; H, 5.1.

For the purpose of identification the chloro compound was transformed into the methoxyl and ethoxyl compounds by dissolving it in solutions of potassium hydroxide in the corresponding alcohols. The products crystallized in large transparent prisms melting at 144 and 172°. In the literature the melting points of these substances are given as 153 and 172° but an examination of the original specimens[3] showed that the melting point of the methoxyl compound is incorrect and should be changed to 144°.

The yield of pure chloro indene—5.75 g. from 10 g. of substance—indicated that acetyl chloride had converted both components of the mixture into the indene derivative. This was confirmed, later, by treating each component separately with acetyl chloride in the same manner. Two grams of the unsaturated ketone gave 1.55 g. and 2 g. of the oxanol gave 1.6 g. of the same chloro compound.

Action of Alcoholic Potassium Hydroxide.—A suspension of 2.27 g. of the finely powdered solid in 150 cc. of a 20% solution of potassium hydroxide in methyl alcohol was boiled for twenty minutes and then filtered, to remove a small quantity of un-

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[2] Japp and Klingemann, *J. Chem. Soc.*, **57**, 669 (1890).

[3] Kohler, *Am. Chem. J.*, **40**, 222 (1908).

changed substance. The filtrate, cooled in a freezing mixture, deposited plates which after repeated recrystallization from ether melted at 153–154°, and were identified as the unsaturated ketone by analysis and mixed melting point.

The filtrate from the unsaturated ketone was diluted with water and then extracted with ether. The ethereal layer was concentrated to a small volume and cooled. It deposited the characteristic flat needles of the alpha hydroxy ketone (VII), completely identified by a comparison with a sample on hand. That the oxanol was the source of the hydroxy ketone was established by dissolving 0.5 g. of pure oxanol in 15 cc. of 20% methyl alcoholic potassium hydroxide, boiling the solution for twenty minutes, then diluting it with water and cooling. The yield of hydroxy ketone was 0.43 g.

Action of Halogen Acids.—A small quantity of the solid was recovered completely after it had been heated in a sealed tube with concentrated hydrochloric acid for two days at 100°. A similar experiment in which 2 g. of the solid was heated with 5 cc. of 48% aqueous hydrobromic acid at 100° for seven days resulted in a brown granular solid which decomposed briskly at 130°. This solid was, doubtless, a mixture of bromo triphenyl indene and oxanol. On recrystallization from benzene and petroleum ether it yielded 0.85 g. of pure oxanol melting at 159° and completely identified by analysis.

The oxanol was obtained more readily by dissolving 1 g. of the substance in 10 cc. of a 30% solution of hydrobromic acid in glacial acetic acid, and allowing the solution to stand overnight. The solvent was removed under reduced pressure, and the oily residue heated with alcohol. The bromo indene was thus converted into the ethoxy indene and the mixture of oxanol and ethoxy indene was separated by recrystallization from alcohol. It yielded 0.4 g. of oxanol.

The oxanol can be obtained from the crystalline product also by treatment with hydriodic acid. Thus 2 g. of the substance was heated with 6 cc. of 45% aqueous hydriodic acid for four hours. The mixture was then diluted with water and extracted with ether. The extract, washed with thiosulfate, dried, and concentrated, deposited 1.85 g. of crude product. By a somewhat troublesome crystallization first from acetone and petroleum ether, and finally from methyl alcohol, the crude product was separated into oxanol melting at 159° and a second pure substance which crystallized in prisms and melted at 135°.

Anal. Calcd. for $C_{27}H_{20}$: C, 94.1; H, 5.8. Found: C, 93.9; H, 6.0.

The substance has the composition and melting point of 1,2,3-triphenylindene. This hydrocarbon was not available for comparison but a sample was obtained by means of a reaction that was much easier to carry out than the one by which it was made originally,[4] namely, by the action of hydriodic acid on 1,2,3-triphenyl-3-ethoxyindene. A suspension of one gram of the ether was heated with 9 cc. of 45% aqueous hydriodic acid for an hour. The mixture was then diluted with water and extracted. The ethereal layer was washed with thiosulfate, dried, and evaporated. It left a colorless oil which after several extractions with petroleum ether readily solidified. The product was the same as that which had been obtained in the preceding experiment.

Action of Hydriodic Acid and Red Phosphorus, 1,2,3-Triphenylhydrindene (XII) and 1,1,2,3-Tetraphenylpropanone.—A suspension of 5 g. of the substance and 1.5 g. of red phosphorus in 12 cc. of constant boiling hydriodic acid was boiled for forty-six hours in an all-glass apparatus equipped with a Bunsen valve to exclude oxygen, then diluted with water and filtered. The filtrate manipulated as in the preceding experiment yielded two products, the one crystallizing in thick needles and melting at 154°, and the other crystallizing in large prisms and melting at 121°.

The higher melting compound has the composition, molecular weight, crystal form and melting point of 1,2,3-triphenylhydrindene, recently described by Schlenk

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[4] Kohler, *Am. Chem. J.,* **40,** 229 (1908).

and Bergmann.[5] Moreover, any open chained hydrocarbon having the composition represented by $C_{27}H_{22}$ would necessarily have an ethylenic linkage and would therefore be attacked by ozone, but our hydrocarbon was recovered almost completely after it had been treated with ozonized oxygen for four hours. The dihydro compound is doubtless formed by further reduction of 1,2,3-triphenylindene which was obtained in the preceding experiment but which was not found among the products of the more effective combination of hydrogen iodide and phosphorus.
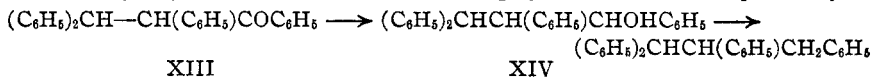
The lower melting compound is likewise a hydrocarbon.

Anal. Calcd. for $C_{27}H_{24}$: C, 93.1; H, 6.9. Found: C, 93.2; H, 6.7.

Since a hydrocarbon with this composition is necessarily open chained and saturated, it is presumably tetraphenylpropane, the final reduction product of the unsaturated hydrocarbon. We therefore undertook its preparation from the corresponding saturated ketone—tetraphenylpropanone (XIII) with sodium amalgam as follows. Eighty grams of 5% sodium amalgam was added to a solution of 6 g. of the ketone in 80 cc. of dry benzene and 100 cc. of absolute alcohol. After fifteen hours the colorless solution was decanted and evaporated in a current of air. The residue, freed from alkali and water in the usual manner, was crystallized from ether. It did not behave well in this solvent but it crystallized readily from acetone, from which it separated in clusters of needles containing a molecule of solvent, and melting at 160–161°.

Anal. Calcd. for $C_{30}H_{30}O_2$: C, 85.2; H, 7.2. Found: C, 85.1; H, 7.3.

The second step in the reduction was effected with hydriodic acid. One gram of tetraphenylpropanol was heated in a sealed tube with 0.5 g. of red phosphorus and 2 cc. of constant boiling hydriodic acid for six hours at 160°. After the usual manipulations, this procedure yielded 0.3 g. of a solid which crystallized in prisms, melted at 121°, and was in every way identical with the lower melting hydrocarbon obtained previously.

$(C_6H_5)_2CH$—$CH(C_6H_5)COC_6H_5 \longrightarrow (C_6H_5)_2CHCH(C_6H_5)CHOHC_6H_5 \longrightarrow$

$$(C_6H_5)_2CHCH(C_6H_5)CH_2C_6H_5$$

XIII   XIV

Reduction.—Tetraphenylpropenone, one of the components of the crystalline product, is very readily reduced to tetraphenylpropanone with zinc and acetic acid, and since solutions of the former are yellow, while those of the latter are colorless, it is easy to follow the course of the reduction by observing the color. When solutions of the crystalline product itself in glacial acetic acid are boiled with zinc dust, they likewise soon become colorless but the result is a mixture of products that is difficult to separate. Thus when 4 g. of zinc dust was added to a solution of 10 g. of the substance in 50 cc. of boiling glacial acetic acid, the solution became colorless in thirty minutes. By dilution with water, extraction with ether and the customary treatment of the ether extract, the solution yielded 9.6 g. of solid melting at 153–156°. From this solid it was comparatively easy to separate 3.4 g. of pure tetraphenylpropanone melting at 180° by fractional crystallization from acetone and ether, but further separation of the remaining material was exceedingly difficult. It was finally accomplished by resorting to carbon disulfide, in which the oxanol is readily soluble and from which it crystallizes well. The yield of pure oxanol was 4.4 g. and that of the saturated ketone 4.5 g.

Reaction with Phenylmagnesium Bromide.—To an ethereal solution of phenylmagnesium bromide prepared from 1.35 g. of magnesium was added 5 g. of the finely powdered solid. It dissolved immediately with evolution of heat and the solution became yellow in color. After boiling the mixture for half an hour a sample was withdrawn and decomposed with iced acid; it regenerated the solid melting at 162°. Ben-

[5] Schlenk and Bergmann, *Ann.*, **463**, 52 (1928).

zene was therefore added and ether distilled until the boiling point was raised to 52°. After the solution had been boiled at this temperature for twenty minutes, it was decomposed with iced acid and manipulated in the usual manner. The washed and dried ethereal layer, upon dilution with petroleum ether, deposited 2.4 g. of a solid substance which after recrystallization from alcohol melted at 184–186°. By analysis and by comparison with an authentic sample this substance was identified as the glycol represented by VIII.

The filtrate from the glycol contained mainly oily products but ultimately yielded a small quantity of a substance which melted at 123° and which was identified as the hydroxy ketone, VII. This experiment was subsequently repeated with pure oxanol and it was thus established that this substance is the source of both the hydroxy ketone and the glycol.

Reaction with Ethylmagnesium Bromide, Preparation of the Oxanol.—Fifteen grams of the substance was added, gradually and with vigorous stirring, to a solution which had been prepared from 4.1 g. of magnesium and which was kept in a freezing mixture throughout the reaction. The mixture was stirred at this temperature for forty-five minutes, then decomposed with iced acid. The·dried ethereal extract on concentration gradually deposited a solid which after a few recrystallizations yielded 7.2 g. of pure oxanol. In another experiment in which the stirring was continued for three hours the yield dropped to 4.2 g.

The filtrate from the oxanol yielded a second product which was subsequently obtained also by the action of ethylmagnesium bromide on the unsaturated ketone but which has not yet been identified.

II. ACTION OF OXYGEN ON THE MAGNESIUM DERIVATIVE FROM BENZAL-DESOXYBENZOIN AND ETHYLMAGNESIUM BROMIDE

To an ethereal solution of ethylmagnesium bromide, prepared from 26 g. of magnesium, 100 g. of benzaldesoxybenzoin was added slowly and with vigorous stirring while the solution was cooled in a freezing mixture. After stirring for forty-five minutes, a rapid stream of dry oxygen was passed into the solution, the stirring and cooling being maintained throughout the operation. After twenty minutes the gray color of the reagent changed to yellow and twenty-five minutes later the color was again gray and a precipitate began to form. The stream of oxygen was maintained for four hours.

On decomposition with iced acid the mixture of solid and solution deposited 32 g. of a new solid melting at 148–152°. The ethereal filtrate on concentration and gradual dilution deposited first 25 g. of a granular solid melting at 100–130°, and finally 3.5 g. of still another solid melting at 169°. The residual oils, distilled under diminished pressure, yielded 6.5 g. of the product melting at 169° and about one gram each of two hydrocarbons which melted the one at 123° and the other at 143°. These hydrocarbons were not investigated.

The product melting at 169° was readily identified as the saturated ketone, $(C_6H_5)(C_2H_5)CHCH(C_6H_5)COC_6H_5$, which is the sole product when the reaction is carried out in the absence of oxygen.[6] The granular solid melting at 100–130° was a mixture which by a laborious fractional crystallization from benzene and ether was separated into a chloro compound which has not yet been identified and the hydroxy ketone which was the principal product of the reaction.

α-**Hydroxy-α,β-diphenylbutyrophenone,** $C_2H_5CH(C_6H_5)CH(C_6H_5)OHCOC_6H_5$.— The principal product of the reaction, after recrystallization, melted at 154°. It is moderately soluble in most common organic solvents and crystallizes readily from nearly all of them in tufts of needles.

⁶ Kohler, *Am. Chem. J.*, **35**, 399 (1906).

Anal. Calcd. for $C_{23}H_{22}O_2$: M, 330; C, 83.6; H, 6.7. Found: M, 329; C, 83.5; H, 6.9.

The substance was made synthetically in the following manner.   α-Chloropropyl-benzene was prepared from ethylphenylcarbinol essentially as directed by Errera,[7] but by distillation under diminished pressure it was obtained as a colorless liquid boiling without decomposition at 104° (17–18 mm.). A solution of 12 g. of the chloro compound in absolute ether was added gradually to 1.5 g. of magnesium turnings suspended in a little ether which was increased to 100 cc. after the reaction had started. The mixture was boiled for twenty minutes, then cooled and filtered rapidly into a separating funnel from which it was added, drop by drop, to a solution of 10 g. of benzil in 20 cc. of absolute ether. A deep purple color was produced and it persisted throughout the reaction. After stirring for an hour, the mixture was poured into iced acid—whereupon the color changed to yellow. The washed and dried ethereal solution, on gradual dilution with petroleum ether, deposited first 4.2 g. of benzil and then 2.1 g. of the hydroxy ketone.

Reduction.—A suspension of two grams of the hydroxyl compound and 0.6 g. of red phosphorus in 5 cc. of constant boiling hydriodic acid was digested on a steam-bath for forty hours, then diluted with water and extracted with ether. The ethereal solution by suitable treatment yields along with a considerable quantity of oily products 0.6 g. of the corresponding saturated ketone—establishing both the character of the carbon chain and the location of the hydrocarbon residues.

$$\overset{\displaystyle OCOCH_3}{\underset{\displaystyle |}{}}$$

Action of Acetyl Chloride, $C_2H_5CH(C_6H_5)C(C_6H_5)COC_6H_5$.—A solution of 5 g. of the hydroxy ketone in 40 g. of acetyl chloride was heated for fifteen hours. The excess of acetyl chloride was removed under diminished pressure, leaving 5.25 g. of a crystalline residue, which after repeated crystallization yielded 3.1 g. of the pure acetate. It crystallized in large transparent prisms and melted at 160–161°.

Anal. Calcd. for $C_{25}H_{24}O_3$: C, 80.6; H, 6.5. Found: C, 80.5; H, 6.5.

Action of Hydrogen Chloride, $C_2H_5CH(C_6H_5)CCl(C_6H_5)COC_6H_5$.—A solution of 3 g. of the substance in 300 cc. of absolute alcohol was saturated with dry hydrogen chloride and set aside for forty hours. The solvent was removed under diminished pressure; it left an oily residue which on treatment with ether and methyl alcohol yielded 2.1 g. of the chloro compound. By recrystallization from methyl alcohol, it was obtained in elongated prisms melting at 93–95°.

Anal. Calcd. for $C_{23}H_{21}OCl$: C, 79.1; H, 6.0. Found: C, 79.0; H, 6.1.

The Methyl Ether, $C_2H_5CH(C_6H_5)C(OCH_3)C_6H_5COC_6H_5$.—Attempts to regenerate the hydroxy ketone from the chloro compound were unsuccessful because the hydroxyl compound is both reduced and cleaved by bases. It was comparatively easy, however, to replace the chlorine with methoxyl. Thus a solution of one gram of the chloro compound in dry methyl alcohol was shaken for twelve hours with 0.5 g. of dry silver oxide, then diluted and extracted with ether. The ether on evaporation deposited a halogen-free solid which after recrystallization from petroleum ether melted at 81–82°.

Anal. Calcd. for $C_{24}H_{24}O_2$: C, 83.7; H, 6.9; OCH_3, 9.0. Found: C, 83.6; H, 6.8; OCH_3, 8.7.

Summary

The structure of the magnesium derivatives which are formed by adding Grignard reagents to unsaturated ketones cannot be determined by converting them into peroxides.

[7] Errera, *Gazz. chim. ital.*, **6**, 222 (1886).

In one of the two cases investigated the action of free oxygen on the magnesium derivative resulted in the formation of equimolar quantities of an unsaturated ketone and a new type of oxanol. In the other case the oxidation product was an alpha hydroxy ketone.

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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]
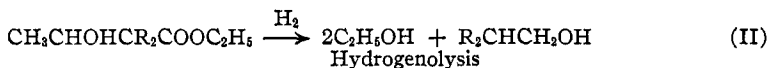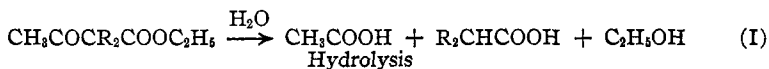
HYDROGENOLYSIS OF OXYGENATED ORGANIC COMPOUNDS

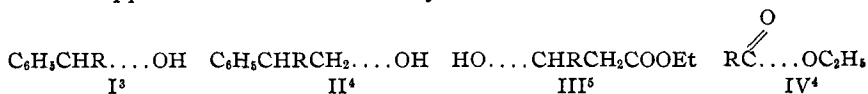BY RALPH CONNOR[1] AND HOMER ADKINS

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This paper deals with the cleavage of carbon to carbon or carbon to oxygen bonds accompanied by the addition of hydrogen. This type of reaction applied to hydrocarbons has been referred to by Ellis[2] as "hydrogenolysis," since it is clearly analogous to the reactions commonly termed hydrolysis, alcoholysis and ammonolysis which involve the *cleavage* of a bond *accompanied* by the *addition* of water, alcohol or ammonia.

$$CH_3COCR_2COOC_2H_5 \xrightarrow{H_2O} CH_3COOH + R_2CHCOOH + C_2H_5OH \qquad (I)$$
$$\text{Hydrolysis}$$

$$CH_3CHOHCR_2COOC_2H_5 \xrightarrow{H_2} 2C_2H_5OH + R_2CHCH_2OH \qquad (II)$$
$$\text{Hydrogenolysis}$$

The cleavage of oxygenated organic compounds with addition of hydrogen has been observed several times to occur as the result of the action of hydrogen in the presence of a catalyst. Recently the use of higher pressures of hydrogen and especially of the copper–chromium oxide catalyst has greatly extended the field of operation and rendered more important the application of hydrogenolysis as a tool in the transformation of organic compounds.

Previous work in this Laboratory has shown that the linkages indicated by dotted lines in the formulas I to VII are susceptible to hydrogenolysis over a copper–chromium oxide catalyst.

$$C_6H_5CHR....OH \qquad C_6H_5CHRCH_2....OH \qquad HO....CHRCH_2COOEt \qquad R\overset{O}{\overset{\|}{C}}....OC_2H_5$$
$$I^3 \qquad\qquad\qquad II^4 \qquad\qquad\qquad III^5 \qquad\qquad\qquad IV^4$$

[1] The authors are indebted to E. I. du Pont de Nemours and Company for the support of a fellowship enjoyed by Dr. Connor during the academic year 1931–1932.

[2] C. Ellis, "Hydrogenation of Organic Substances," 3d ed., D. Van Nostrand Company, New York, 1930, p. 564.

[3] Adkins and Connor, THIS JOURNAL, **53**, 1091 (1931).

[4] Adkins and Folkers, *ibid.*, **53**, 1095 (1931).

[5] Folkers and Adkins, *ibid.*, **54**, 1145 (1932).