The Cleavage of Cyclo-Beta-Diketones. I.
Tetramethyl-1,3-Cyclobutanedione. II.
Tetraphenyl-1,3-Cyclobutanedione.

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THE CLEAVAGE OF CYCLO BETA DIKETONES

I. TETRAMETHYL-1,3-CYCLOBUTANEDIONE
II. TETRAPHENYL-1,3-CYCLOBUTANEDIONE

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
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in

The Department of Chemistry

by

Garry Carlton Kitchens
B.S., University of Georgia, 1935
M.S., University of Georgia, 1937
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ABSTRACT
This investigation was undertaken to determine the course of the reaction between several cyclic β-diketones and organo-magnesium and lithium compounds. Open-chain β-diketones, which do not enolize, undergo cleavage of the molecule.

\[
\begin{align*}
R & \quad \quad \quad + \quad R'\text{MgX} \quad \rightarrow \quad R \quad R' \text{MgX} \\
R-G-C-G-R \quad + \quad R'-G-R \quad \rightarrow \quad R'-C-R \quad + \quad R \text{MgX}
\end{align*}
\]

Cyclic β-diketones have been reported to differ from open-chain diketones in their behavior towards these reagents. In every case, where both carbonyl groups are part of the cycle, cleavage of the ring has not been observed and usually normal addition products have been isolated.

In the present work tetramethyl-1,3-cyclobutanedione (I) was treated with (1) methyl, (2) ethyl, (3) phenyl and (4) mesityl magnesium bromide, (5) lithium phenyl and (6) lithium mesityl. Tetraphenyl-1,3-cyclobutanedione (XI) was treated with (1) phenyl magnesium bromide, (2) lithium phenyl and (3) lithium mesityl.

Treatment of I with methyl magnesium bromide yielded the β-hydroxy ketone, 5-hydroxy-2,4,4,5-tetramethyl-3-hexanone (IV) via the unstable monoaddition product, and the primary cleavage product III.
Treatment with ethyl magnesium bromide also caused cleavage of I yielding 5-hydroxy-2,4,4-trimethyl-3-heptanone (VI). The formation of V is a result of cleavage of the ring, followed by reduction of the carbonyl group and subsequent hydrolysis to yield VI.

All attempts to prevent the reduction of V were unsuccessful. The product of this reaction has been erroneously described by other investigators as the cyclic glycol.

Phenyl magnesium bromide effected the cleavage of I, but in
In this case, the \( \beta \)-hydroxy ketone VIII was unstable and decomposed to give benzophenone and di-isopropyl ketone. All attempts to isolate the primary cleavage product arising from VII, and the \( \beta \)-hydroxy ketone VIII were unsuccessful.

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\text{C}_6\text{H}_5\text{MgBr} \quad \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \quad \text{C} = \text{C} \quad \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \quad \text{C} = \text{C} \quad \text{C}_6\text{H}_5
\end{align*}
\]

The behavior of I toward lithium phenyl was found to be analogous to its behavior towards phenyl magnesium bromide. However, the benzophenone produced by the decomposition of VIII did not survive the hydrolysis process and was converted to triphenyl carbinol.

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\text{C}_6\text{H}_5\text{MgBr} \quad \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \quad \text{C} = \text{C} \quad \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \quad \text{C} = \text{C} \quad \text{C}_6\text{H}_5
\end{align*}
\]
In order to ascertain the nature of the primary cleavage product it was necessary to adopt a reagent which would produce a cleavage product containing a highly hindered carbonyl group, thus preventing further addition of the reagent and giving rise to formation of a β-diketone. Mesityl magnesium bromide fulfills these conditions, but failed to react with I. It then became necessary to resort to lithium mesityl, which reacted with I to produce dimethyl isobutyryl mesityl methane (X).

\[
\begin{align*}
&\begin{array}{c}
\text{(CH}_3\text{)}_2\text{C} - \text{C}=\text{O} \\
\text{O}=\text{C} - \text{C(CH}_3\text{)}_2
\end{array} \\
\xrightarrow{(\text{CH}_3)_2\text{C}_6\text{H}_5\text{Li}} \\
\begin{array}{c}
\text{(CH}_3\text{)}_2\text{C}_6\text{H}_5\text{Li} \\
\text{O}=\text{C} - \text{C(CH}_3\text{)}_2
\end{array}
\end{align*}
\]

Tetraphenyl-1,3-cyclobutanedione (XI) failed to react with phenyl magnesium bromide or with lithium mesityl. This failure was attributed to the hindrance to the carbonyl group offered by the phenyl groups.

Lithium phenyl caused the cleavage of XI yielding presumably the decomposition products of the β-hydroxy ketone, which decomposes into sym-tetraphenyl acetone, benzophenone and triphenyl carbinol.
It has been suggested that the formation of an intermediate involving the magnesium atom and the two carbonyl groups in a chelated ring may be a necessary condition for the cleavage of β-diketones. Since the steric configurations of the 1,3-cyclobutanediones are such that such chelated intermediates are impossible, it is definitely established that cleavage may occur where chelation is impossible.

The cleavage of the 1,3-cyclobutanediones as well as open-chain β-diketones can be explained on the basis of a reversible aldol condensation.

Maintenance of the cyclic member of the equilibrium would lead to addition without cleavage, while maintenance of the open
chain member of the equilibrium would lead to cleavage. Since
a four membered ring represents a strained configuration, it
is to be expected that it would be readily broken and that the
cyclic member would not be maintained in the above equilibrium.
This expectation is fulfilled by the fact that cleavage was
observed with each of the β-diketones studied.
REVIEW OF LITERATURE
Organo-magnesium compounds undergo a normal addition reaction with compounds containing one carbonyl group. If, however, another functional group is present in the beta position, the consequences of addition are sometimes peculiar, and in some cases lead to cleavage of the molecule. These functional groups may occur either in an open chain or as part of a cycle. Such substances contain the following linkages in the molecule:

\[ -\overset{\_}{C}-\overset{\_}{C}-\overset{\_}{C}- \]

Beta-dicarbonyl compounds

\[ -\overset{\_}{C}-\overset{\_}{C}-\overset{\_}{O}H \]

Beta-hydroxy carbonyl compounds

\[ -\overset{\_}{C}\overset{\_}{O}-\overset{\_}{C} \]

Alpha-oxido carbonyl compounds

The behavior of these general types of compounds toward organo-magnesium and lithium reagents is reviewed.
The reaction between open chain beta-diketones and organic metallic compounds has been studied by a number of workers. Zelinsky treated acetylacetone with methyl magnesium bromide and observed a vigorous reaction, but obtained only a small quantity of product. His only information on the product was that it boiled at 101-102° at 15 mm., and that its composition corresponded approximately to C₇H₁₆O₂. Zerewitinoff reported later that acetylacetone liberates one mole of methane from methyl magnesium iodide, but made no attempt to isolate products.

Smedley added dimethyl dibenzoyl methane to methyl magnesium iodide, and concluded that the reagent added to both carbonyl groups, giving on hydrolysis the expected ditertiary alcohol, C₆H₅(CH₃)COHC(CH₃)₆C(OH)(CH₃)C₆H₅. However, it has been demonstrated by Kohler and Erickson that her results were in error, and that she was analyzing a mixture of cleavage products whose composition corresponded to the ditertiary alcohol.

Vorlander, Osterburg and Mayn added dibenzoyl methane to phenyl magnesium bromide, and demonstrated conclusively that the resulting compound hydrolyzed to a β-hydroxy-β,β-diphenyl propiophenone. Vorlander and his collaborators observed that the β-hydroxy ketone apparently did not react further with phenyl magnesium bromide. Kohler and Erickson found that it reacted rapidly, yielding the corresponding glycol and triphenyl carbinol. The carbinol resulted from a cleavage of the molecule:
The glycol was the result of addition without cleavage:

\[
\text{(C}_6\text{H}_5)_2\text{C} \bigg(-\begin{array}{c}
\text{CH}_2 \\
\text{C} \bigg) - \text{C}_6\text{H}_5 \xrightarrow{\text{C}_6\text{H}_5\text{MgX}} \text{(C}_6\text{H}_5)_2\text{C} \bigg(-\begin{array}{c}
\text{CH}_2 \\
\text{C} \bigg) - \text{C}_6\text{H}_5
\end{array}\bigg)
\]

A number of different beta-diketones were examined by Kohler and Erickson\(^2\), who found that those diketones which have mono- and di-substituted methylene groups form magnesium addition compounds, which were unstable and underwent cleavage, giving a ketone, which added a second molecule of the Grignard reagent:

\[
\text{C}_6\text{H}_5\text{C}=\text{CHC}_6\text{H}_5 + \text{(C}_6\text{H}_5)_2\text{CO} \xrightarrow{\text{C}_6\text{H}_5\text{MgX}} \text{(C}_6\text{H}_5)_3\text{CO}_2\text{MgX}
\]

On the other hand, those beta-diketones which are largely or entirely enolic, underwent normal addition with organic magnesium compounds:

\[
\text{C}_6\text{H}_5\text{COCH}_3\text{COC}_6\text{H}_5 \xrightarrow{\text{C}_6\text{H}_5\text{MgX}} \text{C}_6\text{H}_5\text{COCH}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)_2
\]

\[
\text{C}_6\text{H}_5\text{C}=\text{CHC}_6\text{H}_5 \xrightarrow{\text{C}_6\text{H}_5\text{MgX}} \text{C}_6\text{H}_5\text{C}=\text{CHCOC}_6\text{H}_5 \xrightarrow{\text{C}_6\text{H}_5\text{MgX}} \text{C}_6\text{H}_5\text{COCH}_3\text{COC}_6\text{H}_5
\]

\[
\text{C}_6\text{H}_5\text{C}=\text{CH-} \bigg(-\begin{array}{c}
\text{C}_6\text{H}_5 \\
\text{C} \bigg)
\end{array}\bigg) \xrightarrow{\text{H}^+} \text{C}_6\text{H}_5\text{COCH}_3\text{COCH}(\text{C}_6\text{H}_5)_2
\]
In these cases, no cleavage of the molecule occurred. However, it was necessary to exercise great care in acidifying the magnesium derivatives because they can pass into intermediate monomagnesium compounds that undergo cleavage:

\[
\text{C}_6\text{H}_5\text{C}==\text{CH}-(\text{C}_6\text{H}_5)_2\rightarrow \text{C}_6\text{H}_5\text{COCH}_3(\text{C}_6\text{H}_5)_2\rightarrow \text{C}_6\text{H}_5\text{C}==\text{CH}_2 + (\text{C}_6\text{H}_5)_2\text{CO}
\]

The following list of compounds and the final products obtained from them illustrate the conclusions reached by Kohler and Erickson:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Final Products</th>
</tr>
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<tbody>
<tr>
<td>I C₆H₅COCH₃COC₆H₅</td>
<td>(C₆H₅)₂C(OH)CH₂COC₆H₅</td>
</tr>
<tr>
<td>II CH₃COCH₃COCH₃ (a)</td>
<td>(CH₃)₂C(OH)CH₂COC₆H₅</td>
</tr>
<tr>
<td>III C₆H₅COCH(C₆H₅)COC₆H₅</td>
<td>C₆H₅COCH₂C₆H₅ + (C₆H₅)₂COH</td>
</tr>
<tr>
<td>IV C₆H₅COCH(CH₃)COC₆H₅</td>
<td>C₆H₅COCH₂CH₃ + (C₆H₅)₂COH</td>
</tr>
<tr>
<td>V CH₃COC(CH₃)₂COCH₃</td>
<td>CH₃COCH(CH₃)₂ + (C₆H₅)₂(CH₃)COH</td>
</tr>
<tr>
<td>VI CH₃COC(CH₃)₂COCH₃ (b)</td>
<td>CH₃COCH(CH₃)₂ + CH₃COC₆H₅(CH₃)₂</td>
</tr>
<tr>
<td>VII C₆H₅COCHBrCOC₆H₅</td>
<td>C₆H₅COCH₂COC₆H₅</td>
</tr>
<tr>
<td>VIII C₆H₅COCHBr₂COC₆H₅</td>
<td>(C₆H₅)₂COCHBrCOC₆H₅</td>
</tr>
<tr>
<td>IX C₆H₅COCHOCOC₆H₅</td>
<td>C₆H₅COCHOHC₆H₅ + (C₆H₅)₂COH</td>
</tr>
</tbody>
</table>

(a) With methyl magnesium iodide.
(b) With mesityl magnesium iodide.

Erickson and Stansbury found that the behavior of β-diketones toward lithium phenyl is exactly analogous to their behavior toward Grignard reagents. The substituted β-diketones, which were incapable of enolization, cleaved upon reaction with
The unsubstituted $\beta$-diketones reacted with two moles of lithium phenyl to give as a hydrolysis product, a $\beta$-hydroxy ketone.

Cyclic Beta-Diketones

The simplest cyclic $\beta$-diketone, cyclopropanedione, has not been reported in the literature.

Chick and Wilsmore assigned the structure of cyclobutane-1,3-dione to the dimer of ketene. One of the reactions which they performed was the reaction of the compound with methyl magnesium iodide. When the reaction was carried out at low temperature and the product hydrolyzed with water, only a resinous material was recovered from the reaction. Upon performing the reaction at low temperature and hydrolyzing with cold, dilute sulfuric acid at $-36^\circ$ to $-40^\circ$, two fractions of material were separated by distillation, neither of which was identified. They stated that apparently some diacetone alcohol was produced and proposed the following course of reaction:
The following formulas have been proposed for diketene:

Formula I, 1,3-cyclobutanedione, proposed by Chick and Wilsomore\textsuperscript{13}, is inadequate. According to Hurd and Williams\textsuperscript{88}, it is inconsistent with the expected dipole moment, molecular refraction, and heat of formation. Formula II, proposed by Hurd and Williams\textsuperscript{88}, and also by Chick and Wilsomore\textsuperscript{13}, fails to account for the exclusive formation of γ-bromoacetocacetyl bromide upon the addition of bromine to the compound, and for the formation of β-butyrolactone by hydrogenation. They proposed Formula III, β-crotonolactone, as a resonance isomer with II. On the basis of Formula III, proper products from the addition of bromine and hydrogen can be accounted for. Formula II would give the observed ozonization product, pyruvic aldehyde. Formula IV, proposed by Wilson\textsuperscript{11}, vinylacetolactone, successfully accounts for all physical and chemical properties except the formation of...
pyruvic aldehyde upon ozonolysis.

Wedekind and Miller have allowed tetramethyl-1,3-cyclobutanedione to react with ethyl magnesium bromide and found that it reacted with two moles of the reagent and yielded the corresponding cyclic glycol, 1,3-diethyl-2,2,4,4-tetramethyl-1,2-cyclobutanediol.

\[
\text{HO-} \quad \begin{array}{c}
\text{(CH}_3\text{)}_2\text{C} \quad \text{O} \\
\text{O} \quad \text{=O} \\
\text{O} \quad \text{=O} \\
\text{(CH}_3\text{)}_2\text{C}
\end{array} 
+ \quad \text{C}_8\text{H}_5\text{MgBr} \quad \overset{\text{H}^+}{\rightarrow} 
\begin{array}{c}
\text{(CH}_3\text{)}_2\text{C} \quad \text{O} \\
\text{O} \quad \text{(CH}_3\text{)}_2\text{C} \\
\text{OH} \quad \text{C}_8\text{H}_5
\end{array}
\]

This cyclic glycol was transformed by hydriodic acid into the diiodide, which was reduced, by means of zinc and acetic acid, to the corresponding cyclic hydrocarbon, 1,3-diethyl-2,2,4,4-tetramethylycyclobutane.

\[
\begin{array}{c}
\text{(CH}_3\text{)}_2\text{C} \quad \text{OH} \quad \text{C}_8\text{H}_5 \\
\text{C}_8\text{H}_5 \quad \text{O} \quad \text{(CH}_3\text{)}_2\text{C} \\
\text{OH} \quad \text{C}_8\text{H}_5 \\
\text{(CH}_3\text{)}_2\text{C}
\end{array} 
\xrightarrow{\text{HI}} 
\begin{array}{c}
\text{(CH}_3\text{)}_2\text{C} \quad \text{I} \quad \text{C}_8\text{H}_5 \\
\text{C}_8\text{H}_5 \quad \text{C} \quad \text{(CH}_3\text{)}_2\text{C} \\
\text{I} \quad \text{(CH}_3\text{)}_2\text{C}
\end{array}
\]

\[
\text{Zn} + \text{HAc} \rightarrow 
\begin{array}{c}
\text{(CH}_3\text{)}_3\text{C} \quad \text{CHC}_8\text{H}_5 \\
\text{C}_8\text{H}_5 \quad \text{C} \quad \text{(CH}_3\text{)}_2\text{C}
\end{array}
\]

Hurd, Jones and Blunk treated the dimer of ethyl ethyl ketene carboxylate with phenyl and ethyl magnesium bromides. In both cases, they observed cleavage of the cyclic molecule,
producing a $\beta$-keto ester. The authors compared the cleavage of this cyclobutanediene with the results of Kohler and Erickson\textsuperscript{33} on the cleavage of open chain $\beta$-diketones.

\[ \text{RMgX} \quad \text{RC} = \text{C} - \text{R} \quad \xrightarrow{\text{H}^+} \quad \text{RC} = \text{C} \quad \text{H} = \text{C} \]

The reaction of ethyl magnesium bromide with two $\beta$-diketones was described by Grateau\textsuperscript{33}. The compounds studied had five-membered rings containing one carbonyl, and a side chain containing the other. Ethyl magnesium bromide added to either carbonyl group in 2-p-toluoyl cyclopentanone, giving as final products unsaturated ketones, which were the dehydration products of the corresponding hydroxy ketones. In addition, cleavage of the molecule was observed in one case, which was explained as the results of hydrolysis of the unsaturated compound:
Grateau concluded that Grignard reagents added to only one carbonyl in 2-p-xyloyl cyclopentanone, since the one next to the xylyl group was highly hindered.

Bauer studied the action of phenyl and ethyl magnesium bromides on α-benzoxy cyclohexanone. He found that Grignard reagents formed addition products with β-diketone, from which the starting materials were regenerated upon hydrolysis.

Both hexamethyl phloroglucinol and pentamethyl phloroglucinol methyl ether were treated by Herzig and Erthalm with methyl magnesium iodide. They found that the hexamethyl compound gave a compound, C_{18}H_{36}O_3, which was the addition compound resulting from the addition of three moles of Grignard reagent. Pentamethyl phloroglucinol methyl ether gave a compound, C_{15}H_{24}O_3, which they explained as probably being the heptamethyl phloroglucinol, as it contained no methoxy group.

Weiss and Luft, in studying the derivatives of 1,3-di-keto-2,2-dimethyl-hydrindene, treated the compound with one mole of
phenyl magnesium bromide and obtained two products. One product, obtained in 20% yield, 3-hydroxy-3-phenyl-2,2-dimethyl-1-hydrindone, m.p. 139-141°, was transformed into the methyl ether that melted at 160-162°, and the other, a crude product, was probably di-hydroxy-diphenyl dimethyl hydrindene.

They treated 3-methoxy-3-phenyl-2,2-dimethyl-1-hydrindone with phenyl magnesium bromide and isolated the addition product, 1-hydroxy-3-methoxy-1,3-diphenyl-2,2-dimethyl hydrindene.

Geissman and Tulagin repeated the work of Weiss and Luft on 1,3-diketo-2,2-dimethyl-hydrindene. They treated the compound with one mole of phenyl magnesium bromide and isolated two products in approximately equal amounts, a monoaddition product, 1-phenyl-2,2-dimethyl-3-keto-hydrindene-1, which was previously isolated by Weiss and Luft, and a diaddition product, 1,3-diphenyl-2,2-dimethyl-hydrindene-1,3-diol. In the same manner they
obtained the monoaddition product in good yields as the main product of the reaction when phenyl magnesium bromide was added to a large excess of the diketone, the diaddition product in good yield when the diketone was added to an excess of the reagent. Under the conditions of their experiment, no cleavage of the cyclic β-diketone was observed.

Geissman and Morris\(^{20}\) in continuing their studies on cyclic β-diketones, treated 8,8-dimethylperinaphthindione-7,9 with phenyl magnesium bromide. By suitable control of experimental conditions, they obtained any one of three substances: the normal monoaddition compound, 7-phenyl-7-hydroxy-8,8-dimethylperinaphthindione-9, the normal diaddition compound, 7,9-di-phenyl-7,9-dihydroxy-8,8-dimethyl-perinaphthindane, and a compound which was formed by normal addition to one of the carbonyl groups, followed by 1,4-addition to the conjugate system. In this case, no cleavage was observed.
Geissman and Tulagan treated 2-methyl-2-benzoyl hydrindone with phenyl magnesium bromide. They obtained the normal diaddition product, 1-phenyl-1-hydroxy-2-methyl-2-diphenylhydroxy-methyl indane, and the cleavage products, 2-methyl hydrindone and triphenyl carbinol. About one fifth of the total amount of reaction followed the route leading to cleavage, the remainder leading to the glycol.

Geissman and his co-worker have postulated two possible mechanisms for the cleavage of $\beta$-diketones. (1) The monoaddition compound of the diketone assumes a form analogous to the chelated enolate of an enolizable $\beta$-diketone, and the cleavage reaction involves a bond shift which closely resembles the interconversion of the resonance forms of such enolates.
Intereconversion of the resonance forms of enolates.

(1) The monoaddition product of the diketone assumes an ionic form in which MgX⁺ is the positive ion and the organic residue is the negative ion. This negative ion decomposes in such a way as to give the carbonyl compound and a halomagnesium enolate. This mechanism is a strict analogy with the reversal of the aldol condensation, as suggested by Kohler.

Geissman and his co-workers have interpreted their work on the cyclic β-diketones in the light of these two possible mechanisms. In discussing Mechanism I as a possible explanation of the course of the reaction, they state that no cleavage occurs in those cases, in which a chelated intermediate is impossible. The cyclic β-diketones, 1,3-diketo-2,2-dimethylhydrindene and 8,8-dimethyl perinaphthindandione-7,9 do not permit the formation of such chelated complexes from the monoaddition products since both carbonyl groups are part of the ring structure and must therefore remain relatively apart. They state that the fact that no cleavage was observed in these compounds was accounted for on this basis and was regarded as
strong support for the postulation of such intermediates. However, in the case of 2-methyl-2-benzoyl hydridone, the first addition of the Grignard reagent can take place either at the carbonyl group involved in the ring or on the extracyclic carbonyl, and in neither case is there any hindrance to the formation of chelated intermediates.

It was anticipated that of the two carbonyl groups, the carbonyl group in the cycle would be more reactive, thereby favoring the production of I, which should yield cleavage products if a chelated intermediate is a sufficient condition for cleavage. The actual products obtained from the reaction were a glycol and the cleavage product shown:
The glycel could have arisen as the second addition product from either of the two monoaddition intermediates postulated. The cleavage products could have arisen only as the result of cleavage of II. According to the authors, this cleavage does not prove that the formation of a chelated intermediate is a necessary condition for cleavage. However, the lack of cleavage through the intermediate I, does prove that the formation, or possibility of formation, of such a chelated intermediate, is not a sufficient condition for cleavage. In all cases, which they examined, in which such an intermediate can not form, no cleavage was observed.

In discussing Mechanism II, the authors state that there is no evidence that halomagnesium alcooilates, as those postulated as intermediates in the cleavage reaction, are ionic in nature as indicated. However, they state that the properties of halomagnesium enolates are in harmony with their formulation as the resonance forms shown as final products of the reaction. They suggest that in those cases in which cleavage does not occur, the spacial distribution of the groups might favor the maintenance of the cyclic member of the equilibrium.

The spacial distribution of the groups in the cyclic diketone studied is such that this might be the case. However, the authors have drawn no conclusions from their results indicative
of the tenability of this mechanism.

Beta-Ketonic Esters.

Grignard treated acetoacetic ester with methyl magnesium iodide, and found that the starting material was recovered in every case, although several different procedures were tried. He postulated that the enolic form of the ester reacted with one mole of the reagent, and that the original compound was regenerated upon hydrolysis.

Ethyl ethylacetoacetate reacted with methyl magnesium bromide to give a β-hydroxy ester, the product of addition of one mole of reagent to the carbonyl group. Some of the starting material was also recovered.

Methyl diethyl acetoacetate yielded a β-hydroxy ester when treated with one mole of reagent. When the reaction was carried out in an autoclave at 100° for eight hours, a hydrocarbon, \((\text{C}_2\text{H}_5)_2\text{C}≡\text{C}('\text{C}_2\text{H}_5)\_2\) was obtained. It was postulated that this was a dehydration product of the tertiary alcohol, \((\text{C}_2\text{H}_5)_2\text{C}('\text{O})\text{CH}('\text{C}_2\text{H}_5)\_2\). This alcohol was not isolated.

Ethyl ethylidene acetoacetate, when treated in a similar fashion, gave only polymerization products, which were not identified.

Grignard found that several procedures yielded only the starting material when ethyl acetyl succinate was treated with methyl magnesium iodide.

Grignard's results are summarized below:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_3\text{COCH}_2\text{CO}_2\text{C}_2\text{H}_5)</td>
<td>Starting Material</td>
</tr>
<tr>
<td>Ethyl acetoacetate</td>
<td></td>
</tr>
</tbody>
</table>
Slavjanoff obtained the following products from the reaction between ethyl dimethylacetoacetate and methyl magnesium iodide:

1. Isobutyric acid, \((\text{CH}_3)_2\text{CHCOOH}\)
2. Tetramethyl ethylenelactic acid, \((\text{CH}_3)_2\text{C(OH)}\text{C(CH}_3)_2\text{COOH}\)
3. Hexamethyl trimethylene glycol, \((\text{CH}_3)_2\text{C(OH)}\text{C(CH}_3)_2\text{C(CH}_3)_2\text{OH}\)

The last two compounds were products of the addition to the carbonyl and carboxyl groups. No mechanism for the production of isobutyric acid is given.

Barbier and Locquim found that isobutyl and phenyl magnesium bromides add to the carbonyl group in methyl acetylpyrotrtartrate, leaving the ester groups unattacked. In both cases, the monohydroxy compounds were formed:

\[
\text{CH}_3\text{COCH}-(\text{C}_2\text{H}_5)\text{CO}_2\text{C}_2\text{H}_5 \xrightarrow{\text{C}_6\text{H}_5\text{MgX}} \text{CH}_3\text{CO}-(\text{C}_2\text{H}_5)\text{CO}_2\text{C}_2\text{H}_5
\]
These authors found that methyl ketones could be prepared from the reaction product of acetoacetic ester and its derivatives with the Grignard reagent by hydrolysis with potassium hydroxide in methyl alcohol.

Belt* found that \( \beta \)-diketonic esters which do not enolize can be cleaved with Grignard reagents. Those which enolize react in the enol form, regenerating the starting material, and a small quantity of \( \beta \)-hydroxy ketone. His results are summarized below:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_6\text{H}_5\text{COC}(\text{CH}_3)_2\text{CO}_2\text{C}_2\text{H}_5 )</td>
<td>Starting material ( (\text{C}_6\text{H}_5)_2\text{G(OH)CH}_2\text{COC}_6\text{H}_5 )</td>
</tr>
<tr>
<td>Ethyl benzyl acetate</td>
<td></td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5\text{COC}(\text{CH}_3)_2\text{CO}_2\text{C}_2\text{H}_5 )</td>
<td>( (\text{C}_6\text{H}_5)_2\text{GCH} )</td>
</tr>
<tr>
<td>Ethyl alpha-benzoyl isobutyrate</td>
<td>( (\text{CH}_3)_2\text{CHGOC}_6\text{H}_5 )</td>
</tr>
<tr>
<td>( \text{CH}_3\text{COC}(\text{CH}_3)_2\text{CO}_2\text{C}_2\text{H}_5 )</td>
<td>( (\text{C}_6\text{H}_5)_2\text{C(OH)(CH}_3 )</td>
</tr>
<tr>
<td>Dimethyl acetoacetic ester</td>
<td>( (\text{CH}_3)_2\text{CHGOC}_6\text{H}_5 )</td>
</tr>
<tr>
<td>( \text{CH}_3\text{COCH}(\text{CH}_3)_2\text{CO}_2\text{C}_2\text{H}_5 )</td>
<td>( (\text{C}_6\text{H}_5)_2\text{C(OH)(CH}_3 )</td>
</tr>
<tr>
<td>Methyl acetoacetic ester</td>
<td>( \text{CH}_2\text{CH}_2\text{COC}_6\text{H}_5 )</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5\text{COCH}(\text{CH}_3)_2\text{CO}_2\text{C}_2\text{H}_5 )</td>
<td>( (\text{C}_6\text{H}_5)_2\text{GCH} )</td>
</tr>
<tr>
<td>Ethyl alpha benzoyl propionate</td>
<td>( \text{CH}_3\text{CH}_2\text{COC}_6\text{H}_5 )</td>
</tr>
</tbody>
</table>

**Malonic Esters**

Valeur* treated ethyl malonate with ethyl magnesium iodide, and obtained the unsaturated alcohol, \( \text{C}_{11}\text{H}_{22}\text{O} \). He concluded that the unsaturated alcohol was produced by the loss of water from the bitertiary alcohol, \( (\text{C}_6\text{H}_5)_2\text{C(OH)CH}_2\text{C(OH)(C}_6\text{H}_5)_2 \).
Methyl malonate was treated with phenyl magnesium bromide by Vorlander and Siebert\(^4\). Their product melted at \(113^\circ\) and was not converted to tetraphenyl allene with acetic anhydride. No further attempt at identification was made.

Slavjanoff\(^5\) treated dimethyl malonic ester with methyl magnesium iodide. He obtained, in general, the same products as those from dimethyl acetoacetic ester, which has already been discussed.

Kalishev\(^6\) studied the reactions of substituted malonic esters with the Grignard reagent. In the reaction between RHgX and \(R'R''C(C\text{C}_3\text{O}_2\text{H}_2)_2\), glycols were obtained only when \(R, R'\) and \(R''\) are all methyl groups. In all other cases, hydroxy esters were obtained. He studied the reaction between methyl, ethyl, propyl, and phenyl magnesium bromides and dimethyl malonate, di-ethyl malonate, and dipropyl malonate.

Leroide\(^7\) studied the reaction of \(\alpha,\alpha\)-disubstituted malonic esters with Grignard reagents. From dimethyl malonic ester, chiefly cleavage products and a small quantity of the glycol were formed:

\[
(C_2H_5)C(C\text{C}_3\text{O}_2\text{H}_2)_2 \xrightarrow{\text{C}_2\text{H}_5\text{MgBr}} \xrightarrow{\text{H}^+} (\text{CH}_3)\text{C}C\text{C}_3\text{O}_2\text{C}_8\text{H}_8 + \text{C}_3\text{H}_7\text{CCO}_2\text{C}_8\text{H}_8
\]

Ethyl di-\(p\)-tolyl malonate was treated with phenyl magnesium bromide by Mirau\(^8\). Triphenyl carbinol and ethyl benzoate were obtained. The reaction was represented as follows:

\[
(C_6\text{H}_5\text{C}_8\text{H}_8)C(C\text{C}_3\text{O}_2\text{H}_2)_2 \xrightarrow{\text{C}_6\text{H}_5\text{MgBr}} \xrightarrow{\text{H}^+} (C_6\text{H}_5)\text{C}C\text{C}_3\text{O}_2\text{C}_8\text{H}_8
\]

\[
C_6\text{H}_5\text{CO}_2\text{C}_8\text{H}_8 \xrightarrow{\text{C}_6\text{H}_5\text{MgBr}} \xrightarrow{\text{H}^+} (C_6\text{H}_5)_3\text{COH}
\]
**BETA-HYDROXY CARBONYL COMPOUNDS**

**Beta-Hydroxy Aldehydes and Ketones**

Several workers have treated β-hydroxy carbonyl compounds with organic magnesium compounds without observing cleavage.

Franke and Kohn²⁸ ¹⁶ ¹⁷ treated several β-hydroxy aldehydes and ketones with Grignard reagents, obtaining normal addition products in all cases. Their results are summarized in the following table:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reagent</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃)₂C(OH)CH₂COCH₃</td>
<td>CH₃MgI</td>
<td>(CH₃)₂C-OH-CH₂-O(CH₃)₂</td>
</tr>
<tr>
<td>Diacetone alcohol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃CH(OH)CH₂CHO</td>
<td>CH₃MgI</td>
<td>CH₃CH(OH)CH₂CH(OH)CH₃</td>
</tr>
<tr>
<td>Aldol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOCH₂C(CH₃)₂CHO</td>
<td>CH₃MgI</td>
<td>HOCH₂C(CH₃)₂CH(OH)CH₃</td>
</tr>
<tr>
<td>Formisobutyraldol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOCH₂C(CH₃)₂CHO</td>
<td>C₆H₅MgBr</td>
<td>HOCH₂C(CH₃)₂CH(C₆H₅)</td>
</tr>
<tr>
<td>Formisobutyraldol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOCH₂C(CH₃)₂CHO</td>
<td>C₆H₅MgX</td>
<td>HOCH₂C(CH₃)₂CHC₆H₅</td>
</tr>
<tr>
<td>Formisobutyraldol</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Baeyer² obtained normal addition products in several cases when he treated β-hydroxy carbonyl compounds with Grignard reagents. In no case was cleavage observed:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reagent</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-HOC₆H₄CO₂CH₃</td>
<td>C₆H₅MgBr</td>
<td>(C₆H₅)₃C(o-HOC₆H₄)COH</td>
</tr>
<tr>
<td>Methyl Salicylate</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Ademann obtained the corresponding 1,3-glycols when 3-methyl-butan-4-ol-2-one was treated with methyl, ethyl, and α-propyl magnesium halides. High-boiling polymerization products were also obtained.

Lemaire repeated the work of Franke and Kohn on diacetone alcohol. He also obtained the corresponding glycol.

Maitland and Tucker treated diacetone alcohol with 9-fluorenyl magnesium bromide, and isolated four products of the reaction. Of these products, one was the glycol \((C_6H_5)_2CHC(OH)-CH_3CH_2C(OH)(CH_3)_3\), and two others were isomeric hydrocarbons, \(C_{19}H_{18}\), obtained as dehydration products of the glycol. The fourth product was 9-fluorenyl dimethyl carbinol. According to the authors, this product probably came from acetone which may have been present in the original starting material as an impurity, or which may have been produced by shifting the following
equilibrium to the right:

$$\text{(CH}_3\text{)}_2\text{C(OH)CH}_2\text{COCH}_2\rightleftharpoons 2\text{(CH}_3\text{)}_2\text{CO}$$

Sabetay and Bleger obtained glycols by treating $\beta$-hydroxy-$\alpha$-dimethyl propionaldehyde with the Grignard reagent. Where $R$ may be $1$-$C_7H_{13}$-, $1$-$C_6H_{11}$-, or $1$-$C_6H_{12}$-, their reaction may be represented:

$$\text{HOCH}_2\text{C(CH}_3\text{)_2CHO} + \text{RMgX} \rightleftharpoons \text{HOCH}_2\text{C(CH}_3\text{)_2CH(OH)R}$$

Kohler and Erickson found that the hydroxy ketone $\text{(C}_6\text{H}_5\text{)}_2\text{C(OH)CH}_2\text{COC}_6\text{H}_5$ may be cleaved upon the addition of the Grignard reagent:

$$\text{(C}_6\text{H}_5\text{)}_2\text{C(OH)CH}_2\text{COC}_6\text{H}_5 \xrightarrow{\text{C}_6\text{H}_5\text{MgX}} \text{(C}_6\text{H}_5\text{)}_2\text{CCH}_2\text{COC}_6\text{H}_5 \xrightarrow{\text{OMgX}}$$

$$\text{CH}_2\text{C(O(MgX))C}_6\text{H}_5 + \text{(C}_6\text{H}_5\text{)}_2\text{CO} \xrightarrow{\text{C}_6\text{H}_5\text{MgX}} \text{(C}_6\text{H}_5\text{)}_2\text{COMgX}$$

Cleavage was avoided by working at sufficiently low temperatures, and a glycol resulted.

Jacquemain treated diacetone alcohol with Grignard reagents. Using ethyl, $n$-propyl, $n$-butyl, $n$-amyl, isopropyl, and iso-amyl magnesium halides, he obtained glycols of the type $\text{(CH}_3\text{)}_2\text{CH(OH)CH}_2\text{C(CH)CH}_2\text{R}$.

Bickel treated two hydroxy ketones with lithium phenyl, obtaining the corresponding hydroxy compounds, without observing cleavage. His two starting materials were $\text{(C}_6\text{H}_5\text{)}_2\text{C(OH)CH}_2\text{COC}_6\text{H}_4\text{-OCH}_3$ and $\text{C}_6\text{H}_5\text{COCH}_2\text{C(OH)(C}_6\text{H}_5\text{)}\text{C}_6\text{H}_4\text{CH}_3$.

Barnett made a preliminary study of the effect of phenyl magnesium bromide on $\beta$-hydroxy ketones. Later a more detailed
study was made by Fuqua. His results are summarized below:

**Compound**

\[ \text{Hydroacetylacetone} \]

\[ \text{Diacetone alcohol} \]

\[ \text{1,3-diphenyl-3-hydroxy butanone-1} \]

\[ \text{2,2-dimethyl-5,5-diphenyl-5-hydroxy pentanone-3} \]

\[ \text{3,3-dimethyl-9-hydroxy-9,1-fluorenyl butanone-2} \]
Beta-Hydroxy Acids and Esters

Using methyl, phenyl, and benzyl Grignard reagents, McKenzie and Martin*9 obtained glycols from $\beta$-hydroxy-$\beta$-phenyl propionic acid as normal addition products. Their reactions may be represented:

$$\text{C}_6\text{H}_5\text{CH(OH)}\text{CH}_2\text{CO}_2\text{H} + \text{RMgX} \rightarrow \text{C}_6\text{H}_5\text{CH(OH)}\text{CH}_2\text{C}(\text{R})_2\text{OH}$$

Glycols were obtained from $\beta$-$\beta$-diphenyl-$\beta$-hydroxy propionic ester by Berberian*8, who treated the ester with methyl, ethyl, and phenyl magnesium bromides:

$$\text{HOC(C}_6\text{H}_5)_2\text{CH}_2\text{CO}_2\text{C}_6\text{H}_5 + \text{RMgX} \rightarrow \text{HOC(C}_6\text{H}_5)_2\text{CH}_2\text{C(OH)}(\text{C}_6\text{H}_5)_2$$

In the case of the methyl compound, the hydrocarbon $(\text{C}_6\text{H}_5)_2\text{C}=$-$\text{C}($-$\text{CH}_3)_2$ was obtained in small yield as a dehydration product of the glycol, but no mention of cleavage was made.

ALPHA OXIDO CARBONYL COMPOUNDS

Alpha Oxido Ketones and Esters

The first systematic study of cleavage of organo-magnesium compounds was made by Kohler, Richtmyer and Hester*2. They found that in every case studied cleavage of the molecule occurred when alpha oxido ketones and glycidic esters were treated with Grignard reagents.

Alpha oxido ketones $\quad \text{R}_2\text{C}=$-$(\text{R})\text{COR}$

Glycidic esters $\quad \text{R}_2\text{C}=$-$(\text{R})\text{CO}_2\text{R}$
They treated benzalacetophenone oxide with phenyl magnesium bromide and obtained triphenyl carbinol and a resin. The compound reacted with ethyl magnesium bromide in a similar manner yielding diethyl phenyl carbinol and resins. The resins in both cases were evidently due to extensive polymerization of the second cleavage product. Anisalacetophenone oxide reacted in a similar manner yielding triphenyl carbinol and resinous products. These reactions demonstrated that cleavage occurred between the carbonyl group and oxide ring.

\[
\text{RCHCHCO}_2\text{C}_8\text{H}_8 \xrightarrow{(\text{RC}_2\text{H}_2\text{O})\text{MgBr} \ + \ (\text{C}_6\text{H}_5)_2\text{CO}} \xrightarrow{(\text{C}_6\text{H}_5)_3\text{CO}} \text{C}_6\text{H}_5\text{MgBr}
\]

Evidence as to the exact nature of one of the primary cleavage products was obtained by treating benzalacetone oxide with mesityl magnesium bromide. This yielded acetomesitylene, which failed to add a second mole of Grignard reagent due to steric hindrance. The product in this case was a ketone instead of a tertiary alcohol as in the previous cases.

\[
\text{C}_6\text{H}_5\text{CHCHCOC}_8\text{H}_8 \xrightarrow{(\text{CH}_3)_2\text{C}_6\text{H}_5\text{MgBr}} \xrightarrow{(\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{O})\text{MgBr} \ + \ \text{CH}_3\text{CO}_2\text{C}_8\text{H}_8(\text{CH}_3)_3}
\]

The nature of the second cleavage product was demonstrated by the reaction of 1,1-diphenyl-2-benzoylethylene oxide, \((\text{C}_6\text{H}_5)_2\text{CCHCOC}_8\text{H}_8\), with phenyl magnesium bromide. In this case triphenyl carbinol and diphenyl acetaldehyde were obtained, with no resinous products formed. The general reactions of organic
magnesium oxide ketones can then be represented as follows:

\[
\begin{align*}
(C_6H_5)_3C-CHCOC_6H_5 + RMgX & \rightarrow (C_6H_5)_2C=CH(OMgX) + RCOC_6H_5 \\
(C_6H_5)CHCHGOC_6H_5 + RMgX & \rightarrow (C_6H_5)C=CHOMgX) + RCOC_6H_5
\end{align*}
\]

In a study conducted to investigate the intermediate steps in the cleavage reaction, the Grignard reagent was added inversely to benzalacetophenone oxide at -10°. The product was hydrolyzed immediately with iced acid yielding the oxide carbinol, \(C_6H_5CHCH(C_6H_5)_2OH\). This carbinol was stable at temperatures far above its melting point, and was not decomposed by alcoholic potassium hydroxide. It reacted promptly with phenyl magnesium bromide, cleaving to give triphenyl carbinol and a resin. The carbinol was also obtained with excess phenyl magnesium bromide provided that the temperature was sufficiently low, and that the mixture was hydrolyzed immediately. With only one equivalent of reagent at the usual temperature, no carbinol was obtained, but the usual cleavage products occurred. The cleavage was not due, then, to an excess of the reagent, but to a spontaneous decomposition at room temperature of the magnesium compound formed by the addition of one molecule of the reagent to the oxido ketone.
The glycidic ester, \((\text{CH}_3)\text{O-CHCO}_2\text{C}_6\text{H}_5\), behaved in a manner analogous to that of the oxido-ketones. With phenyl magnesium bromide a cleavage took place although only one cleavage product, triphenyl carbinol, was isolated.

\[
(\text{CH}_3)_2\text{C-CHCO}_2\text{C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{MgX} \rightarrow (\text{CH}_3)_2\text{C-CH-C-C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5
\]

\[
(\text{C}_6\text{H}_5)_2\text{COMgX} + Y
\]

Sergmann and Wolff repeated some of the work of Kohler, Richtmyer and Hester and in addition reported two oxido ketones which gave products other than cleavage products. Benzal-p-phenyl-acetophenone oxide, \(\text{C}_6\text{H}_5\text{CHGHCOC}_6\text{H}_5\text{C}_6\text{H}_5\), reacted with phenyl magnesium bromide to give two products. The first was the pinacol of phenyl bi-phenyl ketone, which was obtained through cleavage.

\[
\text{C}_6\text{H}_5\text{C}_6\text{H}_5 \xrightarrow{\text{C}} \text{C}_6\text{H}_5\text{C}_6\text{H}_5
\]

The second product was a compound, \(\text{C}_{33}\text{H}_{22}\text{O}_3\), resulting from the addition of two moles of phenyl magnesium bromide to the ethylene oxide linkage. The authors were in doubt as to the exact structure of the compound.

Benzal-p-methoxyacetophenone oxide, \(\text{C}_6\text{H}_5\text{CHGHCOC}_6\text{H}_4\text{OCH}_3\), underwent addition without cleavage when treated with Grignard reagent, yielding a compound \(\text{C}_{33}\text{H}_{22}\text{O}_3\).
Bickel investigated the compound obtained by Bergmänn and Wolff from benzal-methoxyacetophenone oxide, and established the following structure for the addition compound.

\[
(C_6H_5)_2CH - CH - C \quad \xrightarrow{\text{OH}} \quad C_6H_4OCH_3
\]

Bickel also treated benzal-methoxyacetophenone oxide with lithium phenyl, obtaining results similar to those obtained from the Grignard reagent with benzalacetophenone oxide. In cold solution the only product was the oxanol; at room temperature the molecule was cleaved.

**Alpha-Oxanols**

Two oxanols, \( C_6H_5CHCH(C(OH)(C_6H_5))_2 \) and \( C_6H_5CH(CH(OH)CH(C_6H_5))_2 \), which are closely related to \( \gamma \)-oxide ketones and \( \gamma \)-oxide esters, were studied by Kohler and Bickel. They found that the metal from the Grignard reagent, lithium phenyl, and sodium in liquid ammonia would replace the hydroxyl hydrogen in the oxanol. At low temperature, by hydrolysis, the oxanols were regenerated; while at higher temperatures the molecules of the metallic derivatives cleaved yielding benzophenone and the corresponding metallic derivatives of diphenylacetalddehyde.
THEORETICAL DISCUSSION
It has been already shown that β-diketones, which either do not enolize or are incapable of enolization, undergo a characteristic cleavage when treated with organo-magnesium compounds.

\[
\begin{array}{c}
R-C-C-C-R + R'MgX & \rightarrow & R-C-C-C-R + R'MgX \\
\text{O R O} & \rightarrow & \text{O R O MgX}
\end{array}
\]

The ketone, formed as a primary cleavage product, does not survive in the presence of excess reagent and is converted readily to a tertiary alcohol.

Cyclic β-diketones have been reported to differ from open chain β-diketones in their behavior towards the Grignard reagent. In every case, where both carbonyl groups are part of the cycle, cleavage of the ring has not been observed and usually normal addition products have been isolated.

Wedekind and Miller treated tetramethyl-1,3-cyclobutanediene with an excess of ethyl magnesium bromide and obtained a compound, b.p. 128-130° (30 mm.), which they concluded was the corresponding glycol resulting from the normal addition of two moles of the reagent.

\[
\begin{array}{c}
(CH_3)_2C-C=O \\
O=C-C(CH_3)_2 & \rightarrow & (CH_3)_2C-C-OH \\
\text{HO-C-C(CH_3)_2} & \rightarrow & \text{HO-C-C(CH_3)_2}
\end{array}
\]
Geissman and co-workers have observed that 2,2-dimethyl-1,3-indanedione and 8,8-dimethyl-7,9-peri-naphthindanedione, compounds in which the two carbonyl groups are members of five and six-membered rings respectively, undergo normal addition when treated with phenyl magnesium bromide.

If these few reports are not exceptional, one would be led to the conclusion that the reaction is perfectly uniform, and that only normal addition products are formed. In reality, experiments in this laboratory with tetramethyl-1,3-cyclobutanedione and tetraphenyl-1,3-cyclobutanedione have shown conclusively that the reaction of these compounds with a variety of organo-magnesium and lithium compounds leads to cleavage of the ring in every case where any reaction at all took place.

Tetramethyl-1,3-cyclobutanedione (I) reacted with an excess of methyl magnesium bromide to yield a monoaddition product (II), which was unstable and underwent a reverse aldol condensation, resulting in cleavage of the ring with the formation of a primary cleavage product (III), which, however, did not survive in the presence of the reagent and was converted into the α-hydroxy ketone (IV), 5-hydroxy-2,4,4,5-tetramethyl-3-hexanone, together with small quantities of acetone and di-isopropyl ketone.
When treated with barium hydroxide, IV decomposed almost quantitatively into acetone and di-isopropyl ketone.

Treatment with excess ethyl magnesium bromide also produced cleavage of I, yielding 5-hydroxy-2,4,4-trimethyl-3-heptanone (VI). The formation of V is the result of cleavage of the cyclic ring, followed by the reduction of the carbonyl group and subsequent hydrolysis to yield VI.
The presence of one hydroxyl and one keto group in VI was ascertained by an active hydrogen determination using the Zerewitinoff method. The identity of VI was confirmed by its decomposition products with barium hydroxide, which were propionaldehyde and di-isopropyl ketone.

\[
\text{VI} \quad \text{Ba(OH)}_2 \rightarrow C_8H_8CHO + (CH_3)_2CH-C-CH(CH_3)_2
\]

Attempts to prevent reduction of V by adding only one mole of the reagent inversely failed, as only the reduction product was obtained. This type of reduction is not unusual, as the reduction of sterically hindered ketones by Grignard reagents is well known. Several cases of reduction by ethyl magnesium bromide have been reported. Start treated di-isopropyl ketone with ethyl magnesium bromide and obtained 23% reduction of di-isopropyl ketone and 53% addition to the carbonyl group to form ethyl di-isopropyl carbinol; Leroide treated ethyl trimethyl acetate with this reagent and isolated only the reduction product, ethyl t-butyl carbinol.

These results differ from those of Wedekind and Miller, who erroneously described the product of the reaction as a cyclic glycol.
In view of the fact that Wedekind and Miller's so-called glycol and VI had the same boiling point and approximately the same analysis, their identity was suspected. They failed, however, to recognize their product as the $\beta$-hydroxy-ketone VI, because they did not determine the number of hydroxyl groups in the molecule. Moreover, the b.p. (124-125°) of the cyclic hydrocarbon corresponding to the reduction of the glycol is presumably in error since VI should reduce to 2,4,4-trimethyl heptane, b.p. 151-152°.

Excess phenyl magnesium bromide reacted with I, causing the molecule to cleave. The expected $\beta$-hydroxy ketone (VIII), could not be isolated by any of the various procedures used for the hydrolysis of the magnesium complex. All attempts to isolate VIII led to its decomposition products, benzophenone and di-isopropyl ketone.

$$
\begin{align*}
\text{(CH}_3\text{)}_2\text{C} & \quad \text{C}=\text{O} \\
\text{C}_6\text{H}_5\text{MgBr} & \quad \text{COMgBr} \\
\text{O}=\text{C} & \quad \text{C(\text{CH}_3)_2} \\
\end{align*}
$$

I

$$
\begin{align*}
\text{(CH}_3\text{)}_2\text{C} & \quad \text{C}=\text{O} \\
\text{C}_6\text{H}_5\text{MgBr} & \quad \text{COMgBr} \\
\text{O}=\text{C} & \quad \text{C(\text{CH}_3)_2} \\
\end{align*}
$$

II

$$
\begin{align*}
\text{(CH}_3\text{)}_2\text{C} & \quad \text{C}=\text{C(\text{CH}_3)_2} \\
\text{C}_6\text{H}_5\text{MgBr} & \quad \text{OMgBr} \\
\text{O}=\text{C} & \quad \text{C(\text{CH}_3)_2} \\
\end{align*}
$$

VIII

$$(\text{C}_6\text{H}_5)\text{C}=\text{O} + (\text{CH}_3)\text{C}=\text{C(\text{CH}_3)_2}$$
The inverse addition of only one mole of phenyl magnesium bromide to I was carried out in an attempt to prevent further addition of the reagent to the primary cleavage product and thus render possible the formation of a diketone, which is one step nearer the cleavage process than the β-hydroxy ketone. This effort failed as only the decomposition products of the β-hydroxy ketone, benzophenone and di-isopropyl ketone, were obtained.

It has been established that the behavior of open chain β-diketones towards organo-lithium compounds is the same as their behavior towards organo-magnesium compounds\(^\text{14}\). It is possible that lithium phenyl might yield a more stable primary addition product than that obtained with phenyl magnesium bromide and in this way avoid cleavage of the ring. In order to test this hypothesis, I was treated with lithium phenyl, but it was found that lithium phenyl reacts in a manner exactly comparable to phenyl magnesium bromide. In addition to di-isopropyl ketone and benzophenone, triphenyl carbinol was also obtained. This was surprising, since it was not produced by any of the reactions between I and phenyl magnesium bromide.

\[
\begin{align*}
&\text{(CH}_3\text{)}_2\text{C}=\text{C}(\text{CH}_3)\text{_2} \quad \text{(CH}_3\text{)}_2\text{C} \quad \text{C}_6\text{H}_5 \quad \text{(CH}_3\text{)}_2\text{C} \quad \text{C}_6\text{H}_5 \\
&\text{O}=\text{C} \quad \text{O}=\text{C} \quad \text{O}=\text{C} \quad \text{O}=\text{C} \\
&\text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \\
&\text{I} \quad \text{IX} \quad \text{VIII} \\
&\text{C}_6\text{H}_5\text{Li} \quad \text{C}_6\text{H}_5\text{Li} \quad \text{C}_6\text{H}_5\text{Li} \\
&\text{(CH}_3\text{)}_2\text{CH} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \\
&\text{H} \quad \text{OLi} \quad \text{OLi} \quad \text{OLi} \quad \text{OLi} \\
&\text{IX} \quad \text{VIII} \\
&\text{(CH}_3\text{)}_2\text{CHCOCH(CH}_3\text{)_2} + \text{(C}_6\text{H}_5\text{)_2CO} \quad \text{C}_6\text{H}_5\text{Li} \quad \text{(C}_6\text{H}_5\text{)_2CO} \\
\end{align*}
\]
Experiments were conducted in which lithium phenyl was added slowly to an agitated mixture of iced-acid and benzophenone and also to a mixture of iced-acid and di-isopropyl ketone. No addition occurred in the case of the di-isopropyl ketone, but benzophenone competed favorably with hydrochloric acid for lithium phenyl and was converted to triphenyl carbinol. This proved that benzophenone is capable of reverting to triphenyl carbinol during the hydrolysis process. Since only benzophenone was produced in the reaction between phenyl magnesium bromide and I, these facts indicate, (1) the formation of IX and consequent absence of benzophenone, and (2), that benzophenone was formed by the decomposition of VIII upon hydrolysis with hydrochloric acid.

In order to ascertain the nature of the primary product it was necessary to adopt a reagent which would produce a cleavage product containing a highly hindered carbonyl group, thus preventing further addition of the reagent and giving rise to the formation of a α-diketone. Mesityl magnesium bromide was selected as a reagent which fulfills these conditions, however, no reaction with I under various conditions was observed with this reagent. It then became necessary to resort to lithium mesityl, which reacted with I to produce dimethyl isobutryl mesityl methane (X).

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{C} & \quad \text{C} = \text{O} \\
\text{(CH}_3\text{)}_3\text{C} & \quad \text{C} = \text{O} \\
\text{C} & \quad \text{C} = \text{O} \\
\text{C} & \quad \text{C} = \text{O} \\
\text{I} & \quad \text{H}^+ \\
\text{C}_6\text{H}_5\text{C} & \quad \text{C}_6\text{H}_5\text{C} \\
\text{C}_6\text{H}_5\text{C} & \quad \text{C}_6\text{H}_5\text{C} \\
\text{C}_6\text{H}_5\text{C} & \quad \text{C}_6\text{H}_5\text{C} \\
\text{C}_6\text{H}_5\text{C} & \quad \text{C}_6\text{H}_5\text{C} \\
\text{X} & \quad \text{X}
\end{align*}
\]
For the purposes of identification, dimethyl isobutyryl-mesityloyl (X) was converted to isobutyric acid and isobutyrylmesitylene by alcoholic potassium hydroxide.

\[
\begin{align*}
(CH_3)_2CHC\overset{\cdot}O & \overset{O}{C} \overset{O}{C} C_6H_5(CH_3)_3 & \overset{\text{KOH}}\rightarrow & (CH_3)_2CHCOOK & + & (CH_3)_2CHCC\overset{O}{C}C_6H_5(CH_3)_3 \\
X
\end{align*}
\]

Tetraphenyl-1,3-cyclobutanedione (XI) was treated separately with three organo-metallic compounds, phenyl magnesium bromide, lithium phenyl and lithium mesityl, and found to be much less active in its reaction than the corresponding tetramethyl compound (I). The extreme difference in the rate of addition was attributed to the fact that the phenyl groups offer a great deal more hindrance to the carbonyl groups than do the methyl groups.

Phenyl magnesium bromide failed to react with XI during periods as long as six hours and at temperature as high as 70°C. However, Compound (XI) underwent cleavage when treated with lithium phenyl yielding sym-tetraphenyl acetone, benzophenone and triphenyl carbinol.

\[
\begin{align*}
(C_6H_5)_2C & \overset{\cdot}O \overset{O}{C} \overset{O}{C} C_6H_5 & \overset{\text{LIC}_{6}H_5}{\rightarrow} & (C_6H_5)_2C & \overset{O}{C} \overset{O}{C} C_6H_5 \\
\text{XI} & \overset{\text{LIC}_{6}H_5}{\rightarrow} & (C_6H_5)_2C & \overset{O}{C} \overset{O}{C} C_6H_5 & \overset{\text{LIC}_{6}H_5}{\rightarrow} & (C_6H_5)_2C & \overset{O}{C} \overset{O}{C} C_6H_5 \\
\overset{\text{OLi}}{\rightarrow} C_6H_5 & \overset{\text{OLi}}{\rightarrow} C_6H_5 & \overset{\text{OLi}}{\rightarrow} C_6H_5 & \overset{\text{OLi}}{\rightarrow} C_6H_5 & \overset{\text{OLi}}{\rightarrow} C_6H_5 & \overset{\text{OLi}}{\rightarrow} C_6H_5 & \overset{\text{OLi}}{\rightarrow} C_6H_5
\end{align*}
\]

\[
\begin{align*}
(C_6H_5)_2CHC-CH(C_6H_5)_2 + (C_6H_5)_2CO & \overset{\text{LIC}_{6}H_5}{\rightarrow} (C_6H_5)_2C\text{OLi}
\end{align*}
\]
The sym-tetraphenyl acetone and benzophenone were accounted for as decomposition products of the corresponding β-hydroxy ketone and the formation of triphenyl carbinol in reactions of this type has already been accounted for.

The action of lithium mesityl was investigated in an attempt to isolate a primary cleavage product. However, no reaction was observed, even at 80° and the starting material was recovered.

Kohler et al. have advanced the explanation that cleavage by organic magnesium compounds is fundamentally the same as the reversal of an aldol condensation. They recognized the possibility of explaining the instability of the magnesium complex, formed by the addition of one mole of the reagent to the compound, by an application of ionization or chelation. Geissmann and Tulagin have applied this condition of chelation as a possible explanation of the course of the cleavage reaction and have suggested that the formation of an intermediate involving the magnesium and the two carbonyl groups in a chelated ring may be a necessary condition for the cleavage of β-diketones.

They observed that 2,2-dimethyl-1,3-indanedione and some other closely related five and six-membered ring compounds failed to
undergo cleavage of the cyclic ring when treated with phenyl magnesium bromide. In their explanation of this behavior, they state that chelation of this type is impossible in 2,2-dimethyl-1,3-indanedione, because of its spacial configuration, and suggest that cleavage failed because the formation of a chelated intermediate was impossible.

In the case of the tetra-substituted 1,3-cyclobutanediones, chelation as that suggested above is also impossible, however, cleavage of the ring was observed in every case where any reaction at all occurred. Thus it has been established definitely that chelation is not a condition for cleavage.

The cleavage of the 1,3-cyclobutanediones as well as open chain β-diketones can be explained on the basis of a reversible aldol condensation.

\[ \begin{align*}
(R)_2C & \quad C=O \\
O=C & \quad C(R)_2 \\
\text{R'} & \quad \text{MgX} \\
\end{align*} \]

Maintenance of the cyclic member of the equilibrium would lead to addition without cleavage, while maintenance of the open chain member of the equilibrium would lead to cleavage. Since a four membered ring represent a strained configuration, it is to be expected that it would be readily broken and that the cyclic member would not be maintained in the above equilibrium. This expectation is fulfilled by the fact that cleavage of the cyclobutanediones with organo-magnesium and lithium compounds was observed in every case where reaction took place.
EXPERIMENTAL
Tetramethyl-1,3-cyclobutanediene (I).

\[
\begin{align*}
(CH_3)_2C&-C=O \xrightarrow{Zn} (CH_3)_2C=O \rightarrow (CH_3)_2C\overset{\text{O}}{=}O \\
\end{align*}
\]

This compound was prepared by the method of Wedekind and Weiss". A solution containing 500 g. of absolute ether and 293 g. (1.27 moles) of O-bromo-isobutyryl bromide was mixed with 360 g. (5.52 moles) of granular zinc in an atmosphere of dry nitrogen. The reaction was started by warming the mixture and its rate was controlled by cooling the flask in an ice bath for a period of one and one-half hours. The mixture was heated then for two hours on a water bath, and allowed to stand over night. Upon addition of 400 ml. of petroleum ether, an oily layer containing zinc bromide separated. After the removal of the petroleum ether layer, this oil and zinc bromide layer was extracted several times with hot petroleum ether. The combined extracts were evaporated to a volume of 100 ml., and upon cooling, 7.0 g. (0.05 mole) of (I) crystallized. Upon further evaporation and cooling of the mother liquors, an additional 1.5 g. (0.011 mole) of the product was obtained. After purification of the product by sublimation it melted at 113-115°.

Yield: 8.5 g. (0.061 mole) (10%).

Tetramethyl-1,3-cyclobutanediene (II).

\[
\begin{align*}
(CH_3)_2C&-C=O \xrightarrow{(C_6H_5)_2N} (CH_3)_2C\overset{\text{O}}{=}O \\
\end{align*}
\]
Wedekind and Weissang\textsuperscript{57} have devised a second method for the preparation of this compound. A solution of 100 g. (0.94 mole) of iso-butyryl chloride in 200 ml. of carbon disulfide was added dropwise during a period of about one and one-half hours to 97 g. (0.96 mole) of triethylamine dissolved in 200 ml. of carbon disulfide, in an atmosphere of dry nitrogen. After the reaction ceased, the mixture was refluxed for six hours. The precipitated triethyl ammonium chloride was filtered under suction and washed three times with 200 ml. portions of hot petroleum ether. The combined liquids were allowed to stand, and an additional small amount of amine hydrochloride was filtered off. The liquid was evaporated to a volume of 100 ml. Upon cooling, 12.5 g. of (I) crystallized. Further evaporation and cooling of the mother liquors produced an additional 3.0 g. of this compound. The combined crystalline product was purified by sublimation, m.p. 113.5-116\degree. Yield: 12.0 g. (0.086 mole) (18\%).

Tetramethyl-1,3-cyclobutanedione (I).- This compound was prepared by the method of Wedekind and Weissang\textsuperscript{57} by the reaction of \(\alpha\)-bromo-isobutyryl bromide and zinc with a yield of only 10\%. A second method\textsuperscript{57} using isobutyryl chloride and triethylamine gave only a yield of 18\%.

Better results can be obtained by a modification of the second method in the following manner:

To a solution of 266 g. (2.63 moles) of triethylamine in 700 ml. of anhydrous carbon disulfide under an atmosphere of dry nitrogen was added 266 g. (2.60 moles) of isobutyryl chloride, with vigorous stirring over a period of one and one-half hours.
The mixture was agitated for four hours and then allowed to stand for five days with periodic agitation. Upon addition of petroleum ether, triethyl ammonium chloride precipitated. After filtration and washing with ether, the combined liquids were evaporated. This yielded 80 g. of the crude product (I). After purification by distilling twice from a short neck flask, the yield was 68 g. (0.48 mole) (38%), b.p. 159-161°, m.p. 115-116°.

This procedure was used with benzene as a solvent without the precaution of an inert atmosphere, with no impairment of yield.

Cleavage by Methyl Magnesium Bromide. 5-Hydroxy-2,4,4,5-tetramethyl-3-hexanone (IV).--To a solution of methyl magnesium bromide, prepared from 60 g. (0.632 mole) of methyl bromide and 12.88 g. (0.53 mole) of magnesium in anhydrous ether, was added 15.0 g. (0.106 mole) of I in small portions over a period of fifteen minutes. The mixture was refluxed for thirty minutes to complete the reaction and then hydrolyzed with iced hydrochloric acid. The aqueous layer was extracted three times with ether and the combined ether extract was dried over anhydrous sodium sulfate. The ether was removed by distillation through a 40 cm. column packed with 5/32 inch glass helices, with the temperature of the distilling flask not over 70°. The remaining liquid was fractionated through a 20 cm. column packed with 5/32 inch glass helices, equipped with a partial condensation type head and gave 0.8 g. of acetone, b.p. 54-57°, n_D^0 1.3596, 2,4-dinitrophenylhydrazone, m.p. 127.5-128.2°, 2,4-dinitrophenylhydrazone, mixed m.p. 127-128°. The residue upon distillation
under reduced pressure gave two fractions: (1) 2.4 g., b.p. 30-69° (2 mm.); (2) 14.64 g. of liquid, b.p. 69-72° (3 mm.). Fraction 1 was refractionated yielding 1.8 g. di-isopropyl ketone, b.p. 123-127°, n\(_D^o\) 1.4021, semicarbazone, m.p. 154-155.5°, semicarbazone mixed m.p. 154.2-155.3°. Fraction 2 was refractionated into three fractions, each of which had the same b.p., 71-71.5° at 3 mm., and the same index of refraction, n\(_D^o\) 1.4419, m.p., 16°. Yield: 12 g. (0.0695 mole) (65%) of IV. Anal. Calcd. for C\(_{18}\)H\(_{30}\)O\(_3\): C, 69.6; H, 11.7. Found: C, 69.4; H, 11.9.

Identification of IV. - A mixture of 7.0 g. (0.041) of IV and 0.1 g. of barium hydroxide was heated in a small distilling flask on an oil bath at 170-180° until the distilling flask was dry. This required about three hours with 6.8 g. of material distilling at a vapor temperature of 56-130°. The product was fractionated and yielded 2.2 g. (0.038 mole) of acetone, b.p. 55-556.4°, n\(_D^o\) 1.3581, semicarbazone, m.p. 190-191°, semicarbazone mixed m.p. 190.1-190.8°, 2,4-dinitrophenyl hydrazone, m.p. 127.5-128°, 2,4-dinitrophenyl hydrazone, mixed m.p. 127-128°, and 4.45 g. (0.0391 mole) of di-isopropyl ketone, b.p. 123-127°, n\(_D^o\) 1.4016, semicarbazone, m.p. 153.8-155, semicarbazone, mixed m.p. 154.1-155°. The yield was 95.2% of acetone and 96.3% of di-isopropyl ketone.

Cleavage by Ethyl Magnesium Bromide. 5-Hydroxy-2,4,4-trimethyl-3-heptanone (VI). - To a solution of ethyl magnesium bromide prepared from 18.2 g. (0.75 mole) of magnesium and
85.0 g. (0.81 mole) of ethyl bromide in anhydrous ether was added 21.0 g. (0.15 mole) of solid I. After the reaction ceased, the mixture was heated on a water bath at reflux temperature for fifteen minutes, then cooled, and hydrolyzed with iced dilute hydrochloric acid. The ether extract after drying over anhydrous sodium sulfate was removed under reduced pressure through a packed column. The residue was distilled under vacuum and yielded 21.8 g. of a liquid, b.p. 127-129° (30 mm.). Refractionation of this material yielded only one substance, nD 1.4449. Yield: 21.8 g. (0.126 mole) (84%).


Identification of VI.- A Zerewitinoff determination with methyl magnesium bromide was made on this product. One mole of the compound gave 1.01 moles of methane, indicating one hydroxyl group per molecule. One mole of compound consumed 1.93 moles of reagent, indicating the presence of one carbonyl group per molecule.

A mixture of 7.3 g. (0.0423 mole) of VI and 0.1 g. of barium hydroxide was placed in a small distilling flask and heated in an oil bath at 170-180° for three hours. The distillate, 7.1 g., b.p. 48-127°, was obtained by using an acetone-carbon dioxide bath. Upon refractionation of the products there were obtained 2.1 g. (0.0362 mole) of propionaldehyde, b.p. 48-51°, nD 1.3640, 2,4-dinitrophenyl hydrazone, m.p. 154.9-155.6°, 2,4-dinitrophenyl hydrazone, mixed m.p. 154.5-155.5°; and 4.7 g. (0.0412 mole) of di-isopropyl ketone, b.p. 124-127°, nD 1.4013,

The above experiment was repeated with a small sample of the compound but with the omission of the barium hydroxide. The same two products were identified, but more time was required for complete cleavage.

**Cleavage by Ethyl Magnesium Bromide.- Inverse Addition.-** A solution of ethyl magnesium bromide, prepared from 2.08 g. (0.0856 mole) of magnesium and 11.0 g. (0.0916 mole) of ethyl bromide in 100 ml. of anhydrous ether, was added over a period of forty five minutes to a solution of 12.0 g. (0.0856 mole) of I in 150 ml. of anhydrous ether. The mixture was agitated for one-half hour and then heated for one-half hour at reflux temperature. The reaction mixture was hydrolyzed with iced hydrochloric acid and extracted three times with ether. After drying the solution over anhydrous sodium sulfate, the ether was evaporated through a Widmer column, under vacuum. A small amount of high-boiling material distilled over with the ether. The distillate was redistilled and the residue added to the residue remaining from the first distillation. Upon the addition of a small amount of petroleum ether, 5.5 g. of crystals, I, m.p. 114-115°, mixed m.p. 114-115°, was obtained. The filtrate was freed of petroleum ether by distilling under vacuum using a packed column. The material remaining after the removal of the petroleum ether was vacuum distilled using a 20 cm. packed column. The first 1.8 g. sublimed at 70-80° (30 mm.) and was
shown to be the starting material, making a total of 7.3 g. (0.052 mole) (60%) unreacted of I. The second fraction consisted of 4.8 g. of liquid (0.0278 mole), which was identified as VI, b.p. 127-131° (30 mm.), n_D^20 1.4456. The yield of VI was 83%, based on amount of I not recovered.

The product was shown to be identical with VI in the following way: 4.0 g. (0.0232 mole) of VI, prepared as described above by the inverse addition of ethyl magnesium bromide to I, was heated with 0.1 g. of barium hydroxide in a small distilling flask at 170-180°. The distillate, b.p. 47-130°, was condensed using an acetone-carbon dioxide bath. On fractionating the distillate there was obtained 1.1 g. (0.0190 mole) of propionaldehyde, b.p. 47-49°, n_D^20 1.3663, 2,4-dinitrophenyl hydrazone, m.p. 153.5-154.8°, mixed m.p. with 2,4-dinitrophenyl hydrazone, 155-156°, and 2.5 g. (0.0219 mole) di-isopropyl ketone, b.p. 124-126°, n_D^20 1.4017, semicarbazone, m.p. 154.6-155.5°, mixed m.p. with di-isopropyl semicarbazone, 154.5-155.5°.

Cleavage by Phenyl Magnesium Bromide.- A phenyl magnesium bromide solution was made from 18.24 g. (0.75 mole) of magnesium and 119.62 g. (0.765 mole) of bromobenzene in 150 ml. of anhydrous ethyl ether. To the reagent was added 21.0 g. (0.15 mole) of solid I over a period of ten minutes. A vigorous reaction resulted, and after the reaction had subsided, the mixture was heated on a water bath at reflux temperature for fifteen minutes. The mixture was cooled, hydrolyzed with ice and hydrochloric acid, extracted three times with ether, and the ether dried over anhydrous sodium sulfate. After removing the ether under
vacuum using a packed column and an acetone-carbon dioxide bath to condense the distillate, there remained 44.6 g. of material. From the distillate, by careful fractionation, there was obtained 6.0 g. of di-isopropyl ketone, b.p. 118-127°. The prepared semicarbazone melted at 152.5-154.9°, and when mixed with an authentic sample of the semicarbazone the m.p. was unaltered. The residue (44.6 g.) was distilled at 2 mm. using an acetone-carbon dioxide bath to condense the distillate, and about 15 ml. of distillate was collected. This distillate fraction proved to be benzene and 8.5 g. of di-isopropyl ketone, b.p. 124-127°. Four grams of the remaining material was steamed distilled and yielded 2.8 g. of benzophenone, m.p. 47-48°, mixed m.p. 47-49°. The remainder of the material was crystallized from methyl alcohol, and recrystallized from a mixture of ether and petroleum ether and yielded 23.3 g. of benzophenone, m.p. 47-48.5°; mixed m.p. with benzophenone was not depressed. The benzophenone oxime was prepared, m.p. 144.5-145.5°, mixed m.p. 144.4-145.7°. Yield: 14.5 g. (0.127 mole) (85%) of di-isopropyl ketone and 26.1 g. (0.143 mole) (95%) benzophenone.

Various methods of hydrolysis were tried in order to isolate the cleavage product. A second reaction was carried out using the same amounts of materials and following the same procedure as above with the exception that the reaction mixture was hydrolyzed with a mixture of ice and ammonium chloride solution. The material remaining, after the removal of ether under vacuum at room temperature, was vacuum distilled at room temperature by means of a mercury vapor pump. The distillates consisted of
two fractions, one consisting of diphenyl and the other consisting of 23.4 g. (0.129 mole) of benzophenone, m.p. 45-47°, mixed m.p. 44-49°. No attempt was made to isolate di-isopropyl ketone in this reaction. The yield of benzophenone was 86%.

The same reaction was carried out and hydrolysis was accomplished by adding dropwise to the mixture an ether-dry hydrochloric acid solution, prepared by passing dry hydrochloric acid gas into 53 g. of cold anhydrous ether until the weight increase amounted to 75 g. The addition required about one hour and the temperature was not allowed to rise above 2°, and the mixture agitated continuously. The magnesium chloride was filtered off and washed several times with ether. The ether was distilled under vacuum at room temperature and the remaining material was distilled under vacuum at room temperature, using an acetone-carbon dioxide bath. A small amount of di-isopropyl ketone and 21 g. (0.115 mole) of benzophenone were obtained.

Yield of benzophenone was 77%.

Still another reaction was carried out using the same materials and the same procedure as the first reaction with the exception that the reaction was carried out at -25° by using a carbon dioxide-acetone bath. Eighty per cent of the starting material was recovered.

Cleavage by Phenyl Magnesium Bromide. - Inverse Addition. -
A solution of phenyl magnesium bromide, prepared from 2.6 g. (0.107 mole) of magnesium and 16.79 g. (0.107 mole) of bromobenzene in 100 ml. of anhydrous ether, was added to a solution of 100 ml. of ether and 12 g. (0.0856 mole) of I. The addition
of the reagent was made over a period of one hour and then the mixture was heated on a water bath at reflux temperature for one-half hour. The mixture was hydrolyzed with dilute hydrochloric acid and ice and extracted three times with ether. After evaporation of the ether under vacuum at room temperature and adding a small amount of petroleum ether to the remaining material, 4.0 g. of crystalline material was obtained. This material was proven to be the starting material, I, m.p. 111.5-113°, mixed m.p. 111.8-113.5°. On recrystallizing from petroleum ether the m.p. was 113.5-114.4°. On cooling the supernatant liquids in acetone-carbon dioxide bath 1.0 g. of material crystallized out which after recrystallizing from petroleum ether proved to be the starting material, m.p. 113-114.1°, mixed m.p. 113-114.5°. The ether-petroleum ether mother liquors were evaporated under vacuum leaving 14.0 g. of material. Crystallization from organic solvents failed. The material was vacuum distilled using an acetone-carbon dioxide bath and yielded 2.5 g. of di-isopropyl ketone, b.p. 121-126°, nD 1.4069, semicarbazone, m.p. 154.5-155.6°, mixed m.p. 154.6-155.4°; 2.1 g. of material which proved to be the starting material, m.p. 113.5-114.1°; and an oil, b.p. 118-124° (2 mm.) which was crystallized from petroleum ether and proved to be benzophenone, 5.8 g., m.p. 47-48.5°, mixed m.p. 47-48.4°. Yield: 7.1 g. (0.0506 mole) of the starting diketone (59%), 21.0 g. (0.0184 mole) (53%) of di-isopropyl ketone, and 5.8 g. (0.0032 mole) (31%) of benzophenone.
Cleavage by Lithium Phenyl.- An ethereal solution of lithium was prepared by allowing 4.04 g. (0.576 mole) of lithium to react with 45.0 g. (0.288 mole) of bromobenzene in 150 ml. of dry ether and any unreacted lithium was then removed mechanically. To this reagent was added 5.0 g. (0.0356 mole) of I in small portions. After the reaction subsided, the mixture was heated fifteen minutes on a water bath. The reaction product was then hydrolyzed by iced hydrochloric acid. The aqueous layer was extracted with ether, and the combined ether extracts dried over anhydrous sodium sulfate. After removal of ether under reduced pressure, petroleum ether was added causing the precipitation of 4.5 g. of solid triphenyl carbinol. This compound was recrystallized from alcohol and had a m.p. 161-162°, mixed m.p. 161.5-162°. The addition of more petroleum ether to the petroleum ether filtrate caused a small amount of benzophenone to precipitate. Recrystallized from methyl alcohol it had a m.p. 47-48°, mixed m.p. 47.5-48.2°. The combined filtrates were distilled and after removal of solvents, yielded 3.8 g. of di-isopropyl ketone, b.p. 124-125°, semicarbazone, m.p. 154.4-155.3°. Steam distillation of the residue yielded 1.4 g. of benzophenone, m.p. 46.5-47.5°, mixed m.p. 47.1-48°.

A residue of 0.5 g. of triphenyl carbinol remained after the steam distillation, which after crystallization from alcohol melted at 161.2-161.6°; mixed m.p. 161.5-162°. The total products obtained were 5.0 g. (0.0192 mole) (54%) of triphenyl carbinol, 1.4 g. (0.0077 mole) (22%) of benzophenone, and 3.8 g. (0.0333 mole) (94%) of di-isopropyl ketone.
The following experiment was designed to show that benzophenone if present would not survive during the hydrolysis, but would react with lithium phenyl to produce triphenyl carbinol. A lithium phenyl reagent was prepared by allowing 1.4 g. (0.2 mole) of lithium to react with 15.6 g. (0.1 mole) of bromobenzene in 100 ml. of dry ether. A solution of 3.64 g. (0.02 mole) of benzophenone in 75 ml. of ether was added to an ice, water and hydrochloric acid mixture containing 0.5 mole of hydrochloric acid. The lithium reagent was added slowly with vigorous mechanical stirring to this mixture. The aqueous layer was extracted with ether. After evaporation of the ether from the combined extracts, the addition of petroleum ether caused 4.1 g. (0.0157 mole) of triphenyl carbinol to crystallize, which on recrystallization gave a m.p. 161-162°. After the evaporation of the petroleum ether from the filtrate, steam distillation of the residue yielded 0.6 g. (0.0033 mole) of benzophenone, m.p. 47-48°. The 4.1 g. (0.0157 mole) of triphenyl carbinol represents 79% of the theoretical yield, while 16.5% of the original benzophenone was recovered.

The hydrolysis of the lithium phenyl was repeated in the presence of 4.9 g. (0.043 mole) of di-isopropyl ketone using the same procedure as described above. One hundred ml. of the lithium reagent, prepared as above, was used. After the hydrolysis, 4.1 g. (0.036 mole) of di-isopropyl ketone was recovered by distillation, representing a yield of 84%. After the distillation, there remained a trace of residue, which was not identified.
The hydrolysis of phenyl magnesium bromide was carried out in the presence of benzophenone and di-isopropyl ketone with the result that only these two materials were recovered unchanged from the reaction mixture.

Treatment with Mesityl Magnesium Bromide. Solid I, 5.0 g. (0.036 mole), was added to a mesityl magnesium bromide reagent prepared from 5.37 g. (0.22 mole) of magnesium and 23.88 g. (0.12 mole) of bromomesitylene in anhydrous ether. The mixture was heated on a water bath for thirty minutes, and then decanted from the excess magnesium, and hydrolyzed with ice and dilute hydrochloric acid. The aqueous layer was extracted three times with ether, and the ether dried over anhydrous sodium sulfate. After distilling the ether off under vacuum, cooling of the remaining material caused 2.1 g. of the starting diketone to crystallize, m.p. 113.5-114.4°. On distilling the remaining material, there was obtained 2.3 g. of the starting material, m.p. 114.3-114.5°, 8.6 g. of mesitylene, and 9.0 g. of bromomesitylene. The total recovery of the starting material was 4.5 g. (0.032 mole) (90%).

A second reaction was carried out using the same amounts of materials and following the same procedure except after the addition of the solid I, the ether was replaced by distillation and benzene was added for the solvent. A total of 4.2 g. (0.03 mole) (84%) of the starting material was recovered, but no other products were isolated.

Cleavage by Lithium Mesityl. Dimethyl Isobutyryl Mesityl Methane (X).- Lithium mesityl was prepared by allowing 3.2 g.
(0.46 mole) of lithium to react with 43.78 g. (0.22 mole) of bromomesitylene in anhydrous ether. The mixture was heated during the course of the addition, and for two hours after the bromomesitylene was introduced, and the residual lithium was removed mechanically.

An ethereal solution of 10.1 g. (0.072 mole) of I was added slowly to the reagent. A vigorous reaction resulted, and the mixture was allowed to stand over night. The reaction product was hydrolyzed with ice and hydrochloric acid. The aqueous layer was extracted several times with ether, and the combined ether extracts were dried over calcium chloride. The ether was removed by evaporation under reduced pressure.

Mesitylene and bromomesitylene were removed by distilling under reduced pressure, and the residue gave 23 g. of a substance boiling at 140-150° (2 mm.). Upon refractionation, 18 g. of material, b.p. 140-151° (2 mm.), was obtained which gave 14 g. (0.0537 mole) (75%) crystals (m.p. 34-36°) from absolute alcohol. Three grams of this solid was further purified by crystallizing once from petroleum ether and twice from alcohol, m.p. 35.5-36.5°.

Anal. Calcd. for C_{17}H_{24}O: C, 78.4; H, 9.3. Found: C, 78.1; H, 9.5.

Identification of X.- A Zerewitinoff determination of active hydrogen with methyl magnesium iodide on this product gave no methane, indicating the absence of hydroxyl group. One mole of the compound tested consumed 2.12 moles of the reagent, indicating the presence of two carbonyl groups per molecule, and probably
resulting in cleavage of the molecule.

One gram of X was refluxed with 15 ml. of saturated alcoholic potassium hydroxide for twenty minutes. The alcohol was removed by distillation and 20 ml. of water added, and the mixture was extracted with ether several times. The water portion gave no precipitate on acidification with sulfuric acid. The odor of isobutyric acid was observed. This acidified solution was distilled, the distillate was made alkaline with sodium hydroxide, and evaporated to dryness. The p-toluidine derivative was made as follows: one gram of p-toluidine and 0.5 ml. of concentrated hydrochloric acid was added to the sodium salt and warmed twenty minutes. The mixture was extracted with alcohol and the alcohol extract filtered, diluted with water and part of the alcohol removed by distillation. Crystals of m.p. 103.5-104.5° separated. Mixed m.p. with a prepared sample of isobutyryl p-toluic was 103-104.5°. The ether extracts were evaporated, and the remaining material vacuum distilled, giving 0.8 g. of material, b.p. 140-143 (20 mm.), nD 1.5086. The α-bromo-3,5-dibromo-isobutyryl mesitylene was prepared by covering the material with ice and water and treating it with 3 g. of bromine for ten minutes with shaking and cooling. The material solidified and was broken up and treated with a saturated solution of sodium bisulfite. The solid material was filtered, washed with ether and recrystallized from alcohol, m.p. 106-107°. A mixed m.p. with an authentic sample of α-bromo-3,5-dibromo-isobutyryl mesitylene proved them to be the same.

Tetraphenyl-1,3-cyclobutanedione. (XI).—The Richard's
method, which is inadequately described in the literature, involves the decomposition of phenyl benzoyl phenoxy methane to form XI.

\[
\begin{align*}
C_6H_5CHO & \xrightarrow{KGN} C_6H_5CH-C_6H_5 \xrightarrow{SOCl_2} C_6H_5CH-C_6H_5 \xrightarrow{NaOC_6H_5} \\
C_6H_5C=O & \xrightarrow{(C_6H_5)_2C=C=O} \xrightarrow{(C_6H_5)_3C=O} \xrightarrow{O=C} C(C_6H_5)_2
\end{align*}
\]

Benzoin and desyl chloride were prepared according to methods described in Organic Syntheses.

**Phenyl Benzoyl Phenoxy Methane.** A solution of sodium phenolate in alcohol was prepared by allowing 12 g. (0.52 mole) of sodium to react with 73 g. (0.78 mole) of phenol in 110 ml. of ethyl alcohol. To this solution was added 50 g. (0.216 mole) of desyl chloride dissolved in 300 ml. of absolute methyl alcohol. This mixture was refluxed for three hours, and the alcohol was evaporated under vacuum. The residual oil was washed several times with a sodium hydroxide solution. Sixty five grams of this oil was obtained. After crystallizing twice, once from methyl alcohol and once from ethyl alcohol, 50 g. (0.173 mole) of the ether was obtained, m.p. 79-81°. Yield: 81%.

Fifteen g. (0.0795 mole) of phenyl benzoyl phenoxy methane was heated at 250° for one hour, after which a small amount of phenol was distilled off under vacuum. The residue was extracted with ether leaving an insoluble material. This material when
recrystallized from benzene, gave 0.2 g. (0.00051 mole) of XI, m.p. 243-245°.

**Tetraphenyl-1,3-cyclobutylidine. (XI).**

\[
\begin{align*}
(C_6H_5)_4CHCOOH & \xrightarrow{SOCl_2} (C_6H_5)_4CHCOC\ & (C_6H_5)_4C=C=0 \\
(C_6H_5)_4C & \xrightarrow{C=C} (C_6H_5)_4C
\end{align*}
\]

The procedure used for the preparation of XI was that of Staudinger.

Diphenylacetyl chloride was prepared by treating diphenylacetic acid with thionyl chloride. The product was purified by vacuum distillation.

A solution of 66 g. (0.286 mole) of diphenylacetyl chloride in 150 ml. of dry ether was added slowly with stirring to 30 g. (0.296 mole) of triethylamine in ether. Refluxing and stirring were continued one hour after the addition of the acid chloride. The ether was then evaporated and the residue was heated at 180° for five hours. This residue solidified into a hard resinous mass, which was extracted with boiling ether. Upon cooling, 6 g. of material, m.p. 176°, was obtained. This was assumed to be the trimer of diphenyl ketene. The ether-insoluble residue was extracted with a large volume of boiling benzene. The resulting solution was filtered, and some of the benzene evaporated. Upon cooling, 1.1 g. (0.00284 mole) of XI, m.p. 243-245°, crystallized. Yield: 2%. 

Benzoin, benzil, benzil mono-hydrazone, and diphenyl ketene were prepared according to the methods described in Organic Syntheses.

Richard's procedure gave only a trace of XI. The procedure of Staudinger gave a yield of 2% of XI while a second method by the same author gave a yield of 6%. A modification of the second method of Staudinger was used in the preparation of this diketone, resulting in a considerably easier preparation at the same yield. The modification consists of heating diphenyl ketene in the absence of a solvent at 180-200° for six hours to polymerize the ketene in preference to heating a benzene solution of diphenyl ketene quinoline at 170° for eighty hours.

Diphenyl ketene, 50 g. (0.257 mole) was heated on a bath at 180-200° for six hours under an atmosphere of nitrogen. The diphenyl ketene polymerized completely, after which it was poured into an erlenmeyer flask while hot and allowed to cool and solidify. One hundred ml. of ethyl ether was added, which
dissolved the greater portion of the trimer, m.p. 176°, leaving XI mixed with the 176° melting trimer. One crystallization from benzene almost completely separated the two polymers, giving crystals of XI, m.p. 245-247°. The yield of XI was 3.3 g. (0.0085 mole) (7%).

Anal. Calcd. for C_{20}H_{20}O_{10}: C, 86.6; H, 5.2. Found: C, 86.3; H, 5.4.

The other polymer (trimer) was isolated by the addition of an equal volume of petroleum ether to the ether extract, giving 19.1 g. of crystals, m.p. 176-177°. Upon working up the benzene from the crystallization of I with the ether-petroleum ether mother liquors an additional 8.9 g. of the trimer was isolated. The yield of the trimer was 27.0 g. (0.046 mole) (54%).

Treatment with Phenyl Magnesium Bromide.- To a phenyl magnesium bromide reagent, made by allowing 6.123 g. (0.039 mole) of bromobenzene to react with 0.945 g. (0.039 mole) of magnesium in 100 ml. of dry ether, was added 1.0 g. (0.0026 mole) of solid XI. The mixture was refluxed one and one-half hours. Solid material resembling the starting diketone was observed. The ether was distilled out and 100 ml. of benzene added and the mixture refluxed one and one-half hours. The mixture was hydrolyzed using ice and hydrochloric acid. After extracting the water layer with ether and benzene, evaporation of the benzene and ether on a water bath gave 0.8 g. of material, which was proven to be the starting diketone as no depression of m.p. was observed when mixed with XI. This is a recovery of 80% of the diketone.
The black mp. with a prepared sample of 8-phenylpentanoic acetic
make) mp. 137-131.5°, was shown to be 8-11-0.104
structure, and trace from acetone. The acetate, 13° 12, was
prepared a second fraction of acetate, 4.2, recovered. The latter
add 1.0. 12.5-12.6°. On the addition of more pentane other
terial was identified as trifluoracetone, mp. 121-122°.
- tritium out. After recovery of acetone from acetone, tritium was
the addition of pentane ether, 7.2. of solid material only
separator on a clean bench, drawing a residue of 0.9. few
The aqueous layer was extracted with ether and the ether extracts
The structure was hydrolyzed using ice and hydrochloric acid.
-one-half hour on a waterbath and allowed to stand over night.
reaction had ended, the reaction mixture was heated one and
recovered. After the
(0.0.1029 mole) of solid AX was added to the reaction. After the
50.0. ml. of anhydrous ether. Five grams of
free 1.46° (0.0.05 mole) of titanium, 16.5° 6. (0.104 mole)
pleasure of titanium fluoroacetate. The titanium reagent was made
were isolated.
(60%) of XI, 8.° 2.45-2.47°, was recovered. No other products
and worked up as in the preceding reaction, 15° 6. (0.0031 mole)
and the mixture refluxed 6x hours. After hydrolysis
a b.p. of 66°. Two grams (0.0.0575 mole) of the solid diacetic
part of the ether was replaced by benzene by gentle stirring the solution
benzene in 200 ml. of ether. 8. soon as the reaction was made.
3.8. E. (0.16 mole) of magnesium, 2.4° 8. (0.155 mole) of bromo-
A second reaction was carried out using a reagent made from
was 132-134°. The remaining materials from the crystallizations were combined, the solvent removed by distillation and the residue steamed distilled. A trace of benzophenone, m.p. 47-48.1°, steam distilled over, leaving a residue which after crystallizing from alcohol proved to be triphenyl carbinol, 0.9 g. The total yield was 3.2 g. (0.0123 mole) (95%) of triphenyl carbinol, 4.5 g. (0.0124 mole) (96%) of tetraphenyl acetone, and a trace of benzophenone.

**Treatment with Lithium Mesityl.**—A lithium reagent was made from 2.1 g. (0.3 mole) of lithium, 30.0 g. (0.15 mole) of bromomesitylene and 75 ml. of ether. The solid diketone, XI, was added and the mixture refluxed for three hours. No change in color of the mixture was observed, and on cooling a material resembling the starting material crystallized out of solution. Part of the ether was distilled out, 100 ml. of benzene was added and the mixture was heated one hour. The mixture was hydrolyzed with ice and dilute hydrochloric acid, and the mixture extracted with benzene. Upon the removal of benzene on a steam bath, 3.6 g. (0.0095 mole) (95%) of XI, m.p. 245-246°, was recovered.

A second reaction was carried out using the same amounts of materials and following the same procedure as above with the exception that sufficient ether was replaced by benzene to give a reflux temperature of 70°, and the solution was refluxed for four hours. A resinous material was obtained after removal of solvent, from which no crystalline material could be isolated. None of the starting material was recovered.
Tetramethyl-1,3-cyclobutanedione and tetraphenyl-1,3-cyclobutanedione have been found to undergo cleavage of the ring when treated with organo-magnesium and lithium compounds. Their behavior has been found to be strictly analogous to open chain \( \beta \)-diketones.

Two open chain \( \alpha \)-disubstituted \( \beta \)-hydroxy ketones have been prepared as products of the cleavage reaction. Compounds of this type have not been previously reported.

Possible mechanisms for the cleavage reaction have been discussed.
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BIOGRAPHY
Garry Carlton Kitchens was born in Danville, Georgia, on July 28, 1914. His elementary education was received in the Grammar School of Danville. He was graduated from the high school division of Middle Georgia Junior College, Cochran, Georgia, in June, 1931. In the autumn of 1931 he entered the college division of Middle Georgia Junior College and graduated in 1933.

The following September he entered the University of Georgia, Athens, Georgia, and graduated with the Bachelor of Science in June, 1935. He entered the graduate school of this institution in September, 1935, as teaching fellow in the Department of Chemistry. He was graduated with the degree of Master of Science in June, 1937.

In September, 1937, he entered Louisiana State University as teaching fellow in the Department of Chemistry, where he was engaged in work leading toward the Doctorate, until the fall of 1940.

He was Professor of Chemistry, Arkansas Agricultural and Mechanical College, Monticello, Arkansas, during the 1940-1941 college session. He was employed in the Crossett Research Laboratories, Crossett, Arkansas for one year. Since August, 1942, he has been employed by Givaudan Delawanna Inc., Delawa-anna, New Jersey, and is at present on leave of absence.

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EXAMINATION AND THESIS REPORT

Candidate: Kitchens, Garry C.

Major Field: Chemistry

Title of Thesis: The Cleavage of Cyclo Beta Diketones. I. Tetramethyl-1,3-cyclobutanedione. II. Tetraphenyl-1,3-cyclobutanedione.

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination: March 15, 1945