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The Reaction of Organomagnesium Compounds With Triketones.

Reuben F. Miller
Louisiana State University and Agricultural & Mechanical College

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THE REACTION OF ORGANOMAGNESIUM COMPOUNDS
WITH TRIKETONES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
In Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy

in

The Department of Chemistry

by

Reuben Miller
B. S., College of the City of New York, 1943
M. S., Louisiana State University, 1950
June 1952
MANUSCRIPT THESES

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The author wishes to express his appreciation for the advice and guidance of Professor J. L. E. Erickson, under whose supervision this work was done. He also wishes to express his gratitude to his wife, Jutta, for her constant encouragement and without whose invaluable assistance this work could not have been completed.
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It has already been shown that alpha-oxido ketones, alpha-oxido esters and non-enolizable beta-diketones undergo a characteristic cleavage when reacted with an excess of Grignard reagent. From a consideration of the foregoing results it was believed that the course of the reaction between organomagnesium compounds and diphenylpropanetrione or 2,3,4-pentanetrione could easily be followed. Diphenylpropanetrione reacted with an excess of phenylmagnesium bromide to yield triphenylcarbinol and benzoin as the final products. The inverse addition of one mole of phenylmagnesium bromide to diphenylpropanetrione gave the benzoate of benzoin as a sole product of the reaction. This indicated that an intramolecular rearrangement had occurred. Convincing evidence for a mechanism postulating cleavage anterior to hydrolysis was obtained by treating the monoaddition magnesium complex with benzyol chloride to yield stilbeneglycol dibenzoate. Diphenylpropanetrione, when treated with excess methylmagnesium iodide, reacted to produce methylbenzoylcarbinol and dimethylphenylcarbinol. The inverse addition of one mole of methylmagnesium iodide to diphenylpropanetrione again yielded a rearranged product, the benzoate of methylbenzoylcarbinol. Similarly dimethyl triketone, when treated with an excess of phenylmagnesium bromide, reacted to produce phenylacetylcarnbinol and methyldiphenylcarbinol. A product of an intramolecular rearrangement, the acetate of phenylacetylcarnbinol, was obtained when dimethyl triketone was treated inversely with one mole of phenylmagnesium bromide. An examination of the above results led to a proposed mechanism which may be written as:
\[ \text{R-CO-CO-CO-R} + \text{R'}\text{MgX} \rightarrow \text{R-CO-CR'\text{(OMgX)}}-\text{CO-R} \]
\[ \rightarrow \text{R-C(OMgX)=CR'}-\text{OOCR} \rightarrow \text{R-COR} \]

and in the presence of excess Grignard reagent:

\[ \text{R-C(OMgX)=CR'}-\text{OCOR} + \text{R'}\text{MgX} \rightarrow \text{R-C(OMgX)=C(OMgX)R'} + \text{R'RCO} \rightarrow \text{R}_2\text{RCOMgX} \]
\[ \text{HON} \rightarrow \text{RCO-CHOHR'} + \text{R}_2\text{RCOH} \]

A different situation, however, was represented by the addition of triketonolane to an excess of phenylmagnesium bromide which resulted in the formation of 1,2,3-trihydroxy-1,2,3-triphenylnolane. No cleavage products were obtained, possibly indicating a strong resonating structure for the monoaddition product.
THEORETICAL DISCUSSION
It has been shown in this investigation that the behavior of triketones with organomagnesium compounds is similar in some respects to the behavior of alpha-diketones and beta-diketones. The alpha-diketones add one mole of reagent to produce alpha-hydroxy ketones, which do not survive in the presence of an excess of reagent and revert to glycols.

The behavior of beta-diketones towards organomagnesium compounds has already been investigated. Acetylacetone, when added to methylmagnesium iodide by Zerevitinoff, yielded a monoaddition product which was not identified with certainty, indicating that the diketone reacted in its enol form. A more definite result was obtained by Smedley who added dibenzoylethylene to an excess of phenylmagnesium bromide to obtain the dehydration product of the monoaddition compound, alpha, alpha-diphenyl-beta-benzoylethylene. This product could only be formed if the beta-diketone reacted as though it was an alpha-ketol, followed by a dehydration of the resulting carbinol. Vorlander, Osterburg and Meyer by repeating this work isolated the carbinol and wrote the equation:

\[
C_6H_5CO.CH_2.COC_6H_5 + C_6H_5MgBr \rightarrow (C_6H_5)_2C(OMgX)CH_2COC_6H_5
\]

indicating the enol character of dibenzoylethylene.

Kohler, Richtmeyer and Rester investigated the behavior of representative oxido ketones and esters toward organic magnesium compounds. They reported that alpha-oxido-ketones are cleaved when they react with organomagnesium compounds. This cleavage resulted from a spontaneous decomposition of a monoaddition compound:
Fundamentally, the cleavage of the carbinol may be interpreted as a reversal of the aldol condensation. They also observed that organic magnesium compounds react with only the carbonyl group of alpha-oxido ketones to give the corresponding oxido carbinol. The mode of addition of organomagnesium compounds to alpha-oxido ketones may be written:

\[
(C_6H_5)_2C = CHCOC_6H_5 + RMgX \rightarrow (C_6H_5)_2C = CHOMgX + RCOC_6H_5
\]

\[
C_6H_5CH - CHCOC_6H_5 + RMgX \rightarrow (C_6H_5CH - CHOMgX)_n + RCOC_6H_5
\]

Kohler and Erickson observed a similar cleavage of beta-diketones and also a relationship between the ability of the beta-diketone to enolize and its tendency to undergo cleavage in the Grignard addition reaction. Highly enolized beta-diketones added one equivalent of the reagent and did not cleave if the magnesium derivatives were carefully acidified. The addition was represented as:

\[
C_6H_5COCH_2COC_6H_5 \rightarrow C_6H_5C = CHCOC_6H_5 \rightarrow C_6H_5C = CHCOC_6H_5 + RMgX
\]

\[
C_6H_5C = CH - C - (C_6H_5)_2 \rightarrow C_6H_5COCH_2C(C_6H_5)_2OH
\]

A different situation, however, was represented by beta-diketones incapable of enolization. Here, the monaddition product was unstable and underwent an analogous cleavage process as with the alpha-oxido ketones.
Cleavage was avoided by operating at a sufficiently low temperature and cleavage was decreased in compounds that had less highly branched chains and if alkyl rather than phenylmagnesium halides were used.

In view of the foregoing results it should not be difficult to follow the course of the reaction between organomagnesium compounds and diphenylpropanetrione or 2,3,4-pentanetrione. From general considerations as well as from various reactions, it appears probable that the central carbonyl group in the triketone is the most active of the three. When diphenylpropanetrione (I) reacts with an excess of phenylmagnesium bromide, triphenylcarbinol and benzoin are obtained as the products of the reaction. Apparently the most active carbonyl group combines with a molecule of the reagent to yield a monooaddition product (II) which now behaves like any other disubstituted beta-diketone. Thus, (II) adds another molecule of the reagent to form the unstable diaddition product (III) which undergoes a reverse aldol condensation, resulting in cleavage of the molecule with subsequent formation of two cleavage products, the magnesium halide derivatives of the enol form of benzoin (IV) and benzophenone (V). In the presence of excess reagent, benzophenone is converted into VI.
Hydrolysis with ice and ammonium chloride gave triphenylcarbinol and benzoin which are the expected cleavage products. This interpretation accounts for the products formed and the reaction may be written:

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\text{III} & \quad \text{IV} \\
\text{V}
\end{align*}
\]

When the above reaction is carried out inversely, however, that is, when one mole of phenylmagnesium bromide is added to one mole of diphenylpropanetrione and the resulting magnesium derivative is decomposed with ammoniacal ammonium chloride, the product expected is phenyl dibenzoylcarbinol (VII):
Strangely enough, the product actually obtained proved to be the benzoate of benzoin (XIII). The formation of XIII is difficult to explain using the mechanism of addition postulated above. Evidently an intramolecular rearrangement has occurred. A similar rearrangement has been reported by Blatt and Hawkins\(^7\) in their study of dibenzoylcarbinol. They report that dibenzoylcarbinol undergoes a rearrangement to the benzoate of benzoylcarbinol upon distillation under reduced pressure. Thus, this rearrangement of the alpha-hydroxy-beta-diketone to the ester of an alpha-hydroxy-ketone involves the shift of a group from carbon to oxygen.

Carbonyl compounds show additive properties by virtue of the following electromeric shift: \(\text{C} = \text{O}\). Since the shift is toward the oxygen atom the orientation of the fragments of the addenda is unambiguous. The carbonyl compound is electrophilic, since the electron-poor carbon atom has much more tendency to take up electrons than the electron-rich oxygen atom has to share them. Thus only nucleophilic substances may normally be expected to add to the carbonyl group. Grignard reagents are nucleophilic reagents and may be written as \(\text{R}^-\text{MgX}^+\).\(^9\) The reaction between diphenyl triketone and phenylmagnesium bromide is then resolved into the case of a nucleophilic addend operating on an electrophilic group. At least two different mechanisms based on different premises may be offered to explain the rearrangement encountered in the inverse addition.
reaction. The first mechanism postulates that the rearrangement occurs anterior to hydrolysis and may be written as:

\[
\begin{array}{c}
\text{C}_6\text{H}_5 - \text{C} - \text{C} - \text{C} - \text{C}_6\text{H}_5 + \text{C}_6\text{H}_5\text{MgBr}^+ \\
to
\begin{bmatrix}
\text{C}_6\text{H}_5 - \text{C} - \text{C} - \text{C} - \text{C}_6\text{H}_5 \\
\text{MgBr}^+
\end{bmatrix}
\end{array}
\]

Addition of the nucleophilic phenyl group to the electrophilic carbonyl carbon to give VIII is evidently the first step. The presence of an electron acceptor such as MgBr\(^+\) enables the alpha carbonyl carbon atom to furnish a strong positive center which may now form a coordinated valence bond (IX) with the electron-rich oxygen. Cleavage follows due to the
strong attractive forces between the oxygen and the electrophilic carbon and also to some extent by the repulsive forces exerted between the two adjacent electrophilic carbon atoms. The benzoyl group has thus migrated from a carbon to an oxygen leaving behind a pair of unshared electrons as shown in X. This unstable state is relieved by a shift of the electron pair to form a double bond with the adjacent carbonyl carbon, thereby strengthening the electromeric shift in the carbonyl group. Structure XI is stabilized by resonance and is the form which undergoes hydrolysis to give the enol form XII of the benzoate of benzoin (XIII).

The second mechanism proposes that the rearrangement occurs after hydrolysis. The probable mechanism is:

\[
\text{C}_6\text{H}_5 - \text{C} - \text{C} - \text{C} - \text{C}_6\text{H}_5 + \text{C}_6\text{H}_5 - \text{MgBr}^+ \rightarrow \text{C}_6\text{H}_5 - \text{C} - \text{C} - \text{C} - \text{C}_6\text{H}_5 \text{MgBr}^+ \text{HOH} \rightarrow \]

\[
\text{XIX} \quad \text{XVII} \quad \text{XVIII}
\]

\[
\text{XIV} \quad \text{XV} \quad \text{XVI}
\]
The addition of one molecule of phenylmagnesium bromide gives VIII which upon hydrolysis will give phenyldibenzoylcarbinol. Under conditions of alkaline hydrolysis as presented above, the hydrogen of the hydroxyl group is removed by hydrogen bonding to give XIV. The electron-rich oxygen will now form a coordinated linkage (XV) with the strong positive center furnished by the alpha carbonyl carbon. Cleavage results as in the first mechanism to produce a carbon with an excess of electrons XVI which is stabilized by the addition of a proton to give the benzoate of benzoic. A somewhat similar mechanism may be shown to apply for acid hydrolysis. A proton is added to the carbonyl oxygen thereby increasing the positive nature of the carbonyl carbon. An oxygen bridge is again formed with the hydroxyl oxygen followed by a loss of two protons and subsequent cleavage to give structure XVI.

From the above data no conclusions can be reached as to the correctness of either proposed mechanism. Phenyldibenzoylcarbinol has not been isolated or prepared indicating a possible structural instability. The work of Blatt and Hawkins verify the apparent instability of at least one hydroxy-beta'-diketone, dibenzoylcarbinol. If the first mechanism is correct, then cleavage of triketones in the presence of excess Grignard reagent, cannot be interpreted as a reverse aldol condensation, but is produced as a result of a intramolecular rearrangement. The second mechanism substantiates the reverse aldol condensation cleavage mechanism, as phenyldibenzoyl carbinol magnesium salt should behave similar to a disubstituted beta-diketone. The solution to this problem lies in ones ability to establish the chemical constitution of the magnesium complex prior to hydrolysis.
Convincing evidence for the first mechanism, postulating cleavage anterior to hydrolysis, was obtained by treating the magnesium complex (XI) with benzoyl chloride with the result that there was obtained stilbeneglycol dibenzoate (XVII)

\[
\begin{align*}
\text{MgBr}^+ + C_6H_5COCl & \rightarrow C_6H_5 - C\equiv C - C_6H_5 + \text{MgBrCl} \\
\end{align*}
\]

In view of the evidence gained for the chemical constitution of XI, the reaction between diphenylpropanetrioce and phenylmagnesium bromide differs in behavior from beta-diketones and may now be expressed as follows:

\[
\begin{align*}
\text{MgBr}^+ & \rightarrow (\text{C}_6\text{H}_5)_2\text{CO} \\
C_6\text{H}_5\text{MgBr} & \rightarrow (\text{C}_6\text{H}_5)_3\text{CO}_{\text{H}} + \text{C}_6\text{H}_5 - C\equiv C - \text{C}_6\text{H}_5 \\
\end{align*}
\]

The inverse addition of one mole of methylmagnesium iodide to diphenylpropanetrioce (I) results in a monoaddition magnesium complex (XVIII) which undergoes a rearrangement to (XIX). Upon hydrolysis the benzoate of benzoylmethylcarbinol (XX) is obtained. This product may be accounted for by an analogous mechanism as that of addition of phenylmagnesium bromide.
Diphenylpropanetrione (I) was added to an excess of methylmagnesium iodide and two products, dimethylphenylcarbinol (XXI) and benzoylmethylcarbinol (XXII), were isolated. Here again these products may be accounted for if the mechanism is assumed to be analogous to that of addition of phenylmagnesium bromide and may be written as:
Dimethyl triketone (XXIII) when treated inversely with one mole of phenylmagnesium bromide reacted similarly to diphenylpropanetrione.

The mechanism is identical with that given above. A monoaddition product undergoes a rearrangement and upon hydrolysis yields the acetate of phenylacetylcarbinol (XXIV).

\[
\begin{align*}
\text{CH}_3 - \text{C} & \quad \text{C} \quad \text{C} \quad \text{O} \quad \text{CH}_3 + \text{C}_6\text{H}_5 - \text{MgBr}^+ \\
\text{CH}_3 - \text{C} & \quad \text{C} \quad \text{C} \quad \text{O} \quad \text{CH}_3 + \text{C}_6\text{H}_5 - \text{MgBr}^+ \\
\text{CH}_3 - \text{C} & \quad \text{C} \quad \text{C} \quad \text{O} \quad \text{CH}_3 + \text{C}_6\text{H}_5 - \text{MgBr}^+
\end{align*}
\]
When dimethyl triketone (XXIII) was added to an excess of phenylmagnesium bromide two products, phenylacetylcarbinol (XXV) and methyl-diphenylcarbinol (XXVI), were isolated. The mechanism is identical with that given for diphenylpropanetrione (I) and may be written as:

\[
\begin{align*}
\text{CH}_3 - \text{C} & \equiv \text{C} \quad \text{MgBr}^+ \quad \text{C}_6\text{H}_5\text{MgBr} \quad \rightarrow \quad \text{CH}_3 - \text{C} & \equiv \text{C} \quad (\text{MgBr})_2 + \\
0 & \equiv 0 - \text{C} - \text{CH}_3 & & (\text{MgBr})_2 +
\end{align*}
\]

\[
\begin{align*}
(\text{CH}_3)(\text{C}_6\text{H}_5)\text{CO} & \quad \text{C}_6\text{H}_5\text{MgBr} \quad \rightarrow \quad (\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{COMgBr} \quad \text{HON} \quad \text{CH}_3 - \text{C} & \equiv \text{C} & \equiv \text{C}_6\text{H}_5 + \\
(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{COH}
\end{align*}
\]

The addition of triketoiandane (XXVII) to an excess of phenylmagnesium bromide did not yield any cleavage products but resulted in the formation of a triaddition product, 1,2,3-trihydroxy-1,2,3-triphenylindane (XXVIII). The resistance of the ketohydrindene structure to cleavage by Grignard
reagents has been described by Geissman and Tulagin\textsuperscript{10} in their paper on 1,3-diketo-2,2-dimethylhydrindene. In the case of 1,3-diketo-2,2-dimethylhydrindene cleavage did not occur upon the addition of an excess of phenylmagnesium bromide. Evidently the ketohydrindene structure was stabilized by resonance and conjugation between the carbonyl groups and the aromatic nuclear structure. When triketoindane is added to an excess of phenylmagnesium bromide the first step is addition to the central carbonyl group, as with diphenylpropanetrione (I). Further addition to the adjacent carbonyl groups and consequent hydrolysis resulted in a tricarbinol.

![Chemical structures](image)
From the above discussion of the experimental results, the behavior of diphenylpropanetrione and dimethyltriketone in the presence of excess phenylmagnesium bromide or methylmagnesium iodide was found to be quite alike. Thus it is apparent that both aromatic and aliphatic open-chain triketones are attacked in a similar manner by nucleophilic agents. The products isolated from these reactions were accounted for by a mechanism utilizing an intramolecular rearrangement of the primary magnesium addition product. This mechanism may be considered as a special case of the Whitmore 1,2 shift rearrangement. The element of a positive center for an initiating source is present in the carbonyl carbon which participates in the coordinate bond. This presents a type of a 1,2 shift - a shift from carbon to oxygen - which is unique and has not been previously described.
DIPHENYL TRIKETONE

Diphenyl triketoae was synthesized by the method of Neufville and v. Pechmann, which involves the following steps:

1. \( C_6H_5CHO + C_6H_5COCH_3 \xrightarrow{NaOH} C_6H_5CH=CHCOC_6H_5 + H_2O \)
2. \( C_6H_5CH=CHCOC_6H_5 + Br_2 \rightarrow C_6H_5CHBrCHBrCOC_6H_5 \)
3. \( C_6H_5CHBrCHBrCOC_6H_5 + 2NaOCH_3 \rightarrow C_6H_5C(OCH_3)=CHCOC_6H_5 + CH_3OH + 2NaBr \)
4. \( C_6H_5C(OCH_3)=CHCOC_6H_5 + H_2O \rightarrow C_6H_5C(OH)=CHCOC_6H_5 + CH_3OH \)
5. \( C_6H_5C(OH)=CHCOC_6H_5 \xleftarrow{} C_6H_5COCH_2COC_6H_5 \)
6. \( C_6H_5COCH_2COC_6H_5 + Br_2 \rightarrow C_6H_5COCHBrCOC_6H_5 + HBr \)
7. \( C_6H_5COCHBrCOC_6H_5 + K_2C_2H_2O_2 \xrightarrow{CH_3COOH} C_6H_5COCH(OOCOCH_3)COC_6H_5 + KBr \)
8. \( C_6H_5COCH(OOCOCH_3)COC_6H_5 + Br_2 \rightarrow HBr + C_6H_5COCH(OOCOCH_3)COC_6H_5 \)
9. \( C_6H_5COCH(OOCOCH_3)COC_6H_5 \rightarrow \text{CH}_3COBr + C_6H_5COCOCOC_6H_5 \)

Benzalacetophenone. A solution containing 218 g. (5.5 moles) of sodium hydroxide, 1960 g. of water and 1000 g. (1225 ml.) of 95% alcohol was introduced into a 5-l. flask supplied with a mechanical stirrer and supported in a larger vessel so as to permit cooling with cracked ice. Following the addition of 520 g. (4.3 moles) of pure acetophenone to the alkaline solution, the flask was rapidly surrounded with cracked ice and 460 g. (4.3 moles) of benzaldehyde was added at once to the stirred reaction mixture. After two hours, the mixture became so thick in consistency that the stirring was no longer effective and was discontinued. The mixture was left in the ice chest for about 10 hours and then cooled in an ice mixture, filtered and washed with
200 ml. of 95% alcohol which had previously been cooled to 0°. After
drying thoroughly in the air, the crude product was recrystallized from
four times its weight of 95% alcohol. Yield was 740 g. (82%) of light
yellow material m.p. 55-57°.

**Benzalacetophenone Dibromide** — To 1200 ml. of carbon tetra-
chloride containing 416 g. (2 moles) of benzalacetophenone was added
320 g. (2 moles) of bromine accompanied by constant stirring and cool-
ing of the reaction mixture. Upon the completion of the reaction, the
dibromide was filtered off and washed with two 500 ml. portions of hot
alcohol. Yield, 600 g. (82%), m.p. 156-157°.

**Dibenzoylmethane** — In a 2-l. three-necked round-bottomed flask,
fitting with a stirrer, reflux condenser and dropping funnel, were placed
400 g. (1.09 moles) of benzalacetophenone dibromide and 370 ml. of
absolute methyl alcohol. A solution of sodium methoxide, previously
prepared from 51 g. (2.2 atoms) of sodium and 500 ml. of absolute methyl
alcohol, was added rapidly to the stirred solution and the mixture was
then refluxed for one hour. The mixture was acidified with 22 ml. of
concentrated hydrochloric acid and after refluxing for about 5 minutes,
300 ml. of cold water was added and the flask was surrounded with an ice
bath. The product was filtered, washed with 50% methyl alcohol and then
with water until free of acid. Recrystallization of the air-dried product
from 300 ml. of hot methyl alcohol yielded 144 g. (60%) m.p. 77-78°.

**Dibenzoyl bromomethane** — To a solution containing 144 g. (0.65
mole) of dibenzoyl methane dissolved in 300 ml. of chloroform was added
dropwise, 103 g. (0.65 mole) of bromine dissolved in 210 ml. of chloroform. The reaction mixture was cooled in an ice bath and stirred during the reaction. A stream of dry air was passed through the solution for two hours to remove the hydrogen bromide as completely as possible. The solvent was distilled off under diminished pressure leaving light brown crystals as a residue. The dried and ground product was recrystallized from a chloroform - petroleum ether mixture and gave 188 g. (96%) of the bromoketone, m.p. 93°.

**Dibenzoylcarbinolacetate.** To a solution containing 90 g. (0.92 mole) of freshly fused potassium acetate in 800 ml. of glacial acetic acid was added 188 g. (0.62 mole) of dibenzoylbromothane and the mixture boiled for one hour. To the clear liquid was added enough water to produce turbidity while the solution was continually stirred and allowed to cool. An oil separated which was crystallized in the form of needles from methyl alcohol. Recrystallization from methyl alcohol yielded 84 g. (53%) of the acetate, m.p. 94°.

**Dibenzoylbromocarbinol Acetate.** The bromination of the acetate was conducted in a manner similar to that of dibenzoylmethane. It was found important to cool the solution well, to add the bromine slowly and to stir constantly to avoid a local rise in temperature. In the course of three hours, 53 g. (0.33 mole) of bromine was added to a solution of 84 g. (0.33 mole) of the acetate in 435 g. of chloroform. A stream of dry air was then passed through the solution to remove the hydrogen bromide as completely as possible. For the purpose of making
the triketone it was found expedient to operate directly with the chloro-
form solution and thus avoid isolating the bromo acetate.

**Diphenyl Triketone.** 6 -- The chloroform solution containing the
dibenzoylbromocarbinol acetate was transferred to a claisen distilling
flask and freed from chloroform by distillation. The flask was heated
at about 120° until the bromo acetate had decomposed and all the acetyl
bromide had distilled. Using another claisen flask as a receiver, the
residue was distilled under diminished pressure and the triketone was
collected as a reddish-brown oil which promptly solidified to a yellow
crystalline mass. This was redistilled again into a claisen flask
receiver and 53 g. (68%) of diphenyl triketone, b.p. 175-177° (2 mm.),
was obtained. The triketone may be recrystallized from boiling petroleum
ether which has been distilled from phosphorus pentoxide. It separates
in golden-yellow needles m.p. 69-70°. As it is extremely hygroscopic
and rapidly becomes coated with the white hydrate when exposed to air,
it must be kept in a vacuum desiccator or in sealed tubes.

The diphenyl triketone used in the following reactions was distilled
directly into a 250 ml. dropping funnel, the fraction distilling at 175-
177° (2 mm.) being collected.

**Reaction between Phenylmagnesium Bromide and Diphenyl Triketone.**--
Approximately 100 ml. of anhydrous ethyl ether containing 6.0 g. (0.025
mole) of diphenyl triketone was slowly added dropwise to a stirred ether-
eal solution of phenylmagnesium bromide prepared from 4.4 g. (0.18 atom)
of magnesium turnings and 28.3 g. (0.18 mole) of bromobenzene. Each drop produced a yellow precipitate which immediately redissolved.

Stirring and refluxing were continued for one hour. The cooled mixture was decomposed with ice and ammonium chloride. The ether phase was separated and the remaining aqueous phase extracted three times with 100 ml. portions of ether. The combined ether phases were dried over calcium chloride, and then concentrated over a steam bath. Upon cooling in an ice bath 2.9 g. (52%) of crystals were gradually deposited which after recrystallization from ethyl alcohol were identified as benzoin, m.p. 133°; m.m.p. 133°. Evaporation of the mother liquor to a small volume and subsequent addition of petroleum ether yielded 4.8 g. (73%) of crystals which after recrystallization from a benzene-petroleum ether mixture were identified as triphenylcarbinol, m.p. 160°; m.m.p. 160°.

**Standardization of the Grignard Reagent.** The Grignard reagent used in the subsequent inverse addition reactions was standardized by titration. An aliquot portion (5 ml.) of the ethereal Grignard solution was poured slowly into 20 ml. of water, excess standard hydrochloric acid was added and the excess acid was titrated with standard sodium hydroxide solution using methyl orange as the indicator.

**Reaction between Phenylmagnesium Bromide and Diphenyl Triketone.**

**Inverse Addition.** To a stirred ethereal solution containing 5.5 g. (0.023 mole) of diphenyl triketone was added 56 ml. of a 0.4529 M (0.025 mole) ethereal solution of phenylmagnesium bromide during a period of half an hour. Each drop produced an insoluble yellow precipitate. The
precipitate was permitted to settle and washed three times by removing
the supernatant ether phase by the use of a filter stick. The mixture
was decomposed with ammoniacal ammonium chloride and the ether phase
was separated. The remaining aqueous phase was extracted three times
with 50 ml. portions of ether and the combined ether phases were washed,
dried over calcium chloride and concentrated on a steam bath. Cooling
the concentrate in an acetone-dry ice bath produced 2.0 g. (34%) of a
crystalline substance which proved to be the benzoate of benzoin, m.m.p. 124°.

**Formation of Stilbeneglycol Dibenzoate**

\[ \text{Triketone} + \text{C}_6\text{H}_5\text{MgBr} + \text{C}_6\text{H}_5\text{COCl} \]

To a solution of 5.2 g. (0.0218 mole) of diphenyl triketone in 100 ml. of
anhydrous ethyl ether was added .023 mole of an ethereal phenylmagnesium
bromide solution dropwise over a period of half an hour. The reaction
mixture was refluxed for half an hour and then 2.9 g. of benzoyl chloride
in 15. ml. of ethyl ether was added. Approximately 100 ml. of ether was
distilled from the reaction mixture and replaced with 100 ml. of benzene.
After refluxing for two hours the yellow precipitate turned into a brown
oil which partially dissolved. The mixture was hydrolyzed with cold
dilute hydrochloric acid solution and worked up as usual. The ethereal
solution was concentrated on a steam bath to give a reddish oil. Upon
the addition of methyl alcohol to the oil and subsequent cooling in an
acetone-dry ice bath 2.9 g. (31%) of white crystals were obtained. These
were recrystallized from methyl alcohol to give colorless needles m.p.
160 - 165°. A mixed melt with an authentic sample of stilbeneglycol
dibenzoate gave no depression.
Reaction between Methylmagnesium Iodide and Diphenyl Triketone.--

To 260 ml. of 0.6060 N (0.16 mole) stirred ethereal phenylmagnesium bromide solution was added dropwise an ethereal solution containing 6.2 g. (0.026 mole) of diphenyl triketone. Each drop produced a slight reddish-brown precipitate which immediately redissolved. Stirring and refluxing were continued for one hour. The cooled mixture was decomposed with an iced ammonium chloride solution and the ether phase separated. The remaining aqueous layer was extracted three times with 100 ml. portions of ether, the combined ether phases were dried over calcium chloride and the solvent distilled, leaving a yellow, viscous oil. Distillation of the oil yielded 2.4 g. (68%) of dimethylphenylcarbinol b.p. 94-96°, (9 mm.) and 2.5 g. (64%) of methylbenzoylcarbinol b.p. 103-105° (4 mm.), n_D^24 1.5309, methylbenzoylcarbinol semicarbazone m.p. 239.5-240°.

Reaction between Methylmagnesium Iodide and Biphenyl Triketone.

Inversion Additon.-- Biphenyl triketone (9.5 g., 0.04 mole) was distilled into a three-necked flask which was fitted with a condenser, stirrer and dropping funnel. Approximately 100 ml. of anhydrous ethyl ether was added to the triketone and the mixture stirred until complete solution of the triketone occurred. To this solution was slowly added 118 ml. of a

0.3466 N CH_3MgI solution (0.041 mole). The reaction mixture was surrounded by an ice bath during the addition. A yellow precipitate developed which later turned to a brown color. Upon completion of the addition (3/4 hour) the reaction mixture was permitted to remain overnight in an ice bath. The following day the supernatant liquid was drawn off and the brown
precipitate was washed with 100 ml. of anhydrous petroleum ether (b.p. 80°) and then hydrolyzed with dilute hydrochloric acid. The ethereal layer was separated and the aqueous layer was extracted with four 100 ml. portions of ether. The combined ethereal extract was washed twice with 50 ml. portions of water containing a small quantity of sodium bisulfite, then dried over Drierite and concentrated to yield 11.1 g. of a red oil. The oil was taken up into petroleum ether "B" and chilled to yield 5.5 g. of diphenyl triketone hydrate. The remaining oil was distilled in vacuo to give 1.8 g. of a yellow oil b.p. 162-165° C (7 mm.) which solidified upon standing to yield white crystals of the benzoate of methylbenzoylcarbinol, m.p. 109-110°.

**Reaction between Mesitylmagnesium Bromide on Diphenyl Triketone.**—To an ethereal solution of mesitylmagnesium bromide, prepared from 13.9 g. (1.07 mole) bromomesitylene and 1.7 g. (0.07 atom) magnesium was added dropwise 2.29 g. (0.0096 mole) of diphenyl triketone dissolved in 50 ml. anhydrous ethyl ether. The reaction mixture turned green at first and later became brown. After refluxing for four hours the mixture was hydrolyzed with cold dilute hydrochloric acid and worked up in the usual way. The ether was removed by distillation to yield a red oil which deposited yellow prisms upon standing. The material was recrystallized from methyl alcohol to yield 1.8 g. (75%) of mesitylphenyl diketone m.p. 136-137°C; 2,4-dinitrophenylhydrazone m.p. 232-232.5°.

**DIMETHYL TRIKETONE**

The method of Sachs and Rohmer for the preparation of dimethyl triketone involves the following steps.
(1) \( \text{C}_6\text{H}_{12}\text{N}[(\text{CH}_3)_2]_2 + \text{HONO} \rightarrow \text{p}-(\text{CH}_3)_2\text{N}-(\text{C}_6\text{H}_4\text{H}_2)\text{NO} + \text{H}_2\text{O} \)

(2) \( \text{CH}_3\text{CO-CH}_2\text{COCH}_3 + \text{p}-(\text{CH}_3)_2\text{N}-(\text{C}_6\text{H}_4\text{H}_2)\text{NO} \rightarrow \text{CH}_3\text{CO-C-COCH}_3 + \text{H}_2\text{O} \)

(3) \( \text{CH}_3\text{CO-C-COCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COCOCOCH}_3 + \text{p}-(\text{CH}_3)_2\text{N}-(\text{C}_6\text{H}_4\text{H}_2)\text{NH}_2 \)

\textbf{p-Nitrosodimethylaniline.} \textsuperscript{16} -- In a 4-l. beaker immersed in ice was placed 200 g. (1.7 moles) of dimethylaniline, 1250 ml. of approximately 5 N hydrochloric acid and 1000 g. of ice. To the stirred mixture was slowly added a cold solution of 125 g. (1.8 moles) of sodium nitrite in 500 ml. of water. The temperature of the reaction mixture was kept below 5\textdegree and there was no liberation of nitrous gases. Upon standing for one hour the orange-yellow hydrochloride was filtered and washed several times with dilute (2 N) hydrochloric acid. The hydrochloride was dried thoroughly in the air and then slowly added to a vigorously stirred saturated aqueous solution of sodium carbonate to yield 224 g. (90%) of the free base, m.p. 86-87\textdegree.

\textbf{Dimethyl Triketone.} \textsuperscript{15} -- To a boiling solution of 48.0 g. (0.48 mole) of acetylacetone and 72 g. (0.48 mole) of \textit{p}-nitrosodimethylaniline in 300 ml. absolute ethyl alcohol was added 8.8 ml. of 33\% aqueous sodium hydroxide solution. The color of the reaction mixture changed after about one minute. The mixture was removed from the heating bath and the reaction, which continued, was moderated by occasional cooling. Upon termination of the reaction, it was cooled in an ice bath and then
diluted with about 700 ml. of ether. The separated sodium acetate (from acetylacetone by hydrolysis) was removed by filtration and the filtrate decomposed in a separatory funnel with a mixture of 300 ml. of sulfuric acid (Sp. gr. 1.16) and 100 ml. of water. The ether phase was separated and the remaining aqueous sulfuric acid phase was extracted six times with 400 ml. portions of ether. Distillation at ordinary pressure removed the ether from the combined ether-alcohol extracts and the alcohol was removed by distillation under reduced pressure, leaving a dark red oil as a residuum. Distillation of the residue yielded 15.4 g. (28%) of dimethyl triketone, b.p. 54-55° (12 mm.). It was noted that dimethyl triketone was hygroscopic and changed on standing in moist air to the monohydrate.

**Reaction between Phenylmagnesium Bromide and Dimethyl Triketone.**

An ethereal solution of 16.8 g. (0.15 mole) of dimethyl triketone was added dropwise during a period of half an hour to a stirred ethereal solution of phenylmagnesium bromide prepared from 21.9 g. (0.90 atom) of magnesium turnings and 141.2 g. (0.90 mole) of bromobenzene. Refluxing and stirring were continued for one hour. The mixture was cooled and then decomposed with an iced ammonium chloride solution. The ethereal and aqueous phases were separated and the latter was extracted three times with 100 ml. portions of ether. The combined ether extracts were washed with water, dried over calcium chloride and concentrated by evaporation to a small volume. Cooling in an acetone-dry ice bath yielded 11.4 g. (39%) of material which after recrystallization from petroleum
ether was proved to be methyldiphenylcarbinol, m.p. 80.5-81°, m.m.p. 81°. The residue was fractionated through a 7 inch column packed with glass helices and yielded 11.1 g. (50%) of phenylacetylarbinol b.p. 105-107° (6 mm.) nD 1.5309; semicarbazone m.p. 194-195°.

Reaction between Phenylmagnesium Bromide and Dimethyl Triketone.

Inverse Addition. To 3.8 g. (0.033 mole) of dimethyl triketone in approximately 100 ml. of anhydrous ether was added dropwise 45 ml. (0.035 mole) of an 0.77 N ethereal solution of phenylmagnesium bromide. The reaction mixture was cooled by an ice bath throughout the addition process. A light yellow insoluble addition product resulted from the reaction and the mixture was hydrolyzed by the slow addition of approximately 100 ml. of a saturated ammonium chloride solution. The aqueous and ethereal layers were worked up in the usual manner but after repeated extractions the aqueous layer still retained a strong yellow color. The ethereal extracts were washed, dried and concentrated to yield a yellow oil which failed to crystallize. The oil was distilled under reduced pressure to yield a forerun of 0.8 g. of a yellow oil, b. p. 85-88° (11 mm.), nD 1.4385, and 1.9 g. of the acetate of phenylacetylarbinol b.p. 130-132° (11 mm.), nD 1.5172. Analysis for C11H23O3: C, 68.73, H, 6.30. Found: C, 68.98, H, 6.52.
TRIKETOHYDRINDENE HYDRATE (NINHYDRIN)

\[
\begin{align*}
\text{C}_6\text{H}_4\text{COC}_2\text{H}_5 + \text{CH}_3\text{COOC}_2\text{H}_5 + \text{Na} & \rightarrow \text{C}_6\text{H}_4\text{COC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH} \\
\text{C}_6\text{H}_4\text{CO. CCH}_3\text{Na. COOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH} & \rightarrow \text{C}_6\text{H}_4\text{CO. CCH}_3\text{Na. COOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH} \\
\text{C}_6\text{H}_4\text{CO. CCH}_3\text{Na. COOC}_2\text{H}_5 & \rightarrow \text{C}_6\text{H}_4\text{CO. CCH}_2 \\
\text{C}_6\text{H}_4\text{CO. CCH}_2 + \text{SeO}_2 & \rightarrow \text{C}_6\text{H}_4\text{CO. CCH}_2\text{O}_2 + \text{Se}
\end{align*}
\]

Sodium 1,3-Diketohydrindene-2-carboxylic Ester.\(^{17}\) -- In a 2-liter round-bottomed flask fitted with an efficient reflux condenser and a dropping funnel were placed 500 g. of diethyl phthalate and 100 g. of powdered sodium. The flask was placed on a steam cone and a mixture of 490 g. of ethyl acetate and 10 g. of absolute ethyl alcohol was dropped in over a period of about ninety minutes. The material in the flask was refluxed gently during the addition of the ethyl acetate mixture. The heating was continued for six hours, the reaction mass cooled and 200 cc. of ether added. As much of the sodium salt as possible was poured on a filter and then washed with ether using as small a volume as possible. The total
yield of the dry, yellow sodium salt was 385 g. (71% of the theoretical).

**1,3-Diketohydrindene.**—To a 3-liter beaker containing 1200-1500 cc. of hot water was added 100 g. of the sodium salt. The solution was cooled to 70° and with vigorous agitation the sodium salt was decomposed with 100 cc. of sulfuric acid solution (3 parts of concentrated sulfuric acid and 1 part of water). The mixture was cooled in an ice-bath to 15° and filtered. The product when dry weighed 59 g. (99% of the theoretical). The total diketohydrindene obtained from 500 g. of diethyl phthalate was 236 g. of a pale yellow solid; m.p. 127-129°. Recrystallization from dioxane-benzene mixture by addition of petroleum ether yielded long glistening needles, m.p. 130-131°.

**Hydrin.**—In a 2-liter three-necked flask fitted with a reflux condenser and mechanical stirrer was placed 55 g. of sublimed selenium dioxide dissolved in 1200 cc. of dioxane and 25 cc. of water. The stirrer was started and the solution heated to approximately 60-70°. The flame was withdrawn, 73 g. of crude diketohydrindene was added and the resulting mixture refluxed for six hours. A solid separated during this period and was filtered off while the mixture was still hot. The filtrate was transferred to a distilling flask and three-fourths of the dioxane distilled. Between 400 and 500 cc. of water was added and the solution boiled to coagulate the tarry precipitate, which was then removed by filtration. The filtrate was concentrated by distillation to approximately 250 cc. and filtered. The filtrate was boiled with 1 g. of norite, filtered
again, concentrated to 125 cc. and allowed to stand at room temperature. The crude ninhydrin which crystallized was filtered, the mother liquor concentrated and a second crop of crystals obtained; total yield of crude 36-38 g.

The impure ninhydrin was contaminated with a trace of selenious acid which acted as a bleaching agent and prevented the formation of the characteristic blue color reaction with alpha-amino acids. It was purified by recrystallization from hot water with the aid of norite. Long colorless prisms of ninhydrin were obtained by crystallization at room temperature. The yield of the pure ninhydrin was 28-31 g. (31-35% of the theoretical). The product gave none of the customary tests for selenium and gave the characteristic color reactions with alpha-amino acids. It lost water of hydration and turned red between 125-130° and finally melted with decomposition at 241-243°.

**Reaction between Phenylmagnesium Bromide and Ninhydrin.** -- An ethereal solution containing 4.9 g. (0.030 mole) of ninhydrin was added dropwise to an ethereal solution containing 0.18 mole of phenylmagnesium bromide. The ninhydrin was fairly insoluble in the ether or benzene and settled to the bottom of the dropping funnel. It was thus added essentially in the solid form to the Grignard reagent. A slight reaction resulted and the reaction mixture at the end of the reaction was reddish in color. The mixture was refluxed for 4 hours at the end of which time there was a tarry deposit on the walls of the reaction flask.
The mixture was decomposed with an ice-ammonium chloride mixture and worked up in the usual manner to yield a dark red oil. The oil was dissolved in methyl alcohol and deposited a white amorphous precipitate when chilled in an alcohol-dry ice bath. The precipitate yielded white crystals from an ethyl alcohol-water mixture and then was recrystallized from ligroin. Yield was 4.8 g. of 1,2,3-triphenyl-1,2,3-trihydroxyindane, colorless needles, m.p. 177-178°. Analysis Calculated for: C_{27}H_{22}O_3; C, 82.2; H, 5.6. Found: C, 82.0; H, 5.8.
SUMMARY
The inverse addition of one mole of phenylmagnesium bromide to diphenylpropanetrione and dimethyl triketone respectively, gave the benzoate of benzoin and the acetate of phenylacetylcarbinol as the respective final products, indicating the occurrence of an intramolecular rearrangement.

The inverse addition of one mole of methylmagnesium iodide to diphenylpropanetrione gave the benzoate of methylbenzoylcarbinol as the final product.

Convincing evidence for a mechanism postulating cleavage anterior to hydrolysis was obtained by treating the diphenylpropanetrione mono-addition magnesium complex with benzoyl chloride with the resultant formation of stilbeneglycol dibenzoate.

Diphenylpropanetrione and dimethyl triketone undergo cleavage when treated with an excess of Grignard reagent. The final products which are tertiary alcohols and alpha-hydroxy ketones may be accounted for by the further addition of the Grignard reagent to the rearranged mono-addition magnesium complex of the above mechanism.

The addition of triketoinane to an excess of phenylmagnesium bromide yielded 1,2,3-trihydroxy-1,2,3-triphenylindane as the sole product.
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Abelmann, P.


The interaction of methylmagnesium iodide (2 moles) and beta-hydroxy-alpha-methylbutaldehyde leads to the formation of OH.CHCH₃.CHCH₃.CHCH₃.OH.

When an excess of methylmagnesium iodide (2.25 moles) is used, the product is contaminated with beta-methylbutane-alpha, gamma-diol, obtained by the reduction of the original aldehyde.


Catalytic Hydrogenation of Diphenyltriketone


Diphenyltriketone in benzene, reduced at 15° with platinum catalyst until 1 mole H₂ is absorbed, gives dibenzoylcarbinol (I) m.p. 110-11.5°, maintained at 106-7°, I melts, resolidifies and again melts; the final equilibrium mixture of isomers m.p. 96.8°; acetyl derivative m.p. 93°. Further reduction of I at room temperature (absorption of 2 moles H₂) gives alpha, gamma-diphenylglycerol (II) m.p. 84.5-5°; monohydrate, m.p. 97-9°; the compound exhibits a very strong tendency to undergo hydration.

II may also be prepared from diphenyltriketone, the reduction requiring about 5 hours in benzene or 2 hours in 95% ethyl alcohol. If the reduction of I is interrupted when 1 mole H₂ is absorbed, there results some II and also alpha, beta-dihydroxy-gamma-keto-alpha, gamma-diphenylpropane (or an isomer) m.p. 87-9°. It is further reduced to (II).

\[
\text{C₆H₅-COCOC₆H₅} \xrightarrow{2\text{H}} \text{C₆H₅-COCH(OH)COC₆H₅} \xrightarrow{2\text{H}} \text{I}
\]
Blaise, E. E.

The interaction between ethyl cyanoacetate and the ether additive compounds of the magnesium alkyl iodides (R.MgI, C₂H₅OC₂H₅), followed by the decomposition of the intermediate products by the addition of water, furnishes a general method for the preparation of the unsubstituted beta-ketonic esters, R.CO.CH₂.CO₂CO₂H₅.

Blatt, A. H., and Hawkins, W. L.
Hydroxy Polyketones. II. Dibenzoylecarbinol.

Dibenzoylecarbinol has been prepared and its chemical behavior is described. The carbinol which does not exist as an ene-diol, is very readily oxidized. It is cleaved by alkali and rearranges on heating to furnish the benzoate of benzoylcarbinol.

Bradley, W., and Robinson, R.
Hydrolytic Fission of Some Substituted Dibenzoylemethanes.

The hydrolytic fission of dibenzoylemethanes is a reaction characteristic of the diketonic phases. The extent of enolization, great as it
is, and the nature of the enols do not affect the result of hydrolytic fission. The hydrolysis is probably the result of the decomposition of a complex anion formed from the diketone and the OH ion. The chief factors controlling the direction of the change are the rates of formation of the two possible complex anions RCO*(OH)CH₂COR, and RCOCH₂CO*(OH)R, and the extent to which each of these breaks down with the formation of carboxylate ions.

Breckpot, R.
The Reaction of Organomagnesium Compounds on Nitriles.

The ordinary reaction of RMgX on nitriles is to yield ketones, but some nitriles yield condensed products similar to those formed by the action of sodium. The latter is explainable on the basis of a pseudo-acid tautomeric form for the nitrile. Thus the reaction should be accompanied by hydrocarbon evolution and should take place with nitriles having labile hydrogen atoms on the carbon atom next to the CN group. This is confirmed by the reactions of C₆H₅CN and CH₂:CHCH₂CN which almost completely yield ketone, while C₆H₅CH₂CN and ClCH₂CN give practically no ketone.

Calvin, Melvin, and Wood, C. L.
Conjugation of Carbonyl Groups and the Absorption Spectrum of Triketopentane.

The absorption spectrum of triketopentane dissolved in an inert hydrocarbon solvent (iso-octane) has been measured and compared with
that of diacetyl and acetone under similar conditions. On the basis of this comparison of absorption spectra, together with a consideration of the molecular dimensions, non-coplanar structure is assigned to the triketopentane.

Dilthey, W., and Last, E.
Action of Magnesium Aryl Haloids on Dicarboxylic Acids.

The action of bromobenzene and magnesium on ethyl oxalate in ethereal solution leads to the formation of benzopinacone and on ethyl succinate in ethereal solution to the formation of the glycol OH.C(C6H5)2-CH2.CH2- C(C6H5)2.OH. The hydroxy ketone, OH.C(C6H5)2-CH2.COC6H5 is obtained when phenylmagnesium bromide is boiled with ethyl malonate in ethereal solution and the product treated with acidified ice-water.

Entermann, C. E., and Johnson, J. R.
Reactivities of Various Functional Groups Toward a Grignard Reagent.

When 1 mol. of MgMeBr in Et2O reacts with 1 mol. each of two reactants, C6H5X, the proportions of the products formed indicate the following reactivities: X=CHO > COCH3 > NCO > COF > COC6H5 > COCl, COBr > CO2C2H5 > CN. The order, COF > COCl, above that Grignard reactions proceed by addition rather than by direct metathesis.

Erickson, J. L. E., and Kitchen, G. C.
The Cleavage of Cyclic Beta-Diketone. I. Tetramethyl-1,3-cyclobutanediones.

The behavior of tetramethyl-1,3-cyclobutanediones with methylmagnesium
bromide, ethylmagnesium bromide, phenylmagnesium bromide, phenyllithium, mesitylmagnesium bromide and mesityllithium has been studied in detail. They report that the compound is cleaved in a manner strictly analogous to open-chain beta-diketones. The cleavage by an excess of the Grignard reagent is represented as:

\[
\begin{array}{c}
\text{CH}_3 - \text{C} = \text{C} = \text{O} \\
\text{O} - \text{C} - \text{CH}_3 \\
\text{CH}_3
\end{array}
\quad \xrightarrow{\text{RMgX}} \quad
\begin{array}{c}
\text{CH}_3 - \text{C} - \text{C} - \text{OMgX} \\
\text{O} - \text{C} - \text{CH}_3 \\
\text{CH}_3
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3 - \text{C} = \text{C} = \text{O} \\
\text{RMgO} - \text{C} - \text{CH}_3
\end{array}
\quad \xrightarrow{(1) \text{RMgX}} \quad
\begin{array}{c}
\text{CH}_3 - \text{O} - \text{CH}_3 \\
\text{CH}_3 - \text{OH} \\
\text{CH}_3
\end{array}
\quad \xrightarrow{(2) \text{H}^+} \quad
\begin{array}{c}
\text{CH}_3 - \text{C} - \text{C} - \text{C} - \text{R} \\
\text{CH}_3 - \text{CH}_3 - \text{R}
\end{array}
\]

Fisher, E., Bergman, M., and Lipschitz, W.  
*New Synthesis of Digallic Acid and Migration of Acyl in the Partial Hydrolysis of Acylated Phenolcarboxylic Acids.*  
Ber., 51: 45-79 (1918).  

Two syntheses have already been described which were expected to lead to p-digallic acid but yielded m-digallic acid instead. A third method is now described. 3:5-diacytelgallic acid is condensed with trisacetyl-galloyl chloride, giving penta-acetyl-p-digallic acid, and this is cautiously hydrolyzed by cold, dilute ammonia solution. Again, the surprising discovery is made that the product is m-digallic acid.
Similarly, if 3:5 diacetylgallic acid is benzoylated and the acetyl groups are removed by hydrolysis, the product is not para, but m-benzoylgallic and when 4-benzoyloxy-3-acetoxybenzoic acid is partly hydrolyzed, the product is 3-benzoylprotocatechuic acid. All of these unexpected products are therefore due to the wandering of one acyl group into the position vacated on hydrolysis by another attached to a neighboring carbon atom.

Thus:

A transference of an acyl group has often been reported before but only from carbon to oxygen or nitrogen and vice versa or from nitrogen in a side chain to nitrogen in the ring but this is the first record of such a migration from one phenolic group to another. The intermediate compound, (III) might perhaps be formed.

Franks, A., and Kohn, M.
Action of Organo-magnesium Compounds on Beta-Hydroxylaldehydes and on Keto-alcohols.
Ber., 37: 4730-31 (1904).

A good yield of pentane-beta-delta-diol, OH.CHCH₃.CH₂CHCH₃.OH, may be obtained by the action of methylimagnesium iodide (2 moles) on aldol. Diacetonealcohol and methylimagnesium iodide yield the glycol, OH.C(CH₃)₂-.CH₂.C(CH₃)₂.OH.
The preparation of glycols by the action of organo-magnesium compounds on keto-alcohols has been investigated. The action of methylmagnesium iodide on acetopropyl alcohol gives the glycol \( \text{OH.C(CH}_3\text{)}_2.\left[\text{CH}_2\right]_3.\text{OH} \). The glycol \( \text{OH.C(CH}_3\text{)}_2.\left[\text{CH}_2\right]_4.\text{OH} \) is formed by the action of methyl-magnesium iodide and acetobutyl alcohol.

Grignard reagents react more readily with CO groups than with ethylene oxides in alpha-oxido ketones (I). Since highly hindered alpha-beta-unsaturated ketones readily form I, the CO group in I is not expected to react with Grignard reagents. When I is refluxed for 3 hours with methylmagnesium iodide in ethyl ether, the corresponding alpha-beta-unsaturated ketone is recovered as the Grignard reagent acts as a reducing agent and one mole of methane is evolved for each mole of I.

When alcoholic solutions of diphenyl triketone and o-phenylenediamine are mixed and cooled, benzoylphenylquinoxaline \( \text{C}_6\text{H}_5.\text{C} = \text{C}.\text{CO.C}_6\text{H}_5 \) is obtained.
Geissman, T. A., and Morris, L.
The Reaction Between Cyclic-Beta-Diketones and Grignard Reagents. II. 8,8-Dimethylperinaphthindandione-7,9.

The reaction between phenylmagnesium bromide and 8,8-dimethylperinaphthindandione-7,9 is studied. The diketonic function is not cleaved under any of the conditions used. Three products are obtained, two of which are the result of normal addition to either one or both of the carbonyl groups, the other being the result of 1,2 addition to one of the carbonyl groups and 1,4 addition to the other.

Geissman, T. A. and Tulagin, V.
The Reaction Between Cyclic-Beta-Diketones and Grignard Reagents. I,3 Diketo-2,2-dimethylhydrindene.

The product resulting from the addition of a mole of Grignard reagent to a beta-diketone resembles 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.
The importance of the steric-configurations of the groups involved is indicated. In the case of 1,3-diketo-2,2-dimethylhydrindene, a chelated complex cannot form and as a result cleavage does not occur.

Geissman, T. A., and Tulagin, V.
The Reaction Between Cyclic-Beta-Diketones and Grignard Reagents. III 2-Methyl-2-benzoylhydrindone.

The reaction between phenylmagnesium bromide and 2-methyl-2-benzoylhydrindone follows two courses, leading to products derived from (a)
diaddition to the carbonyl groups and (b) cleavage. Cleavage occurs only when the initial attack by the reagent is on the extracyclic carbonyl group. It is postulated that the ability of the monoaddition product to form an intramolecular coordination complex is not a sufficient condition for cleavage.

Grignard, V.  
Action of Organo-magnesium Compounds on Beta-Ketonic Esters.  

In addition to small quantities of methane and hydrogen, ethyl acetacetate and magnesium methiodide yield products from which water regenerates the unchanged ester and magnesium iodide; the ester reacts in its enolic form. From ethyl ethylacetoacetate and magnesium methiodide, the unchanged ester, and an ester OH.C(CH₂)₂.CHC₆H₄.COOC₂H₅ are obtained; on hydrolysis with 10% potassium hydroxide, the latter yields beta-methyl-alpha-ethylbutyric acid OH.C(CH₂)₂.CHC₆H₄.COOH. If the mixture of magnesium methiodide and ethyl ethylacetoacetate is heated at 100° a glycol OH.C(CH₂)₂.CHC₂H₅.C(CH₃)₂.OH is obtained together with unchanged ester.

Grignard, V., and Blanchon, H.  
The Enolization of Ketones.  

The Grignard reagent has an enolizing reaction on ketones and it is possible to esterify the mixture of enol so produced and the accompanying tertiary alcohol from the normal reaction by means of acid chloride or anhydrides. After separation of the esters by distillation, the enolic
ester can be hydrolyzed with $H_2O$. With certain precautions the enol-keto mixture can be isolated by the decomposition of the magnesium complex by ammonium chloride. A systematic study was undertaken to establish a relation between the constitution of the ketone, its aptitude for enolization and the stability of the enol; the present paper dealing with the enolization of ketones and the preparation of the enols. To obtain the maximum amount of enolate iso-propylmagnesium bromide was selected as being the most readily prepared reagent. In general, the ketone was dissolved in an equal volume of ethyl ether and gradually introduced into the reagent. After refluxing for 30 minutes and then cooling to $-5^\circ$, the theoretical amount of acetyl chloride in 5 volumes of ethyl ether was added dropwise with stirring and the resulting yellow mass was dropped into iced water containing sodium bicarbonate. The washed and dried ethyl ether extracts, freed from solvent, were distilled under reduced pressure giving 3 fractions, the keto-enol mixture, the enol acetate and the acetate of the tertiary alcohol. The reaction was run with cyclohexamone, thujone, carvone and mesityl oxide.


The oxidation of certain beta-keto carboxylic acid esters and beta-diketones with $BzO_2H$ (I) in $CHCl_3$ was oxidized in a cold-water bath by adding the calculated amount of I in 3 portions over 0.5 hr.; the reaction was stopped after 14 hours and removal of $CHCl_3$ in vacuo left a yellow
crystal mass which, fractionally crystallized from absolute MeOH gave 5 fractions (a) containing BzOH (III) and BzCH2OBz (IV), (b) containing IV and Bz2CHOH (V), (c) containing II and V, and (d) containing V, III, and II. Treating a sample in MeOH with 3-4 ml. saturated NaHCO3 solution resulted in CO2 evolution with III, V gave a yellow color, II and IV gave a white milky turbidity; when a sample in MeOH was diluted with water and extracted with ether, the residue gave an intense brown-violet FeCl3 reaction with II, while IV gave the hydroxamic acid test. V crystallized from ligroin in fine, colorless needles, m. about 110°; 50 mg. dissolved in 150-200 ml. boiling ligroin; its dinitrophenylhydrazone m. 164-5° (from glacial HOAc); V hydrogenated with PtO2 in alcohol absorbed 8 moles H; as soon as V came in contact with PtO2 it gave a yellow color, slowly disappearing on hydrogenation. V (50 mg.) in MeOH with 2 ml. saturated NaHCO3 solution gave a yellow color which soon disappeared; addition of 8 ml. water, extraction with ether, and recrystallization of the residue from alcohol gave IV, colorless needles, m. 119°.

Kohler, E. P., and Erickson, J. L. E.,
Cleavage of Beta-Diketones. I. Cleavage by Organic Magnesium Compounds.

Beta-diketones that have no substituents in the CH2 group react with 2 equivalent of phenylmagnesium bromide; the product is a di-magnesium compound which on hydrolysis yields a beta-hydroxy ketone. The beta-diketones that have 1 or more substituents in the CH2 group likewise
react with 2 equivalents of phenylmagnesium bromide but the result in
this case is a mixture of 2 magnesium compounds because the process
involves a cleavage which is similar to that of oxido ketones. The
following list shows the diketones studied, along with the products
obtained.

<table>
<thead>
<tr>
<th>Diketone</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6H_5COCH_2COCH_3$</td>
<td>$(C_6H_5)_2C(OH)CH_2COCH_3$</td>
</tr>
<tr>
<td>$CH_3COCH_2COCH_3$</td>
<td>$(CH_3)_2C(OH)CH_2COCH_3$</td>
</tr>
<tr>
<td>$C_6H_5COCH(C_6H_5)COCH_3$</td>
<td>$C_6H_5COCH_2COCH_3 + (C_6H_5)_3COH$</td>
</tr>
<tr>
<td>$C_6H_5COCH(CH_3)COCH_3$</td>
<td>$C_6H_5COCH_2CH_3 + (C_6H_5)_3COH$</td>
</tr>
<tr>
<td>$CH_3COCH(CH_3)COCH_3$</td>
<td>$CH_3COCH(CH_3)_2 + (C_6H_5)_2C(CH_3)OH$</td>
</tr>
<tr>
<td>$CH_3COCH(CH_3)_2COCH_3$</td>
<td>$CH_3COCH(CH_3)_2 + (CH_3COCH_3)_2(CH_3)_3$</td>
</tr>
<tr>
<td>$C_6H_5COCOCOC_6H_5$</td>
<td>$C_6H_5COCHOC_6H_5 + (C_6H_5)_3COH$</td>
</tr>
</tbody>
</table>

Kohler, E. P., Richtmeyer, W. K., and Hester, W. F.
Action of Organo Magnesium Compounds on Alpha-Oxido Ketones and Esters.  

When organic magnesium compounds react with alpha oxido ketones,
they combine with the CO group only. By operating at a low temperature
and decomposing the product immediately it is possible to secure the
corresponding oxidocarbinol; otherwise the unstable magnesium derivatives
de decompose spontaneously into magnesium derivatives of aldehydes and
ketones, which may subsequently be transferred into tertiary alcohols.
Organic magnesium derivatives first transform alpha-oxido esters into
alpha-oxido ketones. The final products are therefore the same as
those obtained with these ketones.
Montagne, P. J.
Molecular Rearrangements. XIII. Phenyl Migrations.

Experiments confirm reports that when there is an intramolecular migration of a phenyl group the latter is attached before and after the rearrangement through the same C atom, i.e. the substituents remain in the same positions.

Moubasher, Radwan, Awad, Wm., Ibrahim, M., and Othman, A. M.
Indene Derivatives. VII. New Reactions of Triketoindan and Experiments with Hydrindan and related Compounds.

1,2,3-Indantrione (I) reacted vigorously with PhMgBr, giving 1,2,3-trihydroxy-1,2,3-triphenylindan (II), needles containing 1 mole C_6H_6, m. 124-30°, which lost C_6H_6 when dried in vacuo and m. 178°. II refluxed with concentrated HNO_3 gave o-C_6H_4 Bz_2, yellow, m. 147°. I with an excess CH_2H_2 gave 2,3-methylene-dioxindone, (III) pale yellow crystals, m. 165°. III heated 6 hours with MeOH-HCl gave 3,3'-dihydroxy (2,2'-biindene)-1,1'-dione (IV), violet crystals, m. 298° (from C_6H_6).

Similarly, perinaphthindan-1,2,3-trione with excess CH_2H_2 gave 2,3-methyleneoxyperinaphthindan-1-one C_{14}H_{10}O_3, m. 200°, giving a persistent orange color with H_2SO_4 hydrolyzed to 2,3-dihydroxyperinaphthindan-1-one, (V), red, m. 258°, giving a blue color with aqueous NaOH. I refluxed with 3(2H)-thienaphthenone in C_6H_6 gave 2(2,-3-dihydro-3-keto-2-thianaphthénylidene)-1,3-indandione (VI), violet, m. 275° (decomposition) (from C_6H_6), giving an orange-red fluorescence in xylene and intense blue green in H_2SO_4.
I refluxed with 1,3-indandione in glacial AcOH gave IV. By heating 1 g. 2,2'-dihydroxy (2,2'-biindan)-1,1',3,3'-tetrone (VII) 5 minutes in vacuo (or in CO₂) at 270°, o-C₆H₄(CO)₂O and IV were formed. When 1 g. VII and 5 g. p-quinone in dry C₆H₆ in a Monax tube were exposed to (May) sunlight 7 days, dehydrogenation took place and I was formed. 1,2,3-Perinaphthindantrione hydrate in H₂O with 10% NaOH and excess BzCl gave 2,3-dibenzoxypersinaphthinden-1-one, yellow-green, m. 215° (from C₆H₆ or aqueous AcOH). When this reaction was carried out without BzCl, V was formed. I hydrate with aqueous NaOH gave a deep blue color; acidification with concentrated HCl gave small amounts of hydrindantin m. 220° (decomposition). Aqueous NaOH gave a violet colored solution with hydrindantin, which was recovered on acidification.

Moubasher, Radwan, and Othman, A. M.
Reactions between Cyclic Triketones and Amines. Color Reactions of Ninhydrin and Perinaphthindane triones.

Triketohydrindene hydrate (ninhydrin) (I) reacts with EtNH₂, BuNH₂, and PhCH₂NH₂ separately to form NH₃, RCHO, and probably 2-hydroxydiketohydrindene (II), which then reacts with I, giving hydrindantin (III),
m. 225° (decomposition). Aldehydes are identified as the 2,4-dinitrophenyl-hydrazone. A mechanism is suggested for the over-all reaction. The intense blue color is believed to result from the formation of a double salt by the amine present in excess with the reduction product of the triketone. On acidification this color is lost and the reduction product is regenerated. Perinaphthindantrione (IV) with the above three amines formed dihydroxyketoperinaphthindene (V), m. 255°.

Similarly, the m-nitro derivative of IV gives the m-nitro derivative of V, m. 265°. Satisfactory products are also obtained from sec-BuNH₂, 1,3-C₆H₂(CH₂NH₂)₂, putrescine, histamine, cadaverine, glucosamine, spermine, and insulin.

Neuberg, C., and Cahill, W. M.
Phytochemical Reduction of Triketopentane.

Triketopentane is reduced by fermenting yeast to dimethylglycerol.

Pace, E.
Pinacols and Pinacolins.

In a previous paper it was shown that gamma-diketones when treated with Grignard reagents give bitertiary glycols which are very readily converted to heterocyclic derivatives of tetrahydrofurfuran, tetrahydro-pyrrole and tetrahydrothiophene. The same reaction has been applied to alpha and beta-diketones. The beta compounds do not react but the alpha derivatives give pinacols and pinacolins. Diacetyl with methylmagnesium iodide gives \[(\text{CH}_3)_2\text{C(OH)}^-\]₂.
Diphenyl Triketone

Dibenzoylmethane is dissolved in chloroform and treated with bromine in molecular proportion, mixed with 3 parts of chloroform. During the addition of the bromine, a stream of dry air is drawn through the liquid in order to remove hydrogen bromide. The residue obtained, after evaporation of the chloroform, consists of dibenzoyl bromomethane, CHBr(COC₆H₅)₂.

Dibenzoylcarbinyl acetate CH(COC₆H₅)₂·O.COC₆H₅ is prepared by the action of anhydrous potassium acetate on the bromide. Dibenzoylbromocarbinyl acetate, C(COC₆H₅)₂·Br·O.COC₆H₅ is obtained by the action of bromine on the previous compound. By heating the compound either alone or in solution, acetyl bromide is eliminated and the triketone formed. Diphenyl triketone CO(COC₆H₅)₂ is very hygroscopic and forms a stable hydrate C(COC₆H₅)₂(OH)₂.

The hydrate readily dissolves in alkalis with the formation of phenylbenzoylhydroxyacetic acid C₆H₅·CO·C(OH)C₆H₅·COOH which has not yet been isolated. After the solution has remained for some time, this compound is decomposed by the further action of the alkali; part yields benzoic acid and phenylhydroxyacetic acid, while carbon dioxide and benzoin are produced from the remainder:

(a) C₆H₅·CO·C(OH)C₆H₅·COOH + H₂O = C₆H₅·COOH + C₆H₅·CH(OH)COOH

(b) C₆H₅·CO·C(H)C₆H₅·COOH = C₆H₅·CO·COH·C₆H₅ + CO₂

By the action of excess phenylhydrazine on the triketone two substances are obtained and may be separated by treatment with benzene at ordinary temperatures; one crystallizes and has not yet been further investigated.
The second compound is soluble in benzene and consists of benzeneazotriphenylpyrazole,

![Chemical structure of benzeneazotriphenylpyrazole]

Diphenyltriketanilide, \( C_{6}H_{5}C(\text{NC}C_{6}H_{5})_{2}O(\text{OH})_{4}CO.C_{6}H_{5} \) is formed by treating the triketone with two parts of aniline at ordinary temperatures. The dianilide \( C(\text{OH})_{2}C_{6}H_{5}:\text{NC}C_{6}H_{5} \) is obtained by boiling the triketone with an alcoholic solution of aniline. Attempts to prepare other triketones from acetophenone, benzoyleacetone, acetylacetone and ethylacetoacetate have been unsuccessful.

Sachs, F., and Barschall, H.

Triketopentane. I.


The preparation of dimethyl triketone is described. Triketopentane reduces potassium permanganate in the cold without producing a precipitate of the dioxide; ammoniacal silver nitrate and chromic acid are also readily reduced; FeHling's solution and copper acetate yield cuprous oxide even in the cold, whilst metallic copper is precipitated from a boiling solution of the sulfate. The dihydrate reddens litmus. A bis-phenylhydrazone \( C_{6}H_{5}O(\text{N.NEC}C_{6}H_{5})_{2} \) and a dianil \( C_{6}H_{5}O(\text{NC}C_{6}H_{5})_{2} \) are obtained but the structures are uncertain. The interaction of o-phenylenediamine hydrochloride and triketopentane in the presence of sodium acetate results in the formation of 2:3-acetylethylquinoxaline N: C.CO.CH₃

![Chemical structure of 2:3-acetylethylquinoxaline]
The method of Ehrlich and Sachs of condensing aromatic nitroso compounds with "acid" methylene derivatives in the presence of an alkaline condensing agent and subsequent hydrolysis with mineral acids whereby the elements of water are taken up in such a way that oxygen replaces the hydrogen atoms of the methylene group, has been extended to other fatty aromatic triketones. o-Methoxyphenyltriketobutane, 2:4-dimethoxyphenyltriketobutane and 2:3:4-triketohexane have been prepared.

The preparation of triketopentane has been improved and is described in detail. The free keto-group in the bisphenylhydrazone does not react with phenylhydrazine in alcoholic solution or with semicarbazide. The configuration of the 2-acetyl-3-methylquinoxaline is confirmed by the formation of the phenylhydrazone, \( \text{C}_6\text{H}_4\cdot\text{N}:\text{C}(-\text{N}:\text{H}:)\text{CO}(-\text{N}:\text{H}:)\text{CH}_3 \), the oxime, \( \text{C}_6\text{H}_4\cdot\text{N}:\text{C}\cdot\text{CH}_3 \), the p-nitrophenylhydrazone and of the semicarbazone. The bis-semicarbazone of triketopentane \( \text{C}_3\cdot\text{C}(-\text{N}:\text{NH}:)\text{CO}(-\text{N}:\text{NH}:)\cdot\text{CH}_3 \) dissolves in alkalies and is reprecipitated by acids. Hydrazine hydrate reacts violently with triketopentane with the evolution of nitrogen and the formation of 4-hydroxy-3:5-dimethylpyrazole \( \text{C}_3\cdot\text{C}(\text{OH})\cdot\text{C}(-\text{N}:\text{NH})_3 \).
phenylbutane can be prepared by analogous methods to those described for triketopentane. The trikete COCH₃.CO.COC₆H₅ forms a beta-phenylhydrazone CH₂C(=N.HNH.C₆H₅)CO.CO.C₆H₅ which condenses with o-phenylenediamine. An excess of phenylhydrazine forms 1:5-diphenyl-3-methylpyrazole-4-azo-benzene N:N.C₆H₅. A beta-monosemicaflzone is formed. Condensation

\[
\text{CH}_3\cdot\text{C}:\text{C}:\text{C}_6\text{H}_5
\]

\[
\text{N}:\text{N}_6\text{H}_5
\]

with o-phenylenediamine gives 2-acetyl-3-phenylquinazoline CH₃.CO.C——C₆H₅.

Hydrazine reacts with triketophenylbutane to give 4-hydroxy-5-phenyl-3

methylpyrazole CH₃.C(COH):C.C₆H₅.

Schonberg, A.
Degradation Reaction in Organic Chemistry.

The degradation of the group COCOCO or COCH₂CO (I) into the group COCO (II) by warming the acids may take place through formation of a N containing intermediate. Bz₂CH₂ and PhNO yield Bz₂C:N(=O)Ph (III), yellow crystals, m. 144°C, and PhNHCH₂; acids convert III into Bz₂.

Schonberg, A., and Azzam, R.C.
Reactive Methylene Groups and Nitroso Compounds. Abnormal Action of Acids on 1,2,3-Triketones.

Dibenzoylmethane (3.4 g.) and C₆H₅NO in absolute ethyl alcohol when heated 20 - 30 minutes on the steam bath, give 2.2 g. of diphenyl triketone beta-anil oxide. Hydrolysis with H₂SO₄ give benzil. Diphenyl
triketone and H₃PO₄ in acetic acid give benzoin; with H₂SO₄ obtain benzil. Diphenyl triketone and AlCl₃ when heated for one hour at 100⁰ also give benzil.

Schonberg, A., Moubasher, R., and Mostafa, A.  
Formation of Methylene Ethers by the Action of Diazomethane on Alpha-Keto Lactones and on Diphenyl Triketone.  
C. A., 35: 6258 (1941).

Diphenyl triketone (1 g.) yields 0.2 g. of alpha, beta-methylenedioxy-beta benzoyle-alpha-phenylethylene, C₆H₅COC-CC₆H₅-0.CH₂.O when treated with an excess of diazomethane.

Schonberg, A., Moubasher, R., and Mostafa, A.  
Synthesis of Acenaphthene. II.  

Diphenyl triketone (0.5 g.) when heated with 4 g. Se at 250⁰ gives benzil.

Sharp, D. B.,  
Mechanism for the Cleavage of Certain Phenylhydrazones by bromine.  

Experiments are reported to elucidate the mechanism of the cleavage of compounds of the type ArNHN:C(COR)COR¹ by bromine in cold AcOH-AcONa to give ArNHN:CBrCOR. EtO(CO)₃Ph (I) and Ph(CO)₃Ph (II) are recovered unchanged after standing 1 - 3 days at room temperature with Br in AcOH-AcONa; EtO(CO)₃Me (III) decolorizes Br in AcOH. The 2-(p-nitrophenylhydrazones) (IV) of I and III in AcOH containing excess AcONa, treated at room temperature or less with 1 mole Br in AcOH, give 93-4%
Et bromoglyoxylate p-nitrophenylhydrazone, m. 199-201°, whereas that of II gives PhCOBr\((\text{NNHC}_6\text{H}_4\text{NO}_2-p)\) m. 245-7°; without AcONa there was no reaction. The IV of III and Ac$_2$O containing several drops concentrated H$_2$SO$_4$ give 8% Et 2,3-dioxobutanoate 2- [acetyl(p-nitrophenyl) hydrazone] (V), m. 135-6°; the IV of I gives 18% Et 3-phenyl-2,3-dioxopropanoate 2- [acetyl (p-nitrophenyl) hydrazone](VI), m. 141-2°; the IV of II gives 33% of 1,3-diphenyl-1,2,3-propanetrione 2- [acetyl (p-nitrophenyl) hydrazone] (VII), yellow, m. 202-2.5°. V-VII are not affected by Br in AcOH-AcONa. p-OgSCGH$_4$ r KST% and X in KtOH-AcOH, kept 1 hour at room temperature give 74% Et 3-phenyl-2,3-dioxopropanoate 2- [ethyl (p-nitrophenyl) hydrazone], yellow, m. 126-9°; II gives 1,3-diphenyl-1,2,3-propanetrione 2- [ethyl (p-nitrophenyl) hydrazone], m. 166-7°; these compounds are not cleaved by Br in AcOH-AcONa. A base-catalyzed mechanism is proposed for the Br cleavage.

Sharp, D. B., and Hoffman, H. A.
Chemistry of Vicinal Tricarbonyl Compounds. I. Condensation Reactions of 1,3-diphenyl-1,2,3-propanetrione.
G. A., 2920a (1951).

Bz$_2$CO (I) (14 g.) in 140 ml. C$_6$H$_6$, refluxed 3 hours with a mole portion of CEMa(CO$_2$Et)$_2$ gives 4.1 g. BzOH and 9.6 g. Bz$_2$. I (3.25g.) and 1 ml. H$_2$O, heated 15 hours at 220°, give 1.26 g. BzOH and 1.42 g. Bz$_2$. I (2.8 g.) and 2.75 g. pO$_2$NC$_6$H$_4$CH$_2$CN containing 2 drops piperidine give 43% of a 1:1 addition product, C$_{25}$H$_{16}$O$_5$N$_2$, m. 155-7°. I (5.43 g.) in 8 ml. C$_3$H$_7$N at 5°, treated with 2.4 g. CH$_2$-(CO$_2$H)$_2$ and 3.4 ml. piperidine at 5°, stirred until small bubbles begin to form, and the
product poured into excess HCl and extracted with AcOEt, gives 44% of the 1:1 addition compound (II) C₁₈H₁₄O₇, m. 149°. II (3.02 g.) and 10 ml. 20% NaOH, heated 15 minutes give 74% PhAc, 85% BzOH, and 25% H₂O₂CH₂O; these 3 compounds account for all but one of the C atoms in II; CO₂ could not be detected. Pure compounds could not be obtained from II and hot AcOH, Ac₂O,POCl₃, or concentrated H₂SO₄.


Hydrogenation over Raney nickel at 50-125° converts 1,3 diketone into a variety of products. The proportion of these products varies with the structure of the diketone and with the duration of the hydrogenation. In most instances the glycol corresponding to the diketone has been obtained in quite satisfactory yields. It seems probable that the process may be interrupted and the beta-keto alcohols obtained in similar yields. Certain diketones underwent cleavage by H at either a C to O or at a C to C linkage. Ketones or alcohols having the same C chain as the original diketone are formed by hydrogenolysis of O, particularly in those compounds which had branched radicals adjacent to one CO. The hydrogenolysis of the C chain occurs with the formation of aldehydes and ketones under quite mild conditions (50°), particularly in the case of the substituted 1,3 diketones. The relative labilities of the 2 bonds c and d of the unsymmetrical diketone C₁₈H₁₄O₇ in an unsymmetrical diketone
seem to be approximately the same irrespective of whether the reaction is alcoholysis or hydrogenolysis. Diacetyl methane $\text{CH}_3\text{COCH}_2\text{COCH}_3$ at $125^\circ$ for 1 hour gives $\text{C}_2\text{H}_5\text{OH}$, $(\text{CH}_3)\text{CHOH}$, unsaturated compounds and 80% pentane-2-4-diols. Dibenzoylmethane at $125^\circ$ for 0.8 hour, gives $\text{C}_6\text{H}_5\text{CCH}_3$,

11% $\text{C}_2(\text{CH}_2\text{C}_6\text{H}_5)_2$, 20% 1,3-diphenylpropan 1-ol and 51% 1,3-diols.

The results with other 1,3 diketones are also given and discussed.

Stieglitz, J., and Stagner, B. A.

It has now been established that $\text{C}_6\text{H}_5\text{NHCH}_3$ is formed in quantity by the hydrolysis of the rearrangement product of $(\text{C}_6\text{H}_5)_3\text{CN}(\text{CH}_3)\text{OH}$ and that $(\text{C}_6\text{H}_5)_2\text{CO}$ is also formed. The formation of $\text{C}_6\text{H}_5\text{NHCH}_3$ opens up the whole problem of the theory of molecular rearrangements of $\text{NCH}_2\text{OH}$ derivatives previously proposed by Stieglitz, according to which an univalent N derivative is first formed under the influence of the reagent used to effect the rearrangement, the free or latent valences of the unsaturated N atom being then assumed to have the power to take the radical R from the C atom; e.g. $\text{RCONHCH}_3$ $\rightarrow$ $\text{RCON}$ $\rightarrow$ CO:NR. In the case of $(\text{C}_6\text{H}_5)_3\text{CN}(\text{CH}_3)\text{OH}$ the formation of a simple univalent N derivative $(\text{C}_6\text{H}_5)_3\text{CN}$ is impossible. Of the various theories which suggested themselves when the first indication of this rearrangement was obtained, one is excluded by the observation that $(\text{C}_6\text{H}_5)_2\text{CO}$ is formed, namely that there is a primary dissociation into a bivalent N derivative, $(\text{C}_6\text{H}_5)_3\text{CNCH}_3$ for then hydrolysis of the product should yield $\text{HON}\left[(\text{C}_6\text{H}_5)_2\text{C}\right]$ $\rightarrow$ $\text{C}^-$ and not
(6_5)^2 CO, and not the slightest indication of the presence of the pinacol was obtained. Of the other theories only 2 need to be taken into account: Beckmann's that the rearrangement simply involves direct exchange of radicals,

\[ \text{R}_2\text{R}'\text{CN}(\text{CH}_3)\text{OH} \xrightarrow{\text{PCl}_3} \text{R}_2\text{C} (\text{OH}) \text{N} (\text{CH}_3)\text{R}' \xrightarrow{\text{PCl}_3} \text{R}_2\text{CClN} (\text{CH}_3)\text{R}' + \text{PCl}_3 \]

or as modified by Kühara:

\[ \text{R}_2\text{R}'\text{CN}(\text{CH}_3)\text{OPCl}_4 \rightarrow \text{R}_2\text{C} (\text{OPCl}_4) \text{N} (\text{CH}_3)\text{R}' \rightarrow \text{R}_2\text{CClN} (\text{CH}_3)\text{R}' + \text{PCl}_3 \]

or that involving the intermediate formation of univalent or other unsaturated N derivatives, the observation that \( \text{P}_2\text{O}_5 \) effects the rearrangement of \( \text{NH}_2\text{OH.HCl} \) suggesting the possibility that salts of \( \text{NH}_2\text{OH} \), by the loss of \( \text{H}_2\text{O} \) or its equivalent may form salts of univalent N compounds which then rearrange, thus:

\[ \text{R}_2\text{R}'\text{CNCH}_3\text{Cl} \rightarrow \text{R}_2\text{R}'\text{CNCH}_3\text{Cl} \rightarrow \text{R}_2\text{C} \cdot \text{NCH}_3\text{R'} \text{Cl} \rightarrow \text{R}_2\text{CClNCH}_3\text{R'} \].

Stieglitz and Stagner discuss the evidence in favor of and against each view and conclude that unless definite evidence is brought that salts leading to the intermediate formation of salts of univalent N derivatives are involved in their rearrangement, the rearrangement of \((6_5)_2\text{CNCH OH, the relation of stereoisomerism of oximes to their rearrangement products and the spontaneous rearrangement of (C_6H_5)_2\text{C:NO}_2\text{C}_6^3\text{H}_5 \) are inconsistent with the theory of the intermediate formation of univalent N derivatives. Other facts, such as the rearrangement of azides and especially the non-rearrangement of chloroimidobenzophenones, chloroimido esters and \((6_5)_3\text{CN}(\text{CH}_3)\text{Cl}, are inconsistent, without further specific assumptions with
Beckmann's theory of a direct exchange of radicals but in striking agreement with Stieglitz's theory of the intermediate formation of unsaturated N derivatives in the rearrangements of chloroamines, hydroxylamines and azides. Unless further experiments should modify these facts, it should be considered that both types of rearrangements may take place. Common to both theories and the most important feature in their modern forms is that the rearrangements originate from the tendency of unstable positive atoms Cl⁺, -O⁺, N⁺, etc., to go over into their stable negative forms, Cl⁻, -O⁻, N⁻, by a capture of electrons from other atoms in the same molecule, a change which is effected in the rearrangements in question. The same fundamental cause, the charge on unstable atoms, with consequent shifting of electrons, underlies the rearrangement of peroxides, hydrazines, acylhalogenanilides, arylhydroxylamines and similar compounds.

Vorlander, D., Osterburg, J., and Meye, O.
Beta-Phenylbenzalacetophenone.

Dibenzoylmethane with 2 moles of phenylmagnesium bromide give beta, beta-diphenyl-beta-hydroxypropiophenone.

Wegmann J., and Dahn H.
Carbonyl Groups and Aromatic Hydrocarbons. V. The Effect of Neighboring Substituents upon the Addition Capacity of Carbonyl Groups.

Benzil does not react with hydrocarbons in the presence of catalysts probably because of the hindering effect of the Ph group. To study this effect further, BzAc (I) and BzCOCH₂Br (II) are allowed to react
with \( \text{C}_6\text{H}_6 \) in the presence of \( \text{AlCl}_3 \). \( \text{I, b} \_15 \text{ 110-15}^\circ \), is prepared in 60% yield by refluxing 20 g. \( \text{PhCH}_2\text{Ac} \) with 17 g. \( \text{SeO}_2 \) in 100 cc. dioxane for 4 hours. When \( \text{I} \) is allowed to react with \( \text{C}_6\text{H}_6 \) in the presence of \( \text{AlCl}_3 \), \( \text{BrSOH} \) is the only reaction product isolated. Bromination by addition of 3.5 g. \( \text{Br} \) in 5 cc. \( \text{CHCl}_3 \) to the boiling solution of 2 g. \( \text{I} \) in 15 cc. absolute \( \text{CHCl}_3 \) gives 90 percent \( \text{II} \), yellow oil, \( \text{b} \_10 \text{ 149}^\circ \). \( \text{II} \), when mixed with a cold saturated solution of \( \text{o-C}_6\text{H}_4(\text{NH}_2)_2 \), gives 2-phenyl-3-(bromomethyl)quinoxaline, long needles, m. 121-2\(^\circ\).

When 2.5 g. \( \text{II} \) in 50 cc. \( \text{C}_6\text{H}_6 \) is stirred with 3 g. \( \text{AlCl}_3 \) at 70\(^\circ\) for 1 hour the mixture decomposed with ice-HCl, the \( \text{C}_6\text{H}_6 \) layer washed with \( \text{NaHCO}_3 \) and \( \text{H}_2\text{O} \), and the dried \( \text{C}_6\text{H}_6 \) solution evaporated to dryness, the residual oil crystallizes on standing. After washing with petroleum ether, the product is chromatographed on \( \text{Al}_2\text{O}_3 \) and eluted with \( \text{C}_6\text{H}_6 \) petroleum ether (1:1), giving (bromomethyl) benzoin (III), m. 93-4\(^\circ\). The structure of III is proven by heating it with \( \text{CrO}_3 \) in \( \text{AcOH} \) for 10 minutes at 60\(^\circ\), giving 40% \( \text{PhCOCH}_2\text{Br} \) and 65% \( \text{BzOH} \).

When 2 g. \( \text{BzCOBz.H}_2\text{O} \) (IV) is treated in 70 cc. of \( \text{C}_6\text{H}_6 \) with 2 g. \( \text{AlCl}_3 \), the deep blue solution heated at 60\(^\circ\) for 1 hour and the mixture worked up in the usual way, 1 g. benzil, m. 97\(\text{^o}\), is the only product isolated. The same result is obtained when IV is treated with \( \text{C}_6\text{H}_6 \) and \( \text{H}_2\text{SO}_4 \) at 0\(^\circ\).

Whitmore, F. C.

Common Basis of Intramolecular Rearrangements.


Many of the "abnormal" reactions of organic chemistry including most intramolecular rearrangements are correlated by the following simple
assumptions: A non-ionic attachment between an atom like C or N and an electronegative atom or group is broken during the reaction. At the instant of removal of the electronegative group it takes a completed octet of electrons with it. The atom that had shared an electron pair with the electronegative group is thus left with only a sextet of electrons. This deficiency of 2 electrons may induce a migration of an electron pair from an adjacent atom, thus giving rise to "abnormal" or rearranged products. In the case of CO compounds a C with an open sextet may be formed by the addition of a positive ion to the O. In this case, also, the presence of the open sextet induces rearrangement. The application of these simple principles is already proving helpful in experimental studies of "abnormal" reactions of simple aliphatic compounds.

Wieland, H., and Bloch, S.
Action of Nitrous Gases on 1:3-Diketones.

Bis-nitrosodibenzoylmethane, CH(C₆H₅CO)₂-N₂O₂·CH(C₆H₅CO)₂, obtained by passing the nitrous fumes evolved from arsenious oxide and nitric acid into an absolute ethereal solution of dibenzoylmethane is decomposed by boiling alcohol or more easily by cold alcoholic potassium hydroxide or ammonia, giving the oxime C₆H₅.CO.C(=N.OH).CO.C₆H₅. This oxime is rapidly hydrolyzed by 20% sodium hydroxide forming benzoic acid and hydrogen cyanide. From the ethereal mother liquors of bis-nitrosodibenzoylmethane diphenyl triketone, C₆H₅.CO.CO.CO.C₆H₅, separates as a crystalline hydrate.

In order to convert the whole of the dibenzoylmethane into the triketone,
the bisnitroso derivative is converted by cold dilute alcoholic potassium hydroxide into the foregoing oxime and this is then decomposed in ethereal solution by the nitrous gases.

Zelinsky, N.
Behavior of Biketones Towards Organo-magnesium Compounds.

Diacetyl when mixed with a cold suspension of methylmagnesium iodide in absolute ether is readily converted into pinacolone. Acetylacetone and the organo-magnesium compound interact energetically but the yield of product is small and consists of a glycol corresponding in composition with the formula C\(_7\)H\(_{16}\)O\(_2\). Acetonylacetone when similarly treated gives a quantitative yield of the glycol OH.C(CH\(_3\))\(_2\).CH\(_2\).CH\(_2\).C(CH\(_3\))\(_2\).OH.

Zerevitinoff, T.,
Estimation of Active Hydrogen in Organic Compounds.

An extension of the method previously described to the determination of the number of replaceable hydrogen atoms in hydroxy-, thiol-, amino-, and imino-compounds. Frequently the results obtained are high owing to the development of heat from the formation of the compound of pyridine with methylmagnesium iodide, and the further interaction of the pyridine and iodide with evolution of gas. The mixture is therefore cooled after the first evolution of gas has occurred. The hydroxy-compounds of the flavone type have been examined and good results obtained even where the hydroxyl group is in the ortho-position. The method also succeeds
with mercaptans, such as propyl, isobutyl or phenyl derivatives and with imido-compounds such as succinimide, oxanilide or phthalimide. The acid amides, like acetamide, react in the cold with one mole of methylmagnesium iodide, and on heating at $85^\circ$, with another mole. The error due to the action of the pyridine is estimated by carrying out a blank experiment.

The reaction has been applied to tautomeric compounds such as acetylacetone and ethyl acetoacetate and at $100^\circ$ these possess one active hydrogen atom. Malonic acid contains three replaceable hydrogen atoms.
VITA
Reuben Miller was born in New York City on September 21, 1922. His primary and secondary education was obtained in the public schools of the City of New York.

After graduating from Samuel J. Tilden High School in January 1939, he attended the College of the City of New York, from which he received the Bachelor of Science degree in Chemistry, in January 1943. He entered the United States Army Air Forces as an Aviation Cadet in January 1943 and received a commission as a 2nd Lieutenant in November 1943. He then served two years with the 13th Air Force in the Asiatic-Pacific Theater of Operations as Operations Officer, Combat Intelligence Officer, and Photo Intelligence Officer. Following his return to inactive duty in May 1946, he accepted a position as chemist in the Penicillin Department of the Lederle Laboratories, Division of the American Cyanamid Company and worked there until September 1947. He married Jutta Ginette Popik of Montreal, Canada, on April 20, 1947.

In September 1947 he entered the Graduate School of Louisiana State University and received the degree of Master of Science in Chemistry in June 1950. He is a member of the American Chemical Society, The Louisiana Academy of Sciences and Phi Lambda Upsilon.

He remained at Louisiana State University serving as a Teaching Graduate Assistant in the Organic Laboratory and is now a candidate for the degree of Doctor of Philosophy in Chemistry.