Addition of organometallic compounds to conjugated systems

Robert Havens Kirby
Iowa State College

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UMI®
ADDITION OF ORGANOMETALLIC COMPOUNDS
TO CONJUGATED SYSTEMS

by

Robert H. Kirby

A Thesis Submitted to the Graduate Faculty
for the Degree of
DOCTOR OF PHILOSOPHY
Major Subject Organic Chemistry

Approved:
Signature was redacted for privacy.

In charge of Major work
Signature was redacted for privacy.

Head of Major Department
Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
1937
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ACKNOWLEDGEMENT

The author wishes to express his appreciation to Dr. Henry Gilman for valuable suggestions and encouragement given during the progress of this investigation.
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</tr>
</tbody>
</table>
INTRODUCTION

When an organometallic compound reacts with a substance containing an unsaturated linkage, reduction, enolization, condensation or addition may occur. If alternate multiple and single bonds, a conjugated system, are present, the reaction may be further complicated by the competitive processes of 1,2-, 1,4- and in a few cases, 1,6-addition. Fortunately, under controlled conditions, addition reactions predominate and the amount of each product may be determined. In the following example, chalcone (A), which contains a conjugated system composed of one ethylenic and one carbonyl linkage, adds phenyllithium and the product of the reaction consists of about five times as much of the unsaturated carbinol resulting from 1,2-addition to the carbonyl group, as saturated ketone from 1,4-addition to the conjugated system.

\[
\begin{align*}
    \text{C}_6\text{H}_5\text{CH}=&\text{CHOC}_6\text{H}_5 & \text{C}_6\text{H}_5\text{Li} \\
    \text{HOH} & \rightarrow \text{C}_6\text{H}_5\text{CH}=&\text{CHOC}_6\text{H}_5 & \text{C}_6\text{H}_5\text{Li} \\
    \text{OH} & \rightarrow \text{C}_6\text{H}_5\text{CH}=&\text{CHOC}_6\text{H}_5 & \text{HOH} \\
    \text{C}_6\text{H}_5\text{CH}=&\text{CHOC}_6\text{H}_5 & \text{C}_6\text{H}_5\text{Li} & \rightarrow \text{C}_6\text{H}_5\text{CH}=&\text{CHOC}_6\text{H}_5 & \text{C}_6\text{H}_5\text{Li} & \rightarrow \text{C}_6\text{H}_5\text{CH}=&\text{CHOC}_6\text{H}_5 & \text{HOH} \\
    \text{A} & \rightarrow \text{C}_6\text{H}_5\text{CH}=&\text{CHOC}_6\text{H}_5 & \text{C}_6\text{H}_5\text{Li} & \rightarrow \text{C}_6\text{H}_5\text{CH}=&\text{CHOC}_6\text{H}_5 & \text{C}_6\text{H}_5\text{Li} & \rightarrow \text{C}_6\text{H}_5\text{CH}=&\text{CHOC}_6\text{H}_5 & \text{HOH} \\
\end{align*}
\]

In this thesis an effort has been made to record and correlate all important data concerned with the addition of
organometallic compounds to substances having conjugated systems. The three brief reviews which have been published are confined to discussions of Grignard reagents (1). Studies dealing with the reactions of many conjugated systems composed of the elements carbon, oxygen, nitrogen and sulfur, with a limited number of organometallic compounds are numerous. Investigations of the reactions of a variety of organometallics with a single unsaturated compound are few and include only the more common metallic compounds. This thesis records the results of some studies treating principally the influence of the metallic atom upon the mode of addition of conjugated systems.

The relative reactivity of the organometallic compound is undoubtedly one of the many factors influencing addition reactions. The value of a knowledge of such reactivities in predicting the course of the reactions of polyfunctional reagents cannot be over-emphasized if the full worth of organometallic compounds to problems of synthetic and theoretical

interest is to be realized. Accordingly, contributions from
the study of conjugated systems to our knowledge of the rela-
tive reactivity of organometallic compounds are of specific
interest.

Investigations of the addition reactions of conjugated
systems have also contributed to problems of functional group
reactivity, synthesis, reaction mechanism, steric hindrance
and structure in aromatic rings.
HISTORICAL

Years ago, Wagner (2) reacted diethylzinc with acrolein and obtained ethylvinylearbinol. This reaction appears to be the first recorded addition of an organometallic compound to a substance having a conjugated system. Somewhat later, it was found that methylmagnesium iodide added to the carbonyl group in mesityl oxide (3). It is appropriate that the first 1,4-addition (interpreted in a different manner) of an organometallic compound was carried out by Grignard when he added ethyl ethylideneacetoacetate to methylmagnesium iodide (4). However, it remained for Kohler and his co-workers to elucidate the many factors influencing such reactions as well as the reaction mechanism in a series of classical investigations extending over a period of more than thirty years.

α-Ethylenic Aldehydes

Until the recent investigations of Stevens (5), it had been generally accepted that the α-unsaturated aldehydes added Grignard reagents only to the carbonyl group. Table I

(2) Wagner, Bull. soc. chim., (2) 42, 330 (1884).
(3) Grignard, Compt. rend., 130, 1322 (1900).
(4) Grignard, ibid., 134, 850 (1902).
gives the percentage yields of unsaturated carbinol (the 1,2-addition product) and saturated aldehyde (the 1,4-addition product) obtained from the reactions of crotonaldehyde and various Grignard reagents. Table II records the reactions run by earlier investigators and in all cases only 1,2-addition was

TABLE I

ADDITION REACTIONS OF CROTONALDEHYDE (5)

<table>
<thead>
<tr>
<th>Grignard Reagent</th>
<th>Unsaturated Carbinol (a)</th>
<th>Saturated Aldehyde (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅MgBr</td>
<td>90</td>
<td>0.1</td>
</tr>
<tr>
<td>C₂H₅MgBr</td>
<td>70.3</td>
<td>0.1</td>
</tr>
<tr>
<td>n-C₃H₇MgBr</td>
<td>78.3</td>
<td>Trace</td>
</tr>
<tr>
<td>CH₂=CHCH₂MgBr</td>
<td>----</td>
<td>Trace</td>
</tr>
<tr>
<td>iso-C₃H₇MgBr</td>
<td>46.5</td>
<td>0.3</td>
</tr>
<tr>
<td>tert.-C₄H₉MgBr</td>
<td>3</td>
<td>10.8</td>
</tr>
<tr>
<td>tert.-C₄H₉MgCl</td>
<td>30.6</td>
<td>20.6</td>
</tr>
<tr>
<td>tert.-C₅H₁₁MgCl</td>
<td>16.3</td>
<td>22.6</td>
</tr>
</tbody>
</table>

(a) The general formulas for the carbinol and saturated aldehyde are CH₃CH=CHCHR and CH₃CHRCH₂CHO, respectively, where R represents the organic radical of the Grignard reagent used.
**TABLE II**

**ADDITION REACTIONS OF α-ETHYLENIC ALDEHYDES (a)**

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Organometallic</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂=CHCHO</td>
<td>C₆H₅MgBr</td>
<td>6, 7</td>
</tr>
<tr>
<td></td>
<td>CH₃MgI</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>C₂H₅MgX (b)</td>
<td>7, 9, 10</td>
</tr>
<tr>
<td></td>
<td>(C₃H₅)₂Zn</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>n-C₆H₁₄MgX</td>
<td>9, 10</td>
</tr>
<tr>
<td></td>
<td>iso-C₆H₁₁MgX</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>n-C₆H₁₂MgX</td>
<td>9, 10</td>
</tr>
<tr>
<td></td>
<td>iso-C₆H₁₃MgX</td>
<td>10</td>
</tr>
</tbody>
</table>

CH₂=CHBrCHO

|                | CH₃MgBr       | 11        |
|                | C₂H₅MgX       | 11        |

CH₂CH=CHCHO

|                | α-C₆H₁₄H₇MgBr | 12        |
|                | CH₃MgI        | 13        |
|                | C₂H₅MgBr      | 9, 14     |
|                | n-C₆H₁₁MgBr   | 14, 15    |
|                | iso-C₆H₁₂MgBr | 13        |

(a) Only the 1,2-products were isolated from the reactions given in this table.

(b) In this and succeeding tables, X represents a halogen atom not definitely specified in the literature.

(6) Klages and Klenk, Ber., 39, 2552 (1906).
(8) Wohl and Losanitsch, Ber., 41, 3621 (1908).
(10) Bouis, ibid., (10) 9, 402 (1928).
(11) Lespietau, Compt. rend., 156, 113 (1910); ibid., 158, 979 (1911).
(15) Reif, Ber., 41, 2759 (1908).
TABLE II (Continued)

<table>
<thead>
<tr>
<th>Chemical Compound</th>
<th>Reactant</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CH=CH(CH₃)CHO</td>
<td>CH₃MgBr</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>C₆H₅MgBr</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>n-C₆H₇MgX</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>iso-C₆H₇MgX</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>iso-C₆H₅MgX</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>iso-C₆H₁₁MgBr</td>
<td>16</td>
</tr>
<tr>
<td>C₆H₅CH=CH(CH₃)CHO</td>
<td>CH₃MgI</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>C₆H₅MgBr</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>n-C₆H₇MgX</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>iso-C₆H₇MgX</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>iso-C₆H₅MgX</td>
<td>17</td>
</tr>
<tr>
<td>(CH₃)₂C=CHCH₂CH₃-</td>
<td>C₆H₅MgX</td>
<td>18</td>
</tr>
<tr>
<td>C(CH₃)=CHCHO</td>
<td>CH₃MgI</td>
<td>13, 18</td>
</tr>
<tr>
<td>(Citraldehyde)</td>
<td>C₆H₅MgX</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>iso-C₆H₅MgX</td>
<td>18</td>
</tr>
<tr>
<td>C₆H₅CH=CHCHO</td>
<td>C₆H₅MgBr</td>
<td>19, 20</td>
</tr>
<tr>
<td></td>
<td>p-C₆H₅C₆H₄MgI</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>CH₃MgI (c)</td>
<td>22, 23</td>
</tr>
<tr>
<td></td>
<td>C₆H₅MgI (c)</td>
<td>23</td>
</tr>
<tr>
<td>C₆H₅CH=CBrCHO</td>
<td>C₆H₅MgBr</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>CH₃MgI</td>
<td>22</td>
</tr>
</tbody>
</table>

(c) Some cinnamic alcohol was found in the reaction product.

(16) Abelmann, ibid., 40, 4589 (1907), 43, 1574 (1910).
(17) Bjelouss, ibid., 43, 2330 (1910).
(18) Austerweil and Cochin, Compt. rend., 151, 440 (1912).
(20) Muskat and Ludeman, Ber., 62B, 2284 (1929).
(22) Sand and Singer, Ber., 35, 3186 (1902).
reported. From these tables it is apparent that 1,4-addition to such conjugated systems is highly restricted, not greatly influenced by an α-bromine atom and has been found to occur to an appreciable extent only with the tert.-butyl- and tert.-amylmagnesium compounds.

α-Ethylenic Ketones

A summary of the reactions of ethylenic ketones with organometallic compounds is given in Tables III, IV and V. The data in Table III were obtained by Kohler (7) under comparable reaction conditions. The carbinols were not isolated, but destroyed by oxidation with permanganate and the yields were based upon the amount of ketone remaining. Tables IV and V should not be interpreted without considering that the reactions were carried out by many investigators and under varying experimental conditions. Table V lists only alicyclic compounds. A few additional reactions of ketones may be found under the discussions, "Crossed Conjugated Systems" and "Cis and Trans Isomers."

By combining the data recorded in Tables III, IV and V, it is possible to formulate simple rules helpful in predicting the type of addition which will occur when an organometallic compound adds to any α-unsaturated ketone. The
### TABLE III

**ADDITION REACTIONS OF α-ETHYLENIC KETONES WITH ETHYL- AND PHENYL-MAGNESIUM BROMIDES**

<table>
<thead>
<tr>
<th>Ketone</th>
<th>( \text{Percentage Yields of 1,4-Product} )</th>
<th>( \text{C}_2\text{H}_5\text{MgBr} )</th>
<th>( \text{C}_6\text{H}_5\text{MgBr} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ( \text{CH}_3\text{CH}=\text{CHCOCH}_3 )</td>
<td></td>
<td>75</td>
<td>40</td>
</tr>
<tr>
<td>2. ( \text{(CH}_3\text{)}_2\text{C}=\text{CHCOCH}_3 )</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3. ( \text{C}_6\text{H}_5\text{CH}=\text{CHCOCH}_3 )</td>
<td></td>
<td>60</td>
<td>12 Cf. (19)</td>
</tr>
<tr>
<td>4. ( \text{C}_6\text{H}_5\text{CH}=\text{CHCOC}_6\text{H}_5 )</td>
<td></td>
<td>71</td>
<td>40</td>
</tr>
<tr>
<td>5. ( \text{C}_6\text{H}_5\text{CH}=\text{CHCOCH(CH}_3\text{)}_2 )</td>
<td></td>
<td>100</td>
<td>88</td>
</tr>
<tr>
<td>6. ( \text{C}_6\text{H}_5\text{CH}=\text{CHCO}(\text{CH}_3)_2 )</td>
<td></td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>7. ( \text{p-CH}_2\text{C}_6\text{H}_4\text{CH}=\text{CHCOCH}_3 )</td>
<td></td>
<td>63</td>
<td>13</td>
</tr>
<tr>
<td>8. ( \text{C}_6\text{H}_5\text{CH}=\text{CHCOCH}_2\text{C}(\text{H})\text{(C}_6\text{H}_5)\text{C}_6\text{H}_5 )</td>
<td></td>
<td>100</td>
<td>93</td>
</tr>
<tr>
<td>9. ( \text{C}_6\text{H}_5\text{CH}=\text{CHCOCH}_2\text{CH(C}_6\text{H}_5)_2 )</td>
<td></td>
<td>100</td>
<td>99</td>
</tr>
<tr>
<td>10. ( \text{CH}_2=\text{CHCOC}_6\text{H}_5 )</td>
<td></td>
<td>100 (24)</td>
<td>100 (24)</td>
</tr>
<tr>
<td>11. ( \text{CH}_2\text{CH}=\text{CHCOC}_6\text{H}_5 )</td>
<td></td>
<td>100 (24)</td>
<td>100 (24)</td>
</tr>
<tr>
<td>12. ( \text{(CH}_3\text{)}_2\text{C}=\text{CHCOC}_6\text{H}_5 )</td>
<td></td>
<td>---</td>
<td>95 (24)</td>
</tr>
<tr>
<td>13. ( \text{CCl}_2\text{CH}=\text{CHCOC}_6\text{H}_5 )</td>
<td></td>
<td>---</td>
<td>95</td>
</tr>
<tr>
<td>14. ( \text{C}_6\text{H}_5\text{CH}=\text{CHCOC}_6\text{H}_5 )</td>
<td></td>
<td>99</td>
<td>94 Cf. (25)</td>
</tr>
<tr>
<td>15. ( \text{p-CH}_2\text{OC}_6\text{H}_4\text{CH}=\text{CHCOC}_6\text{H}_5 )</td>
<td></td>
<td>98</td>
<td>96</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Volume (mL)</th>
<th>1.0% Toluene (a)</th>
<th>2.0% Toluene (b)</th>
<th>5.0% Toluene (c)</th>
<th>10.0% Toluene (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>---</td>
<td>0.01</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>41 (19)</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>100</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>100</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>100</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>100</td>
<td>---</td>
<td>0.01</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>99</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
<td>0.05</td>
</tr>
</tbody>
</table>

(continued)
### TABLE IV

**Addition Reactions of α-Ethylene Ketones with Miscellaneous Organometallic Compounds**

<table>
<thead>
<tr>
<th>Ketone</th>
<th>Organometallic Compound</th>
<th>Type of Addition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, ((\text{CH}_3)\text{CH}≡\text{COCCH}_3)</td>
<td>(\text{C}_6\text{H}_5\text{MgBr})</td>
<td>1-2</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>(\text{CH}_3\text{MgI})</td>
<td>1-2</td>
<td>3,13,28</td>
</tr>
<tr>
<td>(\text{tert.-C}_4\text{H}_9\text{MgCl})</td>
<td>1-2</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_5\text{CH}_3\text{MgI})</td>
<td>1-2</td>
<td></td>
<td>29</td>
</tr>
<tr>
<td>2, (\text{CH}_3\text{CH}≡\text{COCCH}_3)</td>
<td>(\text{CH}_3\text{MgI})</td>
<td>1-2</td>
<td>30</td>
</tr>
<tr>
<td>(\text{iso-C}_4\text{H}_9\text{MgCl})</td>
<td>1-2 and 1-4</td>
<td>5,30</td>
<td></td>
</tr>
<tr>
<td>(\text{tert.-C}_4\text{H}_9\text{MgCl})</td>
<td>1-2</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>(\text{iso-C}_5\text{H}_11\text{MgBr})</td>
<td>1-2</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>3, (\text{CH}_3\text{CH}≡\text{C}(\text{CH}_3)\text{COCH}_3)</td>
<td>(\text{CH}_3\text{MgI})</td>
<td>1-2</td>
<td>31</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_5\text{MgBr})</td>
<td>1-2 and 1-4</td>
<td></td>
<td>31</td>
</tr>
<tr>
<td>(\text{n-C}_4\text{H}_9\text{MgBr})</td>
<td>1-2 and 1-4</td>
<td></td>
<td>31</td>
</tr>
<tr>
<td>4, (\text{C}_2\text{H}_6\text{C}(\text{CH}_3)≡\text{C}(\text{CH}_3)\text{COCH}_3)</td>
<td>(\text{CH}_3\text{MgI})</td>
<td>1-2</td>
<td>31</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_5\text{MgBr})</td>
<td>1-2</td>
<td></td>
<td>31</td>
</tr>
<tr>
<td>(\text{n-C}_4\text{H}_9\text{MgBr})</td>
<td>1-2</td>
<td></td>
<td>31</td>
</tr>
<tr>
<td>(\text{n-C}_3\text{H}_7\text{MgBr})</td>
<td>1-2</td>
<td></td>
<td>31</td>
</tr>
<tr>
<td>5, (\text{n-C}_3\text{H}_7\text{CH}≡\text{C}(\text{CH}_3)\text{COCH}_3)</td>
<td>(\text{C}_6\text{H}_5\text{MgBr})</td>
<td>1-2 and 1-4</td>
<td>31</td>
</tr>
<tr>
<td>6, (\text{CH}_3\text{CH}≡\text{C}(\text{CH}_3)≡\text{COC(CH}_3)_3)</td>
<td>(\text{C}_6\text{H}_5\text{MgBr})</td>
<td>1-2</td>
<td>31</td>
</tr>
</tbody>
</table>

(27) Klages, Ber., 37, 2301 (1904).
(28) Fellenberg, ibid., 37, 3578 (1904).
(29) Fellenberg, ibid., 39, 2064 (1906).
(31) Colonge, ibid., (5) 2, 754 (1935).
TABLE IV (Continued)

7. \( n-C_3H_7CH=CHCOCH_3 \)  
   \( C_6H_5MgBr \)  
   \( CH_3MgI \)  
   \( C_6H_5MgBr \)  
   \( n-C_3H_7MgBr \)  
   \( n-C_4H_9MgBr \)  
   \( 1-2 \)  
   \( 1-2 \)  
   \( 1-2 \)  
   \( 1-2 \)  
   \( 1-2 \)  
   \( 32 \)  
   \( 32 \)  
   \( 32 \)  
   \( 32 \)  
   \( 32 \)  

8. \((CH_3)_2C=CHCH=CHCOCH_3\)  
   \( CH_3MgI \)  
   \( 1-2 \)  
   \( 15 \)  

9. \( C_6H_5CH=CHCOCH_3 \)  
   \( CH_3MgI \)  
   \( 1-2 \)  
   \( 1-4 \)  
   \( 13,33 \)  
   \( (C_6H_5)_2CHNa \)  
   \( 1-4 \)  
   \( 34 \)  

10. \( \alpha-C_4H_9OCH=CHCOCH_3 \) \hspace{1em} \((a)\)  
    \( C_6H_5MgBr \)  
    \( n-C_3H_7MgBr \)  
    \( iso-C_4H_9MgBr \)  
    \( iso-C_4H_9MgBr \)  
    \( 1-4 \)  
    \( 1-4 \)  
    \( 1-4 \)  
    \( 1-4 \)  
    \( 35,36 \)  
    \( 35 \)  
    \( 35 \)  
    \( 35 \)  
    \( 35 \)  

11. \( \beta-CH_3OC_6H_4CH=CHCOCH_3 \)  
    \( C_6H_5MgBr \)  
    \( 1-4 \)  
    \( 36 \)  

12. \( \alpha-C_4H_9OCH=CHCOCH_3 \) \hspace{1em} \( n-C_3H_7MgBr \)  
    \( 1-4 \)  
    \( 36 \)  

13. \( \alpha-C_4H_9OCH=CHCOCH_3 \) \hspace{1em} \( iso-C_4H_9MgCl \)  
    \( 1-4 \)  
    \( 36 \)  

14. \( C_6H_5CH=CHCOCH(C_6H_5)_2 \)  
    \( C_6H_5MgBr \)  
    \( 1-4 \)  
    \( 37 \)  

15. \( C_6H_5CH=CHCOCH_3_2 \)  
    \( n-C_3H_7MgBr \)  
    \( C_6H_5MgBr \)  
    \( 1-4 \)  
    \( 38 \)  
    \( 1-4 \)  
    \( 38 \)  

\((a)\) Methyl-, iso-butyl-, iso-amyl- and phenylmagnesium halides gave only resinous products (35).

(37) Rack, Ber., 56, 1150 (1923).
TABLE IV (Continued)

<table>
<thead>
<tr>
<th></th>
<th>Chemical Structure</th>
<th>Products</th>
<th>Literature References</th>
</tr>
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<tbody>
<tr>
<td>16</td>
<td>( C_6H_5CH=CHCOC_6H_4 )</td>
<td>( p-CH_3OC_6H_4MgBr ) 1-4 39</td>
<td>(39) Albesco, Ann. chim., (9) 18, 216 (1922).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( p-CH_2C_6H_4MgBr ) 1-4 39</td>
<td>(40) Smith and Hanson, J. Am. Chem. Soc., 57, 1326 (1935).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( C_6H_5MgBr ) 1-4 39</td>
<td>(42) Badoche, Bull. soc. chim., (4) 43, 337 (1928).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( (C_6H_5)_{2}CHNa ) 1-4 34</td>
<td>(43) Bergmann, J. Chem. Soc., 989 (1935).</td>
</tr>
<tr>
<td>17</td>
<td>( C_6H_5CH=C(CH_3)COC_6H_4 )</td>
<td>( CH_3MgI ) 1-2 40</td>
<td>(44) Lowenbein, Ber., 57, 1519 (1926).</td>
</tr>
<tr>
<td>18</td>
<td>( C_6H_5CH=C(C_6H_5)COC_6H_4 )</td>
<td>( C_6H_5MgBr ) 1-4 39</td>
<td>(45) Ziegler and Ochs, Ibid., 55, 2257 (1922).</td>
</tr>
<tr>
<td>19</td>
<td>( C_6H_5C(OC_6H_5)=CHCOC_6H_4 )</td>
<td>( C_6H_5MgBr ) 1-2 41</td>
<td>(46) MacLean and Widdows, J. Chem. Soc., 105, 2169 (1914).</td>
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<tr>
<td></td>
<td></td>
<td>( C_6H_5MgBr ) 1-2 and 1-4 41</td>
<td>Putative 1,3-addition.</td>
</tr>
<tr>
<td>20</td>
<td>( C_6H_5CH=CHBrCOC_6H_4 )</td>
<td>( p-CH_3C_6H_4MgBr ) 1-4 42</td>
<td>Putative 1,3-addition.</td>
</tr>
<tr>
<td>21</td>
<td>( C_6H_5CH=CHCOC_6H_4Cl-p</td>
<td>( C_6H_5MgBr ) 1-4 43</td>
<td>Putative 1,3-addition.</td>
</tr>
<tr>
<td>22</td>
<td>( C_6H_5CH=CHCOC_6H_4Br-p</td>
<td>( p-BrC_6H_4MgBr ) 1-4 43</td>
<td>Putative 1,3-addition.</td>
</tr>
<tr>
<td>23</td>
<td>( p-HOC_6H_4CH=CHCOC_6H_4</td>
<td>( p-CH_3C_6H_4MgBr ) 1-4 44</td>
<td>Putative 1,3-addition.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( C_6H_5MgBr ) 1-4 44</td>
<td>Putative 1,3-addition.</td>
</tr>
<tr>
<td>24</td>
<td>( C_6H_5CH=CHCOC_6H_4OCH=CH-p</td>
<td>( p-CH_3OC_6H_4MgBr ) 1-4 (b) 45</td>
<td>Putative 1,3-addition.</td>
</tr>
<tr>
<td>25</td>
<td>( p-C_6H_5O_2CC_6H_4CH=CHCOC_6H_4</td>
<td>( C_6H_5MgBr ) 1-4 46</td>
<td>Putative 1,3-addition.</td>
</tr>
</tbody>
</table>

(b) The failure of a sensitive test for the 1,2-product indicated exclusive 1,4-addition.

(40) Smith and Hanson, J. Am. Chem. Soc., 57, 1326 (1935).
(44) Lowenbein, Ber., 57, 1519 (1926).
(45) Ziegler and Ochs, Ibid., 55, 2257 (1922).
<table>
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<th>Concentration</th>
<th>Source</th>
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<td>26</td>
<td>p-CH₃OC₆H₄CH=CHCO₆H₅</td>
<td>C₆H₅MgBr</td>
<td>1-4</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(C₆H₅)₂CHNa</td>
<td>1-4</td>
<td>34</td>
</tr>
<tr>
<td>27</td>
<td>(C₆H₅)₂C=C(C₆H₅)CO₆H₅</td>
<td>CH₃MgI</td>
<td>1-2</td>
<td>48</td>
</tr>
<tr>
<td>28</td>
<td>C₆H₅CH=CHCO₆H₅(CH₃)₂-2,4,6</td>
<td>C₆H₅MgBr</td>
<td>1-4</td>
<td>49</td>
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<tr>
<td>29</td>
<td>C₆H₅C(CH₃)=CHCO₆H₅(CH₃)₂</td>
<td>C₆H₅MgBr</td>
<td>1-4</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₃MgI</td>
<td>1-4</td>
<td>50</td>
</tr>
<tr>
<td>30</td>
<td>(C₆H₅)₂C=CHCO₆H₅(CH₃)₂</td>
<td>C₆H₅MgBr</td>
<td>1-4</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₃MgI</td>
<td>1-4</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₂H₅MgI</td>
<td>1-4</td>
<td>50</td>
</tr>
<tr>
<td>31</td>
<td>α-C₄H₅OCH=CHCO₆H₅</td>
<td>C₆H₅MgBr</td>
<td>1-4</td>
<td>51</td>
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<tr>
<td></td>
<td></td>
<td>CH₃MgI</td>
<td>1-4</td>
<td>51</td>
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<td>C₂H₅MgBr</td>
<td>1-4</td>
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<td>32</td>
<td>α-C₄H₅OCH=CHCO₆H₄CH₃-2</td>
<td>C₆H₅MgBr</td>
<td>1-4</td>
<td>52</td>
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<td>CH₃MgI</td>
<td>1-4</td>
<td>52</td>
</tr>
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<td></td>
<td>C₂H₅MgBr</td>
<td>1-4</td>
<td>52</td>
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<tr>
<td></td>
<td>iso-C₃H₇MgX</td>
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<td>52</td>
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<tr>
<td></td>
<td>iso-C₃H₇MgX</td>
<td>1-4</td>
<td>52</td>
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<tr>
<td>33</td>
<td>α-C₄H₅OCH=CHCO₆H₄OCH₃-2</td>
<td>C₆H₅MgBr</td>
<td>1-4</td>
<td>53</td>
</tr>
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<td>n-C₃H₇MgBr</td>
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<td>α-C₄H₅OCH=CHCO₆H₄Cl-2</td>
<td>C₆H₅MgBr</td>
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<td></td>
<td>n-C₃H₇MgBr</td>
<td>1-4</td>
<td>53</td>
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(47) Vorlander and Friedberg, Ber., 56, 1144 (1923).
(49) Kohler, Tishler and Potter, Ibid., 57, 2517 (1935).
(50) Kohler and Barnes, Ibid., 56, 690 (1933).
(52) Maxim and Angelesco, Bull. soc. chim., 51, 1365 (1932).
(53) Maxim and Angelesco, Ibid., 51, 1128 (1934).
TABLE IV (Continued)

35. \( \alpha-C_4H_5OCH=CHCOC_6H_4Br-p \quad C_6H_5MgBr \quad 1-4 \quad 53 \)
\( \quad C_6H_5MgBr \quad 1-4 \quad 52 \)
\( \quad \alpha-C_6H_5MgBr \quad 1-4 \quad 53 \)

36. \( \alpha-C_6H_5CH=CHCH=CHCOCH_3 \quad C_6H_5CH_2MgCl \quad 1-2 \quad 54 \)

37. \( \alpha-C_6H_5CH=CHCH=CHCOC_6H_6 \quad C_6H_5MgBr \quad 1-4 \quad 19,55,56 \)
\( \quad C_6H_5MgI \quad 1-4 \quad 54,55,56 \)
\( \quad C_6H_5CH_2MgCl \quad 1-4 \quad 54,55,56 \)
\( \quad (C_6H_5)_2CHNa \quad 1-4 \quad 54 \)

38. \( \alpha-C_6H_5CH=CHCH=CHCOC_6H_4OCH_3-p \quad C_6H_5CH_2MgCl \quad 1-4 \quad 55 \)

39. \( \alpha-C_6H_5CH=CHCH=CHCOC_6H_4Br-p \quad C_6H_5CH_2MgCl \quad 1-4 \quad 55 \)

40. \( \alpha-C_6H_5COCH=CHCOC_6H_6 \quad C_6H_5MgBr \quad 1-4 \quad 57 \)

41. \( 2,4,6-(CH_3)_3C_6H_4COCH=CHCOC_6H_6 \quad C_6H_5MgBr \quad 1-4 \quad 57 \)

42. \( \alpha-BrC_6H_4COCH=CHCOC_6H_4Br-p \quad C_6H_5MgBr \quad 1-4 \quad 57 \)

43. \( \alpha-C_6H_5COC(C_6H_5)_2-C(C_6H_5)_2-\)
\( \quad COC_6H_6 \quad C_6H_5MgBr \quad 1-2 \quad 58 \)

44. \( \alpha-C_6H_5COCH=C(C_6H_5)_2COC_6H_6 \quad C_6H_5MgBr \quad 1-4 \quad (c) \quad 58 \)

(c) Of the two possible modes of 1,4-addition, the Grignard reagent reacted with the conjugated system numbered.

(54) Bauer, Ber., 35, 688 (1905).
(55) Bauer and Breit, ibid., 39, 1916 (1906).
(56) Kohler, ibid., 38, 1203 (1905).
(58) Hahn and Murray, ibid., 36, 1484 (1914).
### TABLE V

**ADDITION REACTIONS OF ALICYCLIC α-ETHYLENIC KETONES**

<table>
<thead>
<tr>
<th>Ketone</th>
<th>Organometallic Compound</th>
<th>Type of Addition</th>
<th>Reference</th>
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<tr>
<td>1.</td>
<td>C₆H₅MgBr, CH₃MgI, C₃H₇MgBr</td>
<td>1-2</td>
<td>59</td>
</tr>
<tr>
<td>2.</td>
<td>C₆H₅MgBr, C₃H₇MgBr</td>
<td>1-2</td>
<td>60</td>
</tr>
<tr>
<td>3.</td>
<td>CH₃MgI</td>
<td>1-2</td>
<td>61</td>
</tr>
<tr>
<td>4.</td>
<td>CH₃MgI</td>
<td>1-2</td>
<td>61</td>
</tr>
<tr>
<td>5.</td>
<td>CH₃MgI</td>
<td>1-2</td>
<td>62</td>
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(59) Borsche and Menz, Ber., 41, 207 (1908).
(60) Blaise and Maire, Bull. soc. chim., (4) 3, 413 (1908).
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<th>8.</th>
<th>9.</th>
<th>10.</th>
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<td><img src="image3" alt="Chemical Structure" /></td>
<td><img src="image4" alt="Chemical Structure" /></td>
<td><img src="image5" alt="Chemical Structure" /></td>
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<tr>
<td>C₆H₆MgBr</td>
<td>C₆H₆MgBr</td>
<td>RMgX</td>
<td>CH₃MgX</td>
<td>CH₃MgX</td>
</tr>
<tr>
<td>C₆H₆MgI (Br)</td>
<td>iso-C₆H₇MgI</td>
<td>1-2 65</td>
<td>1-2 69</td>
<td>1-2 69</td>
</tr>
<tr>
<td>C₆H₆MgBr</td>
<td>iso-C₆H₇MgBr (I)</td>
<td>1-2 65</td>
<td>1-2 69</td>
<td>1-2 69</td>
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<tr>
<td>iso-C₆H₇MgCl</td>
<td>1-4 65</td>
<td>1-2 69</td>
<td>1-2 69</td>
<td>1-4 69</td>
</tr>
<tr>
<td>iso-C₆H₇MgI</td>
<td>1-4 66</td>
<td>1-2 69</td>
<td>1-2 69</td>
<td>1-4 69</td>
</tr>
<tr>
<td>C₆H₆CH₂MgCl</td>
<td>1-4 67</td>
<td>1-2 69</td>
<td>1-2 69</td>
<td>1-4 69</td>
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(63) Klages and Sommer, Ber., 39, 2306 (1906).
(64) Rupe and Liechtenhan, ibid., 39, 1119 (1906), 41, 1393 (1908).
(66) Semmler, Jonas and Oelsner, Ber., 50, 1838 (1917).
(67) Rupe and Tomi, ibid., 47, 3084 (1914).
(68) Simonis and Kirschchen, ibid., 45, 567 (1912); Stoermer and Lange, ibid., 50, 981 (1917); Bergmann and Weiss, Ann., 480, 84 (1930).
(69) Auwers, Ber., 49, 2339 (1916).
11. \[ \text{C}_8\text{H}_{12}\text{MgBr} \quad \text{CH}_3\text{MgI} \quad 1-2 \quad 70 \]

12. \[ \text{CH}_3\text{CO} \quad \text{CH}_3\text{MgI} \quad 1-2 \quad 61 \]

13. \[ \text{HC}=\text{C}(\text{CH}_3)_2 \quad \text{C}_8\text{H}_{12}\text{MgBr} \quad 1-2 \quad 71 \]

14. \[ \text{HC}=\text{C}(\text{CH}_3)_2 \quad \text{C}_8\text{H}_{12}\text{MgBr} \quad 1-2 \quad 71 \]

15. \[ \text{CH}_3\text{MgI} \quad 1-2 \quad 13 \]

(70) Baeyer and Piccard, Ann., 384, 208 (1911).
(71) Lipp and Quaedvlieg, Ber., 62, 2311 (1929).
(72) Beville, Compt. rend., 144, 1221 (1907).
16. \[
\begin{array}{c}
\text{C}_6\text{H}_5\text{Mgl} \\
\text{1-4} \\
72
\end{array}
\]
\[
\begin{array}{c}
n-\text{C}_6\text{H}_7\text{Mgl} \\
\text{1-4} \\
72
\end{array}
\]

17. \[
\begin{array}{c}
\text{C}_6\text{H}_5\text{Mgl} \\
\text{1-4} \\
73
\end{array}
\]

18. \[
\begin{array}{c}
\text{C}_6\text{H}_5\text{MgBr} \\
\text{1-4} \\
65
\end{array}
\]

19. \[
\begin{array}{c}
\text{C}_6\text{H}_5\text{MgBr} \\
\text{1-4} \\
65
\end{array}
\]

20. \[
\begin{array}{c}
\text{C}_6\text{H}_5\text{MgBr} \\
\text{1-4} \\
65
\end{array}
\]

21. \[
\begin{array}{c}
\text{C}_6\text{H}_5\text{MgBr} \\
\text{1-4} \\
74
\end{array}
\]
\[
\begin{array}{c}
\text{CH}_3\text{Mgl} \\
\text{1-4} \\
75
\end{array}
\]
\[
\begin{array}{c}
\text{C}_6\text{H}_5\text{MgBr} \\
\text{1-4} \\
74
\end{array}
\]
\[
\begin{array}{c}
\text{iso-C}_6\text{H}_7\text{MgBr} \\
\text{1-4} \\
75
\end{array}
\]

(73) Manolesco, *ibid.*, 172, 1360 (1921).
(74) Boedtker, *ibid.*, 145, 329 (1907).
(75) Boedtker, *ibid.*, 154, 437 (1912).
(76) Boedtker, J. pharm. chim., (3) 6, 193 (1927).
(77) Haller and Bauer, Compt. rend., 142, 971 (1906).
(78) Wolff, ibid., 172, 1357 (1921).
following rules and selected illustrations were derived by comparing the reactions of a given Grignard reagent and various ketones. The striking correlation of the reactivity of a carbon atom with the steric effect of the groups attached to that carbon will be noted.

First, the influence of $R'$ in the compound, $R''C=CRCOR'$, upon the amount of 1,2-addition is similar to the influence of $R'$ in the compound, $CH_3COR'$, upon the rate of reaction with the common carbonyl reagents (sodium bisulfite, hydroxylamine and others) (7). The reactions of compounds 3, 4, 5, 6, 14 and 17 of Table III show that the amount of 1,2-addition decreases as $R'$ changes in the order: $CH_3$, $C_2H_5$, $iso-C_3H_7$, $(CH_3)_2C$, $C_6H_5$, 2,4,6-$(CH_3)_2C_6H_2$.

Second, a group or groups on the $\beta$-carbon atom tend to decrease the amount of 1,4-addition, a phenyl group having greater influence than methyl and two groups having more effect than one. The reactions of compounds 10 and 22 of Table III illustrate this effect of $\beta$-substitution. That the influence of the phenyl group is greater than methyl will be seen from a comparison of the reactions of compounds 1 and 2 of Table III, 1, 3 and 7 of Table III, and 14 and 21 of Table III. The effect of dissubstitution on the $\beta$-carbon atom is illustrated by comparing 22 and 21 with 11 and 14 of Table III, and 3 with 4 of Table IV (31). It has been pointed out (41) that an ethoxyl
group on the β-carbon has an influence similar to a phenyl group (Cf. compounds 19 of Table IV and 22 of Table III).

Third, if \( R' \) in the compound \( RHC-\text{CRCOR'} \) is an aromatic radical, the 1,2-directing influence of monosubstitution on the β-carbon atom is completely overshadowed and 1,4-addition occurs. Compounds 11 through 20 of Table III in which \( R' \) is a phenyl or substituted phenyl group show this tendency toward 1,4-addition. The reactions of compounds 26 and 27 of Table IV indicate that even disubstitution on the β-carbon atom does not overcome the 1,4-directing tendency when \( R' \) is the mesityl group. In compounds 21 and 22 of Table III, \( R' \), a phenyl group, is not effective in directing addition to the 1- and 4-positions because of disubstitution on the β-carbon atom.

Fourth, substitution on the α-carbon atom appears to favor 1,4-addition. The reactions of compounds 5 and 7 of Table IV illustrate this rule. Although it has been stated (79) that an α-halogen "does not materially affect the primary reaction", this may be true only for compounds adding a Grignard reagent exclusively, or nearly so, in the 1- and 4-positions. For example, compound 14 of Table III added both ethyl- and phenylmagnesium bromides largely to the conjugated system, and substitution of the α-hydrogen atom by bromine, obviously cannot greatly increase the (79) Kohler and Johnstin, Am. Chem. J., 33, 35 (1905).
quantity of 1,4-product.

Fifth, the general principles of the above four rules may be applied with equal success to the addition reactions of alicyclic compounds. The reactions of compounds 1 through 5 of Table V indicate that the influence of a methylene group adjacent to the carbonyl is about equivalent to that of a methyl group adjacent to the carbonyl in the open-chain unsaturated ketones. Compounds 9, 10 and 11 of Table V are of particular interest for a comparison of their addition reactions clearly illustrates that an accumulation of groups on the carbons adjacent to the carbonyl favors 1,4-addition.

The five above-mentioned rules appear to hold true throughout the reactions given in Tables III, IV and V, but precaution should be exercised in their application. Comparisons should be as exact as possible, only a single R-group of the ketone being varied and the same organometallic compound being chosen in every case. While some of the yields reported in the literature account for a large part of the reactants, many do not exceed forty to fifty per cent and often the saturated ketone is the only product isolated by the investigators. The sensitivity of the unsaturated carbinols and their dehydration products increases the experimental difficulties of separation and identification, and consequently, knowledge of the entire course of some
reactions is not available. Added to such uncertainties is the absence of exact knowledge relative to the influence of the highly aromatic furyl, anisyl and dimethylaminophenyl groups upon the addition reactions of carbon atoms adjacent to them.

Temperature and solvent have been shown to have little influence upon the quantities of 1,2- and 1,4-addition products. Phenyl- or ethylmagnesium bromide gave the same amount of saturated ketone with ethyl styryl ketone, C₆H₅CH=CHCO₂H₅, at -37° and at the boiling point of ether (7). Ethylmagnesium bromide in benzene or in ether gave the same amount of saturated ketone with benzalacetone (7). Additional investigations of these factors should be of value.

Customarily, the formation of secondary products from the reactions of α-unsaturated ketones and Grignard reagents is avoided by the slow addition of the ketone to a large excess of reagent. The reverse order of addition may greatly increase the amount of complex products. Kohler and Peterson (80) have carefully investigated such reactions and found

\[
\begin{align*}
C_6H_5CH=CHCOC_6H_5 + C_6H_5MgBr & \rightarrow (C_6H_5)_2CHCH=CC_6H_5 \text{OMgBr} \\
\text{(A)} \\
C_6H_5CH=CHCOC_6H_5 + (A) \xrightarrow{\text{HOH}} C_6H_5CH\text{CHCH}_2\text{COC}_6H_5 \\
& (C_6H_5)_2CHCHCOC_6H_5 \\
\end{align*}
\]

the magnesium salts formed in the primary reaction condensed with unreacted unsaturated ketone.

The normal tendency of the carbonyl group to 1,2-addition is greatly disturbed not only by the structure of the ketone, but by the organic radical and the metal of the organometallic compound employed. A consideration of these factors has been deferred to the "Discussion" of this thesis.

**Mechanism of the Addition to α-Ethylene Ketones**

The addition of a Grignard reagent to an unsaturated ketone may give either an unsaturated carbinol, a saturated ketone or a mixture of these two products. The unsaturated

\[
\begin{align*}
\text{RCH} & = \text{CH} - \text{CR'}\text{R''} \\
\text{RCH} = \text{CHCOR'} + \text{R''MgX} \xrightarrow{\text{HOH}} \text{RR''CHCH}_2\text{COR'} \\
\end{align*}
\]

carbinol obviously results from 1,2-addition to the carbonyl
group, but three different mechanisms may account for the ketone.

First, the saturated ketone may be a rearrangement product of the carbinol. If the carbinol suffered an allylic shift of \( R'' \) followed by ketonization, the saturated ketone would result. If \( R' \) represents the same group as \( R'' \), either \( R' \) or \( R'' \) might migrate to yield the identical ketone. Further, if \( R' \) is equivalent to \( R \), and the hydroxyl or \( R'' \) underwent a 1,3-shift, the same ketone would result, and when \( R \) is equivalent to \( R'' \) a similar shift of \( R'' \) would yield the required ketone. If \( R = R' = R'' \) a rearrangement of \( R' \), \( R'' \) or hydroxyl would account for the ketone formed. The shift of a hydroxyl is eliminated for reactions in which \( R \) is not equivalent to \( R' \). Ordinarily the unsaturated carbinols do not rearrange to give ketones, but an interesting exception has recently been found (81). When the carbinol (A) was heated under reduced pressure, a ketone (B) resulted,

\[
\begin{align*}
\text{R-CH}_3\text{OC}_6\text{H}_5\text{CH}=\text{CHCH(C}_6\text{H}_5)_2 + \Delta & \rightarrow \\
\text{P-CH}_3\text{OC}_6\text{H}_5\text{CHCH(C}_6\text{H}_5)_2 \text{CH(C}_6\text{H}_5)_2 & \\
\text{P-CH}_3\text{OC}_6\text{H}_5\text{CH}=\text{HCOC}_6\text{H}_5 + (C_6\text{H}_5)_2\text{CHMgI}
\end{align*}
\]

(81) Studies in progress in this laboratory by Dr. H. Gilman and the author of this thesis.
probably from an allylic shift of the benzohydryl group followed by ketonization. It is unlikely that the carbinol was an intermediate in the Grignard synthesis, for in this reaction the ketone was isolated without heating or other treatment known to attack the carbinol. However, in all reactions of conjugated systems it is necessary to definitely eliminate the possibility of 1,2-addition followed by an allylic shift before 1,4-addition can be established. The rearrangement of (A) may be attributed to the lability of the benzohydryl group.

Second, the ketone may result from a direct addition of the Grignard reagent to the ethylenic bond. This explanation has been used as a mechanism for the closely related reaction of the ester, ethyl methacrylate, $\text{CH}_3=\text{C}(\text{CH}_3)\text{CO}_2\text{C}_2\text{H}_5$, with methylmagnesium iodide (82). However, Kohler (19) has found that the intermediate products fail to show reactions characteristic of compounds having a carbon-magnesium linkage. Also, such intermediates would be expected to react with themselves, to give polymeric substances. Finally, a preponderance of evidence has established that Grignard

(82) Blaise and Courtot, Compt. rend., 140, 370 (1905).
reagents do not add to ethylenic linkages (83).

Third, the Grignard reagent may add to the 1- and 4-
positions of the conjugated system and the saturated ketone
result from hydrolysis followed by ketonization. Most con-
vincing evidence in support of this mechanism has been found
by Kohler (26). In the reaction of benzaldesoxylbenzoin (C),

\[
\text{C}_6\text{H}_5\text{CH} = \text{C}(\text{C}_6\text{H}_5)\text{COC}_6\text{H}_5 + \text{C}_6\text{H}_5\text{MgBr} \rightarrow (\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)\text{CC}_6\text{H}_5 \text{OMgBr} \\
\text{(C)}
\]

the enol (D) may be isolated, converted to the ketone (E)
or oxidized to the peroxide (F) whose structure has been
established by decomposition to known products. Oxidation
of such magnesium salts as (G) failed to aid in the eluci-
dation of their structures (84), but additional evidence
supporting such enolates was found by "anchoring" the
position of the magnesium atom with benzoyl chloride (49).

gives complete references, including the several
studies of Gilman and co-workers.
(84) Kohler and Mydans, ibid., 54, 4667 (1932).
When the magnesium salt from chalcone (I) and phenylmagnesium bromide was treated with benzoyl chloride, a \( \beta \)-diketone (K)

\[
\text{(I)} \quad \text{C}_6\text{H}_5\text{CH}=\text{CHCOC}_6\text{H}_5 + \text{C}_6\text{H}_5\text{MgBr} \rightarrow \text{(J)} \quad \text{(C}_6\text{H}_5\text{)}_2\text{CHCHCOC}_6\text{H}_5 \quad \text{MgBr}
\]

\[
\text{(K)} \quad \text{(C}_6\text{H}_5\text{)}_2\text{CHCHCOC}_6\text{H}_5 \quad \text{C}_6\text{H}_5\text{CO}
\]

was formed (19, 85). The structure of (J) is therefore left in doubt as (K) may have resulted from an enolate similar to (H) or from a compound of the structure, \( (\text{C}_6\text{H}_5\text{)}_2\text{CHCHCOC}_6\text{H}_5 \quad \text{MgBr} \)

Incidentally, the enol from the hydrolysis of (H) is the only compound of this type, not having a group on the \( \alpha \)-carbon atom, from which a peroxide has been formed (49).

Further evidence supporting 1,4-addition is the reaction of only one molecule of phenylmagnesium bromide with dibenzalacetone (86). If direct addition of the Grignard

(85) Kohler and Tishler, \textit{ibid.}, 54, 1594 (1932).
reagent to an ethylenic linkage had occurred, a second molecule of the reagent could have added to the reaction product. Apparently, the carbonyl group was involved in the primary reaction and a second 1,4-addition was prevented.

**α-Ethylenic Esters**

Three primary products have been isolated from the reactions of α-unsaturated esters and organometallic compounds; an ester (E) resulting from 1,4-addition, a saturated ketone (K) and an unsaturated tertiary alcohol (A). The ketone and alcohol may each form in either or both of two reactions.

\[
\begin{align*}
R'CH=CHCOR'' &\xrightarrow{OMgX} R'CH=CHCOR'' + R''MgX \\
RCH=CHCOR'' &\xrightarrow{OH} RCH=CHCOR'' + OH \\
RR''CHCH=GOR'' &\xrightarrow{OMgX} RR''CHCH=COR'' + HOH \\
RR''CHCH=GOR'' &\xrightarrow{OH} RR''CHCH=GOR'' + HOH
\end{align*}
\]

(A)

In Table VI the reactions of various esters have been summarized. The letters A, K and E designate the type of
## TABLE VI

**Addition Reactions of α-Ethylene Esters**

<table>
<thead>
<tr>
<th>Ester</th>
<th>Organometallic Compound</th>
<th>Type of Product</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ( \text{CH}_2=\text{C(CH}_3\text{)}\text{CO}_2\text{C}_2\text{H}_5 )</td>
<td>( \text{CH}_3\text{MgI} )</td>
<td>K</td>
<td>82</td>
</tr>
<tr>
<td>2. ( \text{CH}_3\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5 )</td>
<td>( \text{CH}_3\text{MgBr} )</td>
<td>A</td>
<td>87</td>
</tr>
<tr>
<td>3. ( \text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5 )</td>
<td>( \text{C}_6\text{H}_5\text{MgBr} )</td>
<td>K and E</td>
<td>88</td>
</tr>
<tr>
<td>4. ( \text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{CH}_3 )</td>
<td>( \text{C}_6\text{H}_5\text{MgBr} )</td>
<td>K and E</td>
<td>89</td>
</tr>
<tr>
<td>5. ( \text{C}_6\text{H}_5\text{CH}=\text{C}(\text{CH}_3\text{)})\text{CO}_2\text{CH}_3 )</td>
<td>( \text{C}_6\text{H}_5\text{MgBr} )</td>
<td>K and E(3%)</td>
<td>90</td>
</tr>
<tr>
<td>6. ( \text{C}_6\text{H}_5\text{CH}=\text{C}(\text{C}_6\text{H}_5\text{)})\text{CO}_2\text{C}_2\text{H}_5 )</td>
<td>( \text{C}_6\text{H}_5\text{MgI} )</td>
<td>A</td>
<td>90</td>
</tr>
<tr>
<td>7. ( \text{C}_6\text{H}_5\text{CH}=\text{C}(\text{C}_6\text{H}_5\text{)})\text{CO}_2\text{CH}_3 )</td>
<td>( \alpha=\text{C_10H_7MgBr} )</td>
<td>E</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>( \text{C}_6\text{H}_5\text{MgBr} )</td>
<td>E</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>( \text{C}_2\text{CH}_3\text{C}_6\text{H}_5\text{MgBr} )</td>
<td>E</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}_3\text{MgI} )</td>
<td>A and E</td>
<td>91, 92</td>
</tr>
<tr>
<td>8. ( \text{C}_6\text{H}_5\text{CH}=\text{CHBrCO}_2\text{C}_2\text{H}_5 )</td>
<td>( \text{C}_6\text{H}_5\text{MgBr} )</td>
<td>K and E</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}_3\text{MgI} )</td>
<td>A</td>
<td>79</td>
</tr>
<tr>
<td>9. ( (\text{C}_6\text{H}_5\text{)})_2\text{C}=\text{C}(\text{CH}_3\text{)})\text{CO}_2\text{C}_2\text{H}_5 )</td>
<td>( \text{C}_6\text{H}_5\text{MgBr} )</td>
<td>A</td>
<td>93</td>
</tr>
</tbody>
</table>

(89) Kohler and Heritage, ibid., 33, 21 (1905).
(90) Kohler, ibid., 36, 529 (1906).
(91) Kohler and Heritage, ibid., 33, 153 (1905).
(92) Kohler and Reimer, ibid., 33, 333 (1905).
(93) Bergmann and Weiss, Ann., 480, 64 (1930).
### TABLE VI (Continued)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction</th>
<th>Products</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.</td>
<td>$\alpha$-C$_4$H$_5$OCH=CHCO$_2$C$_2$H$_5$</td>
<td>C$_6$H$_5$MgBr, C$_2$H$_5$MgBr, $\eta$-C$_3$H$_7$MgBr, iso-C$_4$H$_5$MgCl, iso-C$_4$H$_9$MgBr</td>
<td>(94) Maxim and Georgescue, Bull. soc. chim., (5) 3, 2266 (1936).</td>
</tr>
<tr>
<td>11.</td>
<td>$\alpha$-C$_4$H$_5$OCH=C(C$_6$H$_5$)CO$_2$R</td>
<td>C$_6$H$_5$MgBr, C$_2$H$_5$MgBr, A and E</td>
<td>(95) Maxim and Stancovici, ibid., (5) 3, 1319 (1936).</td>
</tr>
<tr>
<td>12.</td>
<td>CH$_2$=CHCH=CHCO$_2$C$_2$H$_5$</td>
<td>C$_6$H$_5$MgBr, K</td>
<td>(96) Kohler and Butler, J. Am. Chem. Soc., 48, 1036 (1926).</td>
</tr>
<tr>
<td>13.</td>
<td>C$_4$H$_8$CH=CHCH=CHCO$_2$CH$_3$</td>
<td>C$_6$H$_5$MgBr, C$_2$H$_5$MgBr, C$_6$H$_5$CH$_2$MgCl, A, K and E</td>
<td>(97) Reynolds, Am. Chem. J., 46, 198 (1911).</td>
</tr>
<tr>
<td>14.</td>
<td>C$_6$H$_5$CH=CHCH=C(CH$_3$)$_2$CO$_2$CH$_3$</td>
<td>C$_6$H$_5$MgBr, C$_2$H$_5$MgBr, C$_6$H$_5$CH$_2$MgCl, A and K</td>
<td>(98) Reimer and Reynolds, ibid., 48, 206 (1912).</td>
</tr>
<tr>
<td>15.</td>
<td>C$_6$H$_5$CH=CHCH=C(C$_6$H$_5$)CO$_2$CH$_3$</td>
<td>C$_6$H$_5$MgBr, CH$_3$Mgl</td>
<td>(99) Reimer and Reynolds, ibid., 49, 428 (1908).</td>
</tr>
<tr>
<td>16.</td>
<td>C$_6$H$_5$CH=CHC(C$_6$H$_5$)=CHCO$_2$CH$_3$</td>
<td>C$_6$H$_5$MgBr</td>
<td>(100) Kay and Perkin, J. Chem. Soc., 89, 839 (1906).</td>
</tr>
<tr>
<td>17.</td>
<td><img src="image" alt="Diagram" /></td>
<td>CH$_3$Mgl</td>
<td></td>
</tr>
</tbody>
</table>

(95) Maxim and Stancovici, ibid., (5) 3, 1319 (1936).
(98) Reimer and Reynolds, ibid., 48, 206 (1912).
(99) Reimer and Reynolds, ibid., 49, 428 (1908).
sequent to hydrolysis are the saturated uronate from
the products of the reaction, obtained and
summarized.

The reactions of α-phenylurethane are summarized
of the these (a)
trion of α-phenylurethane ketones and esters (1). pp. 26 and 37
fluence of α- and β-substitution are smaller in the reac-
the acetylation of α-urea on the α-carbon atom. The in-
9 and 10 yields unsaturated esters, probably because of
revers 1,4-addition. Finally, the reactions of compounds
ions of compounds 1 and 2 indicate that α-substitution
that αCH₂ is more easily replaced than αOCH₃. The rec-
cepted and the reactions of compounds 9 and 10
shows that α-phenyl group decreases the ease of
not indicate that α-phenyl group decreases the ease of
once apparent. However, the reactions of compounds 9
theses reactions may be predicted from the nature of data at
In the formulation of Rules whether the course of
the terminal atoms of the three conjugated double bonds
through the under 1,4-addition and not 1,3-addition to
not been found in the reaction products. Compound 17
saturation ketones of the general formula, ROH=CHR, have
un-saturated ketone and unsaturated ester, respectively,
product isolated and represent the unsaturated ester.

-28-
### TABLE VII

**ADDITION REACTIONS OF α-ETHYLENIC NITRILES**

<table>
<thead>
<tr>
<th>Nitrile</th>
<th>Organometallic Compound</th>
<th>Type of Addition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ( \text{C}_6\text{H}_5\text{CH}=\text{CHCN} )</td>
<td>( \text{C}_6\text{H}_5\text{MgBr} )</td>
<td>1-2</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}_2\text{MgI} )</td>
<td>1-2</td>
<td>102</td>
</tr>
<tr>
<td>2. ( \text{C}_6\text{H}_5\text{CH}=\text{C}(\text{C}_6\text{H}_5)\text{CN} )</td>
<td>( \text{C}_6\text{H}_5\text{MgBr} )</td>
<td>1-2 and 1-4</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}_2\text{MgI} )</td>
<td>1-4</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>( \text{C}_6\text{H}_5\text{MgBr} )</td>
<td>1-4</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>( \text{C}_6\text{H}_5\text{Li} )</td>
<td>1-2</td>
<td>101</td>
</tr>
<tr>
<td>3. ( (\text{C}_6\text{H}_5)_2\text{C}=\text{CHCN} )</td>
<td>( \text{C}_6\text{H}_5\text{MgBr} )</td>
<td>1-2</td>
<td>102</td>
</tr>
<tr>
<td>4. ( \alpha-\text{C}_6\text{H}_5\text{OCH}=\text{C}(\text{C}_6\text{H}_5)\text{CN} )</td>
<td>( \text{C}_6\text{H}_5\text{MgBr} )</td>
<td>1-4</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>( \text{C}_6\text{H}_5\text{CH}_2\text{MgBr} )</td>
<td>1-4</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}_2\text{MgI} )</td>
<td>1-4</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>( \text{C}_6\text{H}_5\text{MgBr} )</td>
<td>1-4</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>( \text{C}_6\text{H}_5\text{MgBr} )</td>
<td>1-4</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>( \text{iso-C}_6\text{H}_5\text{MgCl} )</td>
<td>1-4</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>( \text{C}_6\text{H}_5\text{CH}_2\text{MgCl} )</td>
<td>1-4</td>
<td>104</td>
</tr>
</tbody>
</table>

(101) Studies in this laboratory by Mr. M. Lichtenwalter.  
(104) Maxim and Aldea, Bull. soc. chim., (5) 2, 582 (1935);  
ibid., (5) 5, 1329 (1936).
1,4-addition and an unsaturated ketone from 1,2-addition. When the reactions of methylmagnesium iodide with compounds 1 and 2 are compared, it appears that an \( \alpha \)-substituent favors 1,4-addition, in accordance with the generalization given for unsaturated ketones on page 27 of this thesis.

It is of particular interest that, under forced conditions, compound 2 of Table VII added two molecules of phenylmagnesium bromide and gave \( \alpha,\beta,\beta \)-triphenylpropiophenone (101).

\[
\begin{align*}
C_6H_5CH=\text{C}(C_6H_5)CN + C_6H_5MgBr &\rightarrow (C_6H_5)_2\text{CHC}(C_6H_5)=\text{CC}(C_6H_5)_2N(MgBr)_2 \\
\text{HOH} &\rightarrow (C_6H_5)_2\text{CHCHCOC}_6H_5 \\
C_6H_5
\end{align*}
\]

\( \alpha \)-Ethyleneic Amides

Table VIII summarizes the reactions of the di-\( N \)-substituted amides with Grignard reagents. A comparison with

\[
\begin{align*}
\text{RCH=CHCOR}^+ + \text{R}^\text{mMgX} &\rightarrow \text{HOH} \\
\text{RCH=CHCOR}^+ &\rightarrow \text{R}^\text{mCHCH}_{\text{a}}\text{CNR}_\text{a}
\end{align*}
\]

Tables III and IV indicates that the \( R_aN \)-grouping attached to the carbonyl favors 1,4-addition in much the same manner as an aromatic group in a similar position in the unsaturated ketones. The tendency of methylmagnesium iodide to add
to the carbonyl group will be considered in the "Discussion" of this thesis.

Maxim and Ioanid (105) treated the intermediates in the reactions of the amides of phenylacrylic acid (Compounds 5, 6 and 7 of Table VIII) and phenylmagnesium bromide with acetyl chloride in the hope of establishing that 1,4-addition had occurred, rather than 1,2-addition to the ethylenic bonds. Their supposed esters were later shown to be β-ketonic amides which failed to elucidate the reaction mechanism (106). The closely related reaction of the magnesium compound from chalcone and phenylmagnesium bromide with benzoyle chloride is discussed on page 34 of this thesis.

\[
\begin{align*}
C_6H_5CH=CHCN(C_6H_5)C_6H_5 + C_6H_5MgBr & \rightarrow (C_6H_5)_2CHCHCN(C_6H_5)C_6H_5MgBr \\
CH_3C=O & \rightarrow (C_6H_5)_2CHCHCN(C_6H_5)C_6H_5 \quad \text{COCH}_3
\end{align*}
\]

<table>
<thead>
<tr>
<th>Amide</th>
<th>Organometallic Compound</th>
<th>Type of Addition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $\text{CH}_2\text{CH} = \text{CHCON(C}_6\text{H}_5)\text{}_2$</td>
<td>$\text{CH}_3\text{MgI}$, $\text{C}_2\text{H}_5\text{MgBr}$</td>
<td>1-2 and 1-4</td>
<td>107, 108, 109</td>
</tr>
<tr>
<td>2. $\text{CH}_2\text{CH} = \text{CHCON(C}_6\text{H}_5)(\text{CH}_3)$</td>
<td>$\text{C}_6\text{H}_5\text{MgBr}$, $\text{C}_2\text{H}_5\text{MgBr}$</td>
<td>1-4</td>
<td>110</td>
</tr>
<tr>
<td>3. $\text{CH}_2\text{CH} = \text{CHCON(C}_6\text{H}_5)(\text{C}_6\text{H}_5)$</td>
<td>$\text{C}_6\text{H}_5\text{MgBr}$, $\text{C}_2\text{H}_5\text{MgBr}$</td>
<td>1-4</td>
<td>110</td>
</tr>
<tr>
<td>4. $\text{CH}_2\text{CH} = \text{CHCON(C}_6\text{H}_5)\text{}_2$</td>
<td>$\text{C}_6\text{H}_5\text{MgBr}$, $\text{C}_2\text{H}_5\text{MgBr}$</td>
<td>1-4</td>
<td>108</td>
</tr>
<tr>
<td>5. $\text{C}_6\text{H}_5\text{CH} = \text{CHCON(C}_6\text{H}_5)\text{}_2$</td>
<td>$\text{C}_6\text{H}_5\text{MgBr}$, $\text{C}_2\text{H}_5\text{MgBr}$</td>
<td>1-4</td>
<td>105, 111</td>
</tr>
<tr>
<td>6. $\text{C}_6\text{H}_5\text{CH} = \text{CHCON(C}_6\text{H}_5)(\text{CH}_3)$</td>
<td>$\text{C}_6\text{H}_5\text{MgBr}$, $\text{C}_2\text{H}_5\text{MgBr}$</td>
<td>1-4</td>
<td>105, 111</td>
</tr>
<tr>
<td>7. $\text{C}_6\text{H}_5\text{CH} = \text{CHCON(C}_6\text{H}_5)(\text{C}_6\text{H}_5)$</td>
<td>$\text{C}_6\text{H}_5\text{MgBr}$, $\text{C}_2\text{H}_5\text{MgBr}$</td>
<td>1-4</td>
<td>111</td>
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<tr>
<td>8. $\text{C}_6\text{H}_5\text{CH} = \text{CHCON(C}_6\text{H}_5)\text{}_2$</td>
<td>$\text{C}_6\text{H}_5\text{MgBr}$, $\text{C}_2\text{H}_5\text{MgBr}$</td>
<td>1-4</td>
<td>112</td>
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</table>

(108) Maxim, *ibid.*, 10, 97 (1928) /C. A., 23, 2697 (1929)/.
(109) Nenitzescu and Cantuniari, *ibid.*, 14, 52 (1932) /C. A., 27, 958 (1933)/.
(110) Maxim and Ioanid, *ibid.*, 12, 28 (1930) /C. A., 25, 488 (1931)/.
(111) Maxim and Ioanid, *ibid.*, 10, 29 (1928) /C. A., 23, 4114 (1928)/.
<table>
<thead>
<tr>
<th>No.</th>
<th>Formula</th>
<th>Product</th>
<th>Conc.</th>
<th>Ref.</th>
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<tr>
<td>9.</td>
<td>$\alpha$-$C_4H_3OCH=CHCON(C_6H_5)_2$</td>
<td>$C_6H_5$MgBr</td>
<td>1-4</td>
<td>113</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_9H_8$MgBr</td>
<td>1-4</td>
<td>113</td>
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<td></td>
<td></td>
<td>$n$-$C_9H_7$MgBr</td>
<td>1-4</td>
<td>113</td>
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<tr>
<td>10.</td>
<td>$\alpha$-$C_4H_3OCH=CHCON(C_6H_5)(CH_3)$</td>
<td>$C_6H_5$MgBr</td>
<td>1-4</td>
<td>113</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_9H_8$MgBr</td>
<td>1-4</td>
<td>113</td>
</tr>
<tr>
<td>11.</td>
<td>$\alpha$-$C_4H_3OCH=CHCON(C_6H_5)(C_2H_5)$</td>
<td>$C_6H_5$MgBr</td>
<td>1-4</td>
<td>113</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_9H_8$MgBr</td>
<td>1-4</td>
<td>113</td>
</tr>
<tr>
<td>12.</td>
<td>$\alpha$-$C_4H_3OCH=CHCON(C_2H_5)_2$</td>
<td>$C_6H_5$MgBr</td>
<td>1-4</td>
<td>113</td>
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<td></td>
<td>$C_9H_8$MgBr</td>
<td>1-4</td>
<td>113</td>
</tr>
<tr>
<td>13.</td>
<td>$\alpha$-$C_4H_3OCH=C(C_6H_5)CON(C_6H_5)_2$</td>
<td>$C_6H_5$MgBr</td>
<td>1-4</td>
<td>95</td>
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<tr>
<td></td>
<td></td>
<td>$C_9H_8$MgBr</td>
<td>1-4</td>
<td>95</td>
</tr>
<tr>
<td>14.</td>
<td>$\alpha$-$C_4H_3OCH=C(C_6H_5)CON(C_2H_5)_2$</td>
<td>$C_6H_5$MgBr</td>
<td>1-4</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_9H_8$MgBr</td>
<td>1-4</td>
<td>95</td>
</tr>
</tbody>
</table>

(113) Maxim and Zugravescu, *Bull. soc. chim.*, (5) 1, 1087 (1934).
Compounds with A Miscellany of Conjugated Systems

Few α-ethylenic acid chlorides have been investigated. The chlorides of β-methylcrotonic acid, \((\text{CH}_3)\_2\text{C} = \text{CHCOCl}\), and α-ethyl-β-methylcrotonic acid, \((\text{CH}_3)\_2\text{C} = \text{C}(\text{C}_2\text{H}_5)\text{COCl}\), reacted with ethylzinc iodide and gave the corresponding unsaturated ketones (114). Cinnamoyl chloride and phenylmagnesium bromide gave a mixture of \(\beta,\beta\)-diphenylpropioiophenone and \(\beta,\beta\)-diphenylpropionic acid (89), indicating that at least a part of the Grignard reagent added to the conjugated system of the unsaturated acid chloride prior to addition to the carbonyl group or replacement of the halogen.

Several compounds in which an acetylenic bond is conjugated with a carbonyl group have been reacted with organometallic compounds, but invariably the products of the reactions result from 1,2-addition to the carbonyl group.

Thus, phenylpropiolaldehyde with several Grignard reagents was found to yield carbinols (115, 116); phenyl phenylethynyl ketone with phenylmagnesium bromide (7), phenylethynylmagnesium bromide and phenylethynylsodium (117) gave 1,2-addition; ethyl phenylethynyl ketone with methylmagnesium iodide and phenylethynyl propyl ketone with ethylmagnesium bromide gave 1,2-addition (115); ethyl phenylpropiolate and benzohydride sodium gave the acetylenic tertiary carbinol (34); and phenylpropiolyl chloride with phenylethynylmagnesium bromide and phenylethynylsodium gave 1,2-addition (117). Obviously, such conjugated systems react less readily than the ethylenic-carbonyl groupings.

Compounds containing the cyclopropane ring may be considered unsaturated for they show addition reactions through cleavage. Dimethyl 2-(3,4-bromomethoxyphenyl)-3-benzoyl-

(116) Klages, Ber., 39, 2537 (1906).
(117) Hess and Weltzien, ibid., 54, 2511 (1921).
cyclopropane -1,1-dicarboxylate (A), having several potential conjugated systems, was found to react with phenylmagnesium bromide and gave a 1,4-product (B) (118). Ethylmagnesium bromide, however, added to the ketonic carbonyl group (118).

Another class of compounds having potential conjugated systems is the α-oxido ketones, \( R_2\text{CHCOR} \). Several such compounds have been reacted with phenylmagnesium bromide and phenyllithium, but evidence of 1,4-addition was not found. The primary reaction in every case consisted of 1,2-addition to the carbonyl group or 1,2-addition to the carbonyl and cleavage of the oxido ring giving \( R_2(C_6H_5)CCHCR'(C_6H_5) \) (119).

It is of interest that the relatively inactive benzohydryl-sodium added only to the carbonyl group in benzalanethophenone oxide (34).

(119) (a) Bickel, ibid., 59, 325 (1937); (b) Kohler and Bickel, ibid., 57, 1399 (1935); (c) Bergmann and Wolf, ibid., 54, 1644 (1932); (d) Kohler, Richtmeyer and Hester, ibid., 53, 205 (1931).
Compounds with two or more conjugated ethylenic bonds are polymerized by organoalkali compounds (120), but the initial reactions may be 1,4-addition. It was definitely established that phenylisopropylpotassium added to the conjugated system in butadiene (121). Grignard reagents do not add to ethylenic linkages and, similarly, ethylmagnesium bromide failed to add to 1,4-diphenylbutadiene or cyclohexadiene (122).

Recently, studies have been made of four substances having the conjugated system, C=C=S=O. Styryl p-tolyl sulfoxide (C) was cleaved by ethylmagnesium bromide and gave

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH}=&\text{CHSO}_2\text{C}_6\text{H}_5, \quad \text{D} \\
\text{C}_6\text{H}_5\text{CH}=&\text{CHSO}_2\text{C}_6\text{H}_5, \quad \text{E} \\
\text{C}_6\text{H}_5\text{COCH}=&\text{C}(\text{C}_6\text{H}_5)\text{SO}_2\text{C}_6\text{H}_5, \quad \text{F}
\end{align*}
\]

1,4-diphenylbutadiene, butane and ethyl tolyl sulfide (123). Styryl p-tolyl sulfone (D) added phenylmagnesium bromide to the 1- and 4-positions of the conjugated system and gave \(\beta,\beta\)-diphenylethyl tolyl sulfone in a fifty per cent yield (123).

(120) Ziegler, Angew. Chem., 49, 499 (1936).
(121) Ziegler, Dersch and Wolfsch, Ann., 511, 13 (1934).
(123) Kohler and Larsen, ibid., 57, 1448 (1933).
Compound (E) added phenylmagnesium bromide to the ethylenic-carbonyl conjugated system. A small amount of the product of 1,2-addition to the carbonyl group was also isolated and there was no evidence that 1,4-addition to the system, C=C-S=O, had occurred. Compound (F) gave two products with phenylmagnesium bromide, the first, \((C_6H_5)_2C(OH)CH=C(C_6H_5)SO_2C_6H_5\), as a consequence of a 1,2-addition to the carbonyl group and the second, \((C_6H_5)_2C-\text{CH}-\text{CHSO}_2C_6H_5\), resulting from 1,2-addition to the carbonyl and 1,4-addition to the system, C=C-S=O (124).

An investigation has been made of the reactions of Grignard reagents with two compounds having the conjugated system, C=C-N=O (125). Nitrostilbene (G) and phenylmagnesium bromide gave exclusively the aci form of a nitro compound (H), thus

\[
\begin{align*}
C_6H_5CH=\text{C}(C_6H_5)\text{NO}_2 & \xrightarrow{\text{HOH}} C_6H_5\text{MgBr} \xrightarrow{\text{HOH}} (C_6H_5)_2\text{CH}=\text{NO(OH)} \\
\text{(G)} & \quad \text{(H)}
\end{align*}
\]

affording excellent proof that 1,4-addition had taken place. Compound (H) with dilute aqueous alkali gave the true nitro compound. Triphenylnitrostilbene with phenyl-, ethyl- and benzylmagnesium halides also gave 1,4-addition.

Compounds having the interesting conjugated system,

(124) Kohler and Larsen, ibid., 58, 1518 (1936).
(125) Kohler and Stone, ibid., 52, 761 (1930).
N=N-C=O, are few in number and only two have been investigated (126). Benzoylazobenzene (1) and azodibenzoyl (J) reacted with various Grignard reagents as indicated by the following equations:

\[ \text{C}_6\text{H}_5\text{N} = \text{NCOC}_6\text{H}_5 \xrightarrow{\text{RMgX}} \text{C}_6\text{H}_5\text{RNHNOCOC}_6\text{H}_5 \]

(I)

\[ \text{C}_6\text{H}_5\text{CON} = \text{NCOC}_6\text{H}_5 \xrightarrow{\text{RMgX}} \text{C}_6\text{H}_5\text{CONRNHNOCOC}_6\text{H}_5. \]

(J)

The investigators assumed that 1,4-addition to the conjugated systems had occurred and their mechanism appears entirely reasonable. Some reduction of the azo linkages also took place.

\( \alpha \)-Diketones have a conjugated system, O=C-C=O, but the well established tendency for the R-group of Grignard reagents to add to carbon rather than oxygen, precludes the possibility of 1,4-addition. Actually, organometallic compounds add directly to a single carbonyl group in such ketones (127).

\[ \text{C}_6\text{H}_5\text{CH}_2\text{COCOC}_6\text{H}_5 + \text{C}_6\text{H}_5\text{MgBr} \xrightarrow{\text{HOH}} \text{C}_6\text{H}_5\text{CH}_2\text{COC(OH)} \text{C}_6\text{H}_5 \]

(127) (a) Kohler and Barnes, J. Am. Chem. Soc., 56, 211 (1934); (b) Kohler and Weiner, Ibid., 56, 434 (1934).
Compounds with Crossed Conjugated Systems

Three or more adjacent, unsaturated linkages, not arranged in a continuous chain, may be termed a crossed conjugated system (128). Table IX summarizes the reactions of such compounds. Crossed, partially aromatic systems are not included and a few alicylic compounds may be found in Table V (Compounds 9, 11, 17, 18 and 20). Compounds 8, 12 and 16 of Table IX underwent 1,4-, not 1,6-addition. It has been pointed out (92, 130) that α-substitution by a phenyl, cyano or carbethoxy group in α-ethylenic esters favors 1,4-addition, decreases the tendency for replacement of the OR group and results in the formation of saturated esters.

Compounds having crossed systems of two different types are of particular interest. Compound 14 of Table IX has been shown to add phenylmagnesium bromide to the system, C=C-C=O, and not the system, C=C-C=N (92). The relative reactivity of various functional groups toward phenylmagnesium bromide has been found to decrease in the order: \(-\text{COCH}_3, -\text{CO}_2\text{C}_6\text{H}_5, -\text{CN}\) (134). It is possible that conjugated systems composed of an ethylenic linkage and one of these groups decrease in reactivity in the corresponding order. On this basis, it might

TABLE IX

ADDITION REACTIONS OF COMPOUNDS WITH
CROSSED CONJUGATED SYSTEMS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Organometallic</th>
<th>Type of Addition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $\text{CH}_3\text{CH} = \text{CH}_2\text{CO}$</td>
<td>$\text{CH}_3\text{MgI}$</td>
<td>1-2</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>$\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$</td>
<td>1-2</td>
<td>29</td>
</tr>
<tr>
<td>2. $(\text{C}_6\text{H}_5\text{CH} = \text{CH})_2\text{CO}$</td>
<td>$\text{C}_6\text{H}_5\text{MgBr}$</td>
<td>1-4</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>$\text{C}_6\text{H}_5\text{C} = \text{CMgBr}$</td>
<td>1-2 (a)</td>
<td>117</td>
</tr>
<tr>
<td></td>
<td>$(\text{C}_6\text{H}_5)_2\text{CHNa}$</td>
<td>1-4</td>
<td>129</td>
</tr>
<tr>
<td>3. $(\alpha = \text{ClC}_6\text{H}_4\text{CH} = \text{CH})_2\text{CO}$</td>
<td>$\text{C}_6\text{H}_5\text{MgBr}$</td>
<td>1-4</td>
<td>36</td>
</tr>
<tr>
<td>4. $(\alpha = \text{C}_6\text{H}_3\text{OCH} = \text{CH})_2\text{CO}$</td>
<td>$\text{C}_6\text{H}_5\text{MgBr}$</td>
<td>1-4</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>$\text{C}_6\text{H}_5\text{MgI}$</td>
<td>1-4</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>$\text{n-C}_7\text{H}_7\text{MgBr}$</td>
<td>1-4</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>$\text{iso-C}_6\text{H}_9\text{MgCl}$</td>
<td>1-4</td>
<td>36</td>
</tr>
<tr>
<td>5. $\alpha = \text{C}_6\text{H}_3\text{OCH} = \text{CH}$</td>
<td>$\text{C}_6\text{H}_5\text{MgI}$</td>
<td>1-4 (b)</td>
<td>36</td>
</tr>
<tr>
<td>$\text{p-CH}_3\text{OC}_6\text{H}_4\text{CH} = \text{CH}$</td>
<td>$\text{n-C}_7\text{H}_7\text{MgBr}$</td>
<td>1-4 (c)</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>$\text{iso-C}_6\text{H}_9\text{MgCl}$</td>
<td>1-4 (c)</td>
<td>36</td>
</tr>
<tr>
<td>6. $\alpha = \text{C}_6\text{H}_3\text{OCH} = \text{CH}$</td>
<td>$\text{n-C}_7\text{H}_7\text{MgBr}$</td>
<td>1-4 (c)</td>
<td>36</td>
</tr>
<tr>
<td>$\text{C}_6\text{H}_5\text{CH} = \text{CH}$</td>
<td>$\text{iso-C}_6\text{H}_9\text{MgCl}$</td>
<td>1-4 (c)</td>
<td>36</td>
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<tr>
<td>7. $\alpha = \text{C}_6\text{H}_3\text{OCH} = \text{CH}$</td>
<td>$\text{iso-C}_6\text{H}_9\text{MgBr}$</td>
<td>1-4 (c)</td>
<td>36</td>
</tr>
<tr>
<td>$\text{p-(CH}_3)_2\text{C}_6\text{H}_4\text{CH} = \text{CH}$</td>
<td>$\text{iso-C}<em>6\text{H}</em>{11}\text{MgBr}$</td>
<td>1-4 (c)</td>
<td>36</td>
</tr>
</tbody>
</table>

(a) The structure of the reaction product was not definitely established.
(b) The structure of the product of the reaction, established by an independent synthesis, was $\alpha = \text{C}_6\text{H}_3\text{OCH} = \text{CHCOCH}_2\text{CH} = \text{C}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{H}_3\text{CH}$.
(c) The structure of the product of the reaction was not established, but the formula, $\alpha = \text{C}_6\text{H}_3\text{OCH} = \text{CHCOCH}_2\text{CHRR}^1$, was assigned.

(129) Bergmann and Wagenberg, *Ber.*, 63, 2585 (1930).
<p>| | | | | | |</p>
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<tr>
<td>8.</td>
<td>((C_6H_5CH=CHCH=CH)_2CO)</td>
<td>((C_6H_5))_2CHNa</td>
<td>1-4</td>
<td>129</td>
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<tr>
<td>9.</td>
<td>(C_2H_5OCH=C(CO_2C_2H_5)_2)</td>
<td>(C_6H_5MgBr)</td>
<td>1-4</td>
<td>41</td>
<td></td>
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<tr>
<td>10.</td>
<td>(C_6H_5CH=CH(CO_2C_2H_5)_2)</td>
<td>(C_6H_5MgBr)</td>
<td>1-4</td>
<td>130</td>
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<tr>
<td></td>
<td></td>
<td>(CH_3MgI)</td>
<td>1-4</td>
<td>130</td>
<td></td>
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<tr>
<td>11.</td>
<td>(\alpha-C_4H_8OCH=C(CO_2C_2H_5)_2)</td>
<td>(C_6H_5MgBr)</td>
<td>1-4</td>
<td>131</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>(iso-C_6H_5MgCl)</td>
<td>1-4</td>
<td>131</td>
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<tr>
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<td>(iso-C_6H_5MgBr)</td>
<td>1-4</td>
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<tr>
<td>12.</td>
<td>(C_6H_5CH=CHCH=CH(CO_2CH_3)_2)</td>
<td>(C_6H_5MgBr)</td>
<td>1-4</td>
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<tr>
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<td>(CH_3MgI)</td>
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<tr>
<td>13.</td>
<td>(\alpha-C_4H_8OCH=CCO(C_2H_5)_2)</td>
<td>(C_6H_5MgBr)</td>
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<td></td>
<td></td>
<td>(C_6H_5MgBr)</td>
<td>1-4</td>
<td>131</td>
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<tr>
<td></td>
<td></td>
<td>(n-C_6H_7MgBr)</td>
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<td></td>
</tr>
<tr>
<td>14.</td>
<td>(C_6H_5CH=CCO_2C_2H_5)</td>
<td>(\alpha-C_{10H_7MgBr})</td>
<td>1-4</td>
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<tr>
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<td></td>
<td>(C_6H_5MgBr)</td>
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<td>92</td>
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<tr>
<td></td>
<td></td>
<td>(CH_3MgI)</td>
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<tr>
<td></td>
<td></td>
<td>(iso-C_6H_5MgBr)</td>
<td>1-4</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(C_6H_5CH_2MgCl)</td>
<td>1-4</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(C_6H_5C=C)MgBr</td>
<td>1-4</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>15.</td>
<td>(\alpha-C_4H_8OCH=CCO_2C_2H_5)</td>
<td>(n-C_6H_7MgBr)</td>
<td>1-4</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(iso-C_6H_5MgCl)</td>
<td>1-4</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>16.</td>
<td>(C_6H_5CH=CHCH=CCO_2C_2H_5)</td>
<td>(C_6H_5MgBr)</td>
<td>1-4</td>
<td>133</td>
<td></td>
</tr>
</tbody>
</table>

(133) Macleod, Ibid., 44, 331 (1910).
be predicted that the conjugated systems including the ketone
group in compound 13 of Table IX and also in the ethyl ethyl-
idenacetacetate of Grignard (4) added the organomagnesium
compounds more rapidly than the system, C=\text{C}-\text{CO}_2\text{H}_5.

Compounds with Partially Aromatic Conjugated Systems

The 1,4-addition of organometallic compounds to partially
aromatic systems is of particular interest because of the in-
frequency of such reactions and the difficulties encountered
in establishing the structure of their products. Compounds 1,
4, 5, 9, 10, 11 and 12 of Table X undergo 1,4-addition as
illustrated. For comparative purposes Table X includes a few
closely related compounds which react by 1,2-addition. Com-
ponds 1, 4 and 5 may react by 1,4-addition because of steric
or other influences which decrease the activity of the carbon-
nitrogen linkage, but it is difficult to understand why com-
ounds 10, 11 and 12 should add in the 1- and 4-positions
when compounds 13, 14 and 15 add to the carbonyl group.

Allen and Gilman (135) have pointed out that the bond
structure assigned to naphthacenequinone (Compound 10,
Table X) by Fieser (136) was verified by the mode of addition
of phenylmagnesium bromide. Possibly compounds 11 and 12
likewise have more or less fixed bond structures.

TABLE X
ADDITION REACTIONS OF COMPOUNDS WITH
PARTIALLY AROMATIC SYSTEMS

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Organometallic Compound</th>
<th>Product</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ((C_6H_5)_2C=NC_6H_5)</td>
<td>(C_6H_5MgBr)</td>
<td>(C_6H_5CHNHC_6H_5) (a)</td>
<td>137</td>
</tr>
<tr>
<td></td>
<td>(C_6H_5CH_2MgCl)</td>
<td>No Reaction</td>
<td>138</td>
</tr>
<tr>
<td></td>
<td>(C_6H_5Hg)</td>
<td></td>
<td>139</td>
</tr>
<tr>
<td>2. (C_6H_5C(CH_3)=NC_6H_5)</td>
<td>(RMgX)</td>
<td>Condensation</td>
<td>140</td>
</tr>
<tr>
<td>3. (C_6H_5CH=NR^1)</td>
<td>(RMgX)</td>
<td>(C_6H_5CHNR^1)</td>
<td>R</td>
</tr>
<tr>
<td></td>
<td>((C_6H_5)_2CHNa)</td>
<td>1,2-Addition</td>
<td>138</td>
</tr>
</tbody>
</table>

4. \[\begin{array}{c}
\text{N} \\
\text{CH}=\text{CHC}_6\text{H}_5
\end{array}\] \(C_6H_5MgBr\) \[\begin{array}{c}
\text{N} \\
\text{CH}_2\text{CH(C}_6\text{H}_5)\end{array}\] 142

5. \[\begin{array}{c}
\text{N} \\
\text{R}
\end{array}\] \(RMgX, RLi\) \[\begin{array}{c}
\text{N} \\
\text{R}
\end{array}\] 143

(a) This reaction has been postulated by Hoch, Compt. rend., 208, 799 (1936), to account for the formation of \(N-\{(\text{phenylbenzohydryl})\text{-aniline in the reactions of benzophenone oxime and benzanilide with phenylmagnesium bromide.}\)

(139) Table 12 of this thesis gives additional reactions.
(143) Bergmann and co-workers, Ann., 483, 80 (1930); Ziegler and Zeiser, ibid., 485, 174 (1931).
**TABLE X (Continued)**

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Compound</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.</td>
<td>RMgX, RLi</td>
<td><img src="image1" alt="Structure" /></td>
<td>143,144</td>
</tr>
<tr>
<td>7.</td>
<td>RMgX, RLi</td>
<td><img src="image2" alt="Structure" /></td>
<td>143,144</td>
</tr>
<tr>
<td>8.</td>
<td>CH=CHC₆H₅</td>
<td>C₆H₅MgBr</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td>9.</td>
<td>(C₆H₅)₂C=CCOC₆H₅</td>
<td>C₆H₅MgBr</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>10.</td>
<td>C₆H₅MgBr</td>
<td><img src="image5" alt="Structure" /></td>
<td><img src="image6" alt="Structure" /></td>
</tr>
<tr>
<td>11.</td>
<td>C₆H₅MgBr, C₆H₅CH₂MgCl</td>
<td><img src="image7" alt="Structure" /></td>
<td><img src="image8" alt="Structure" /></td>
</tr>
</tbody>
</table>

CH₃MgI | ![Structure](image9) | 1,2- and 1,4-Addition | 147 |
(CH₃)₃CMgCl | ![Structure](image10) | 1,2-Addition (20%) | 146 |

TABLE X (Continued)

12. \( \text{RMgX} \)

13. \( \text{RMgX} \)

14. \( \text{RMgX} \)

15. \( \text{RMgX} \)

(150) Ullmann and Engi, Ber., 37, 2370 (1904).
(151) Sünzly, Decker and Wittmann, ibid., 37, 2936 (1904).
Cis and Trans Isomers

The cis and trans forms of \( \alpha \)-ethylenic ketones or esters give the same amounts of 1,2- and 1,4-addition. Benzal- and iso-benzaldehydesoxybenzoin with ethylmagnesium bromide gave only the saturated ketone (26). The cis and trans forms of methyl \( \alpha \)-n-propyl-\( \beta \)-ethylvinyl ketone and methyl \( \beta \)-n-propylvinyl ketone, respectively, gave, with ethylmagnesium bromide, equal amounts of saturated ketone and unsaturated alcohol (152). The isomeric methyl esters of cinnamalacetic acid, \( \text{C}_9\text{H}_8\text{CH}=\text{CH}=\text{CHCO}_2\text{CH}_3 \), with phenylmagnesium bromide both gave 1,4-addition and methoxylation replacement to yield \( \text{C}_9\text{H}_8\text{CH}=\text{CHCHCH}_2\text{CO}_2\text{CH}_3 \), but the allo form reacted more rapidly (97).

It is disappointing that reactions so generally influenced by steric factors do not distinguish such isomers. A possible explanation is that the organometallic compound catalyzes a transformation of one form to the other or establishes an equilibrium. Gilman and Nelson (152a) have pointed out that tri-n-propylboron may cause thiokeetonization of

\[
\begin{array}{c}
\text{S} \\
\text{N} \\
\text{C-SH}
\end{array}
\]

However, the cis and

trans forms of methyl \( \alpha \)-phenyl-\( \beta \)-\( p \)-chlorobenzoyl-\( \gamma \)-acylate,

p-C₆H₅COCH=C(C₆H₅)CO₂CH₃, added methylmagnesium iodide to the ketonic linkage and gave the corresponding cis and trans hydroxy esters without transformation occurring (153), and triethylbismuth did not convert oleic to elaidic acid (153a).

1,6-Addition

It has been pointed out (96) that long conjugated systems of the type, C≡C≡C≡C≡O, give 1,2- and 1,4-addition, but, for some reason inherent in the nature of such conjugation, do not yield 1,6-addition. Several such compounds are found in Tables IV, VI and IX and compound 8 of Table X is likewise an illustration (145). However, 1,6-addition by organometallic compounds has been achieved and, years ago, Baeyer and Villiger (154) believed that the phenol (B) was formed when fuchsonone (A) reacted with methylmagnesium iodide, but the structure of their product has only recently been

![Chemical Structures](image)

(153a) Unpublished studies by Mr. J. A. V. Turek in this laboratory.
(154) Baeyer and Villiger, *Ber.*, 36, 2793 (1903).
confirmed (155). In the investigations of several similar reactions it was found that methyleneanthrone (C) added

\[
\begin{align*}
\text{1} & \text{0} \\
\text{C} & \text{H}_2 \\
\end{align*}
\]

(C)

phenyl-, methyl- and ethylmagnesium halides to the 1- and 6-positions while anthrofuchsonne (D) gave 1,2-addition to the carbonyl linkage with phenyl- and methylmagnesium halides (155).

EXPERIMENTAL

The general technique employed was the same for the several experiments. Conventional three-necked flasks fitted with Hopkins condenser, mercury-sealed stirrer and dropping funnel were warmed with a free flame while a rapid stream of pure, dry nitrogen was passed through them. Purification of the nitrogen was effected by passage through two Milligan gas wash bottles containing alkaline pyrogallol solution, two wash bottles containing sulfuric acid and a tower holding phosphorus oxide suspended on glass wool. The high order of reactivity of many of the organometallic compounds used, necessitated unusual care in the purification of all solvents and reactants. The ether was dried over sodium wire and distilled, as required, from a solution of phenylmagnesium bromide stored under nitrogen. Other solvents were dried over sodium and solid reactants were kept over phosphorus oxide for twenty-four hours under reduced pressure in a desiccator. The reactants were added slowly to an excess of the organometallic compound to avoid secondary reactions (156) and hydrolysis was effected with cold ammonium chloride solution prior to the admission of air to the reaction flask.

(156) See page 29 of this thesis.
Chalcone with Diphenylzinc.

Diphenylzinc was prepared by forty-eight hours refluxing of a suspension of 50 g. of mossy zinc in a solution prepared from 7.8 g. (0.022 mole) of diphenylmercury and 75 cc. of xylene (157). A warm solution of chalcone (4.2 g., 0.02 mole) in 25 cc. of xylene was added to the boiling solution of diphenylzinc, previously freed of zinc amalgam by decantation. The mixture was refluxed gently for two hours prior to hydrolysis. The xylene extract was dried over sodium sulfate and evaporated in a current of dry air. The residue was crystallized from petroleum ether (60 - 68°) and gave 5.2 g. (91%) of β,β-diphenylpropiophenone (mixed m. p.) (19). If an appreciable amount of diphenylstyrlylcarbinol had been present, the melting point of the solid obtained from the petroleum ether would have been markedly lower than that of the pure ketone (96°), for a mixture prepared from one part of carbinol (m. p. 111°) and twenty parts of ketone melted from 86 to 89°.

Chalcone with Triphenylaluminum.

A solution containing about 0.027 mole of triphenylaluminum was prepared by refluxing 100 cc. of xylene in which 14.2 g. (0.04 mole) of diphenylmercury had been dissolved,

(158) Gilman and Marple, Rec. trav. chim., 55, 133 (1936).
with 10 g. of aluminum chips for twenty hours (158). The clear, warm solution was decanted from mercury and aluminum, and heated to boiling. A solution of 5.2 g. (0.025 mole) of chalone in 25 cc. of xylene was added slowly, each drop causing a transitory red coloration. The mixture was heated at 130° for one hour, cooled and hydrolyzed. Evaporation of the xylene extract and a single crystallization from ethanol gave 6.7 g. (94%) of β,β-diphenylpropiophenone (mixed m. p.).

Chalone with Phenylmanganous Iodide.

Phenylmanganous iodide was prepared by adding 9.3 g. (0.03 mole) of anhydrous manganous iodide (159) to an ether solution of 0.1 mole of phenylmagnesium iodide, and, after stirring the mixture for twenty hours, the chocolate brown precipitate of the organomanganese compound was washed with seven 200-cc. portions of ether (160). A negative color test (161) established that the final washings were free of Grignard reagent. To a suspension of the precipitate in 100 cc. of

(159) The halide was kindly supplied by Mr. E. Binschadler.
(160) The preparation of organomanganese compounds has been studied in detail by Mr. M. M. Barnett and others in this laboratory. The phenylmanganese derivative was found by them to be qualitatively free of magnesium and to analyze for a mixture of C₆H₅MnI and (C₆H₅)₂Mn, but may not contain divalent manganese.
ether were added 4.2 g. (0.02 mole) of chalcone. The ether refluxed gently, indicating an immediate reaction, but the mixture was stirred for seventeen hours prior to hydrolysis. The residue from the evaporation of the ether extract was crystallized from petroleum ether and gave 4.4 g. (77%) of \( \beta,\beta\)-diphenylpropioiophenone (mixed m. p.).

In a second experiment, 9.3 g. (0.03 mole) of manganous iodide were added to 0.055 mole of phenyllithium in 100 cc. of ether. The reaction was vigorous and, after fifteen minutes of stirring, the brown solution was found to give a negative color test and the precipitate a positive reaction. No attempt was made to extract lithium salts from the mixture. A vigorous reaction was again noted when 4.2 g. (0.02 mole) of chalcone were added. After ten minutes of stirring, hydrolysis was effected and the ether extract evaporated to dryness. The residue was extracted with benzene, the benzene evaporated, and the resulting semi-solid mass gave 2.9 g. (51%) of \( \beta,\beta\)-diphenylpropioiophenone (mixed m. p.) and 1.2 g. of biphenyl.

**Chalcone with Diphenylberyllium.**

A single arylberyllium compound, phenylberyllium iodide, has been reported in the literature (162). Diphenylberyllium

(162) Gilman and Schulze, *ibid.*, 49, 2904 (1927).
may be prepared conveniently from phenyllithium and beryllium halide. To 4 g. (0.05 mole) of anhydrous beryllium chloride, cooled in an ice bath, were added 50 cc. of ether, and the mixture was stirred for thirty minutes to allow formation of the oily, ether-insoluble etherate. A phenyllithium solution prepared from 17.3 g. (0.11 mole) of bromobenzene, 100 cc. of ether and 1.5 g. (0.22 g. atom) of lithium, was added slowly. A white sludge separated immediately and the mixture, which gave a positive color test, was stirred for thirty minutes at room temperature. A solution of 5.2 g. (0.025 mole) of chalcone in 25 cc. of ether was added dropwise and, after ten minutes of stirring, the mixture was hydrolyzed. The ether extract gave 6.4 g. (90%) of β,β-diphenylpropiophenone (mixed m. p.). Diphenylberyllium undoubtedly could have been prepared from beryllium chloride and phenylmagnesium bromide, instead of phenyllithium, but the identification of the organo-beryllium compound by the reaction with chalcone would not have been possible (163).

Chalcone with Phenyllithium.

A solution of 5.2 g. (0.025 mole) of chalcone in 25 cc. of ether was added dropwise to 0.027 mole of phenyllithium in 100 cc. of ether. The mixture was stirred for five minutes,

(163) See page 95 of this thesis.
hydrolyzed, and the ether extract dried and evaporated in a stream of dry air. The residual solid was digested with 40 cc. of warm petroleum ether (60 - 68°), cooled and filtered. The remaining solid was crystallized from a mixture of benzene and petroleum ether, and yielded 4.9 g. (69%) of diphenylstyrylv-carbinal (mixed m. p.) (164). The original petroleum ether extract and the filtrates from the crystallization of the carbinal were combined and evaporated, and the residue was crystallized from ethanol. A 13% yield (0.9 g.) of pure β,β-diphenylpropiophenone resulted. The oil (representing 18% of the reaction products) obtained upon further evaporation of the filtrates was found resistant to crystallization. The lithium used was of 99.5% purity and failed to give qualitative tests for the more common elements. It is unreasonable that the saturated ketone could have resulted from the reaction of organometallic compounds other than phenyllithium.

Chalcone with Phenylcalcium Iodide.

Phenylcalcium iodide was prepared in 100 cc. of ether from 20.4 g. (0.1 mole) of iodobenzene and 0.2 g. atom of bright calcium turnings (165). After the removal of the

(164) Lüttringhaus, Ber., 67B, 1602 (1934).
unreacted metal, 4.2 g. (0.02 mole) of chalcone in 20 cc. of ether were added and, after five minutes of stirring, the mixture was hydrolyzed. The ether extract was evaporated and the residue was crystallized from a mixture of benzene and petroleum ether. The yield was 2.6 g. (45%) of diphenylstyrylcarbinol (mixed m. p.). Evaporation of the filtrates gave dark oils resistant to crystallization (166) and an attempt to isolate the saturated ketone by fractional distillation was unsuccessful. A small amount of an unidentified solid melting at 120° was isolated from the fraction boiling from 160 to 200° (7 mm.). The fraction boiling from 200 to 250° (7 mm.) did not crystallize upon standing for one week and failed to give a solid derivative with phenylhydrazine.

**Chalcone with Phenylsodium.**

To avoid contamination of the reaction products by diphenylmercury, phenylsodium was prepared by the method of Schorigin (167). To 1.4 g. (0.06 g. atom) of bright sodium shavings suspended in 100 cc. of benzene, were added 4.7 g. (0.015 mole) of dibutylmercury. The mixture was stirred for

(166) These results are in agreement with the findings of Mr. R. L. Bebb and Mr. J. C. Bailey in this laboratory. (167) a. Schorigin, Ber., 41, 2723 (1908); ibid., 43, 1938 (1910); b. Gilman and Kirby, J. Am. Chem. Soc., 58, 2074 (1936).
twenty-four hours without heating, and cooled in an ice bath, prior to the addition of 4 cc. of mercury. The brown suspension of phenylsodium was decanted from the amalgam and cooled to 10°. After the addition of 4.2 g. (0.02 mole) of chalcone, the mixture was stirred for ten minutes and hydrolyzed by adding 5 cc. of ethanol followed by an ammonium chloride solution. The benzene extract was evaporated to a small volume in an air stream and 20 cc. of petroleum ether were added to precipitate 2.2 g. (39%) of diphenylstyrylcarbinol (mixed m. p.). Oils resistant to crystallization were obtained by evaporation of the filtrates and, accordingly, they were united and distilled. The fraction boiling from 200 to 230° (8 mm.) was crystallized from ethanol and gave 0.2 g. (3.5%) of β,β-diphenylpropionophenone (mixed m. p.).

Chalcone with Phenylpotassium.

A suspension of phenylpotassium (167b), prepared by stirring 3.9 g. (0.015 mole) of diethylmercury, 2.3 g. (0.06 g. atom) of potassium shavings and 100 cc. of benzene for two days at room temperature, was decanted from the potassium amalgam and cooled to 10°. After the addition of 4.2 g. (0.02 mole) of chalcone, the mixture was stirred for ten minutes and hydrolyzed with butyl alcohol and an ammonium chloride solution. The benzene extract was evaporated to about
10-cc. volume and filtered to remove a small amount of solid material. The addition of petroleum ether precipitated crude diphenylstyrilcarbinol which was removed by filtration. Upon evaporating the filtrate and crystallizing the residue from ethanol, 0.5 g. of quite pure carbinol (m. p. 110°) were obtained. β,β-Diphenylpropiophenone, if present in an appreciable amount, would have crystallized from the ethanol at this point in procedure. The total yield to purified diphenylstyrylcarbinol (mixed m. p.) was 3.0 g. (52%).

Chalcone with p-Dimethylaminophenylmagnesium Halides.

p-Dimethylaminophenylmagnesium halides have not been prepared from the organic halogen compounds and magnesium in satisfactory yields (168). The iodide and bromide were found to give equally poor yields and the addition of benzene to increase the solubility of the Grignard reagent, was not effective. To a solution of 6.2 g. (0.025 mole) of p-iododimethylaniline (169) in 50 cc. of ether and 20 cc. of benzene, were added 5 g. of magnesium turnings and five drops of ethyl

(168) Ehrlich and Sachs, Ber., 36, 4296 (1903); Baeyer, ibid., 38, 2759 (1905); Ann., 354, 152 (1907); Chamberlain and Dull, J. Am. Chem. Soc., 50, 3088 (1928).
bromide. The mixture was refluxed for forty-eight hours and
the unreacted magnesium was removed by filtration. Chalcone
(2.1 g., 0.01 mole) was added and, after ten minutes of stir-
ring, the solution was hydrolyzed and worked up in the usual
manner. Only a 5% yield of β-([p-dimethylaminophenyl]-β-
phenylpropiophenone (mixed m. p. with the material described
on page 72 of this thesis) was isolated. In a similar experi-
ment, an equivalent amount (0.025 mole) of p-bromodimethyl-
aniline was substituted for the iodide. Fractional distilla-
tion and crystallization of the oils obtained subsequent to
hydrolysis gave 0.2 g. (7%) of β-([p-dimethylaminophenyl]-
β-phenylpropiophenone (mixed m. p.) and 1.5 g. of recovered
bromide.

The low yields of Grignard reagents were circumvented by
preparing p-dimethylaminophenylmagnesium iodide from magne-
sium iodide and p-dimethylaminophenyllithium. A solution of
0.024 mole of p-dimethylaminophenyllithium, prepared from
5 g. (0.025 mole) of p-bromodimethylaniline, lithium and
75 cc. of ether, was added slowly to a solution of magnesium
iodide, prepared from 0.06 g. atom of iodine, excess magnes-
sium powder and 35 cc. of ether. Some evolution of heat was
noted and, after ten minutes of stirring, a solution of 4.2 g.
(0.02 mole) of chalcone in 25 cc. of ether was added dropwise.
After five minutes of stirring, the mixture was hydrolyzed
and extracted with ether. A test portion of the residue obtained by evaporating the ether, gave a red solution when treated with alcoholic hydrogen chloride, indicating the presence of p-dimethylaminophenylphenylstyrylcarbinol. However, the carbinol could not be isolated by crystallization and 6.1 g. of crude β-(p-dimethylaminophenyl)-β-phenylpropiophenone were obtained. After crystallization from ethanol, 4.7 g. (71%) of the pure ketone (mixed m. p.) were isolated.

Chalcone with p-Dimethylaminophenyllithium.

To a solution of p-dimethylaminophenyllithium, prepared from 5.0 g. (0.025 mole) of distilled p-bromodimethylaniline, lithium and 75 cc. of ether, were added 4.2 g. (0.02 mole) of chalcone in 25 cc. of ether. The mixture was stirred for five minutes, hydrolyzed and extracted with 200 cc. of ether. The solid obtained by evaporating the ether solution, was digested with warm petroleum ether, cooled and filtered. The filtrate was evaporated and the residue repeatedly crystallized from ethanol. The yield of β-(p-dimethylaminophenyl)-β-phenylpropiophenone (mixed m. p.) was 0.8 g. (12%). The solid remaining from the original petroleum ether digestion was crystallized from a mixture of benzene and petroleum ether, and gave 5.0 g. (75%) of p-dimethylaminophenylphenyl-
styrylcarbinol. The white, crystalline carbinol melted at 131°, was sensitive to the acidic air of the laboratory and gave a ruby red solution with alcoholic hydrogen chloride.

**Anal.** Calcd. for $C_{25}H_{25}NO$: C, 83.8; H, 7.04.
Found: C, 83.6; H, 6.98. Zerewitinoff: Calcd. 1.0.
Found: 0.80.

**Attempted Preparation of p-Dimethylaminophenylcalcium Iodide.**

The preparation of this compound from the halide and metallic calcium was found unsatisfactory. When 6.2 g. (0.025 mole) of $p$-iododimethylaniline (169), 2 g. of calcium turnings, 50 cc. of ether and a large crystal of iodine were heated under reflux with stirring for twenty-four hours, some white precipitate formed and the mixture gave a weak positive color test. The ether-soluble material, obtained subsequent to hydrolysis, was crystallized from ethanol and identified as recovered iodide (75%). These results were checked by a duplicate experiment and indicate a highly restricted reaction.

**4-Dimethylaminochalcone with Phenylmagnesium Bromide.**

A solution of 5 g. (0.02 mole) of 4-dimethylaminochalcone (46) in 50 cc. of benzene was added dropwise to 0.08 mole of phenylmagnesium bromide in 100 cc. of ether. The mixture was stirred for ten minutes, hydrolyzed and extracted with ether.
The ether was dried and evaporated, and the resulting oil, which failed to crystallize, was distilled. The fraction boiling from 230 to 260° (3 mm.) was crystallized from ethanol and gave 3.4 g. (52%) of β-(dimethylaminophenyl)-β-phenyl-propiophenone. An increased yield of this ketone was obtained by cooling a solution of 5.0 g. (0.02 mole) of 4-dimethylamino- chalcone in 75 cc. of benzene to 7° and adding 0.021 mole of phenylmagnesium bromide in 37 cc. of ether dropwise. The ether extract, obtained subsequent to hydrolysis, was evaporated and the solid residue crystallized from ethanol. The crude ketone weighed 5.7 g. and melted from 88 to 89°. This product boiled from 245 to 250° (3 mm.) and when the distilled material was crystallized from ethanol, 5 g. (66%) of the pure ketone melting at 101° were obtained. The ketone gave a colorless solution in alcoholic hydrogen chloride, liberated hydrobromic acid when added to a chloroform solution of bromine and failed to evolve methane with methylmagnesium iodide. The products from the two above experiments, prior to distillation, gave red solutions with alcoholic hydrogen chloride, characteristic of small amounts of p-dimethylaminostyryldiphenylcarbinol. 4-Dimethylaminochalcone gave a light yellow solution with alcoholic hydrogen chloride.
4-Dimethylaminochalcone with Diphenylberyllium.

A solution of 5.0 g. (0.02 mole) of 4-dimethylaminochalcone in 50 cc. of benzene was added dropwise to about 0.04 mole of diphenylberyllium in 100 cc. of ether. A transitory, red coloration was observed as each drop of the chalcone solution came into contact with the organometallic solution. The mixture was stirred for ten minutes and hydrolyzed. A small portion of the oil obtained by evaporating the ether extract, gave a red solution when added to alcoholic hydrogen chloride. The remainder of the oil failed to crystallize and was distilled. The fraction boiling from 260 to 285° (7 mm.) was crystallized from ethanol and gave 4.6 g. (71%) of \( \beta-(p\text{-dimethylaminophenyl})\beta\text{-phenylpropiophenone} \) (mixed m. p.).

4-Dimethylaminochalcone with Phenyllithium.

Five grams (0.02 mole) of 4-dimethylaminochalcone in 50 cc. of benzene were added to 0.024 mole of phenyllithium in 100 cc. of ether. The mixture was stirred for ten minutes, hydrolyzed and extracted with ether. The solid from the evaporation of the ether extract was crystallized from a mixture of benzene and petroleum ether, and gave 4.4 g. (76%) of \( p\text{-dimethylamino styryldiphenylcarbinol} \) melting at 117°. The carbinol was white and crystalline when pure, but traces of acids caused a red coloration.
Anal. Calcd. for C₂₂H₂₃NO: C, 83.8; H, 7.04.
Found: C, 83.5; H, 7.00. Zerewitinoff: Calcd.: 1.0.
Found: 0.85.

The filtrates from the crystallization of the carbinol were evaporated and the residue, after crystallization from ethanol, gave 0.95 g. (14%) of β-(p-dimethylaminophenyl)-β-phenylpropiophenone (mixed m. p.). A duplicate run gave approximately the same amounts of saturated ketone and carbinol.

4-Dimethylaminochalcone with Phenylecalcium Iodide.

To a solution of phenylecalcium iodide (165) prepared from 20.4 g. (0.1 mole) of iodobenzene, calcium turnings and 100 cc. of ether, were added 5.0 g. (0.02 mole) of 4-dimethylaminochalcone in 50 cc. of benzene. After ten minutes of stirring, the mixture was hydrolyzed and extracted with ether. The residue from the evaporation of the ether extract was digested with 200 cc. of warm petroleum ether, cooled and filtered. The insoluble portion was crystallized from a mixture of benzene and petroleum ether and gave 4.2 g. (64%) of p-dimethylaminostyryldiphenylcarbinol (mixed m. p.). Attempted fractional crystallization and distillation of the dark oil obtained by evaporation the filtrates did not result in the isolation of the saturated ketone. It is entirely
possible that the ketone was present in small amounts and that the dark resinous materials, characteristic of the products of the reactions of phenylcalcium iodide, frustrated crystallization.

**Benzophenone-anil with Phenylsodium.**

A suspension of phenylsodium was prepared by stirring a mixture of 3.5 g. (0.01 mole) of diphenylmercury, 1 g. of powdered sodium and 50 cc. of benzene for twenty-four hours (170). The mixture was decanted from the sodium amalgam and 2.6 g. (0.01 mole) of the anil were added. After thirty minutes of stirring, the suspended solid was removed by filtration and hydrolyzed with water. The solid, isolated by extraction with ether, was repeatedly crystallized from propyl alcohol and gave 0.05 g. (1.5%) of triphenylmethylaniline (mixed m. p. with an authentic sample). The solution from the original filtration was also hydrolyzed and evaporated, but failed to give definite compounds.

**Benzophenone-anil with Phenylpotassium.**

A solution of 12.6 g. (0.04 mole) of dibutylmercury in 125 cc. of benzene and 6.3 g. (0.16 g. atom) of finely divided potassium were stirred for forty-eight hours (167b).

The suspension of phenylpotassium was decanted from the amalgam, and 10.3 g. (0.04 mole) of benzophenone-anil were added. The dark red mixture was stirred for five minutes and hydrolyzed with butyl alcohol and an ammonium chloride solution. The benzene extract was dried with sodium sulfate and evaporated. The solid residue was digested with 75 cc. of warm methanol, cooled, filtered and crystallized from propyl alcohol. The yield of triphenylmethylaniline (mixed m. p.) was 9.8 g. (73%).
DISCUSSION

In the reactions of conjugated systems with organometallic compounds the metallic derivative plays a definite part in determining the amounts of 1,2- and 1,4-addition, but this factor has received limited attention. The problem appears complex and only after the correlation of nearly unlimited quantities of experimental data can it be hoped that the key to a complete solution will be found. A number of Grignard reagents can be arranged in an order of increasing ability to add to the 1- and 2-positions of a given conjugated system, but the series may not be duplicated for other conjugated systems or by the corresponding organometallic derivatives of another metal with the same conjugated system. Also, such a series for the phenyl derivatives of various metals may not follow the order of the butyl derivatives of the same metals, as has been shown true in studies of relative reactivities. However, some similarity is certainly to be expected in the general behavior of organometallic compounds and the addition reactions of conjugated systems.

By comparing the reactions of several Grignard reagents with a given conjugated system, an order showing the increasing tendency of organomagnesium compounds to add to the 1- and 2-positions has been formed. In Series I the various R-groups represent organomagnesium compounds and the amount
of 1,2-addition to be expected increases from left to right (decreasing quantity of addition to the conjugated system). Admittedly, the series is not strictly accurate, for many conjugated systems give the same type of addition with several Grignard reagents, yet several isolated reactions indicate such an arrangement. Five reactions of methylmagnesium iodide illustrate the preference of this compound for 1,2-addition: (a) Chalcone (Compound 14, Table III and 16, Table IV) gave 1,2- and 1,4-addition, but only 1,4-addition with \( p \)-anisyl-, \( p \)-tolyl-, phenyl- and ethylmagnesium bromides. (b) \( \alpha \)-Methylchalcone (Compound 19, Table III and 17, Table IV) gave 1,2-addition while with phenyl- and ethylmagnesium bromides only 1,4-addition occurred. (c) Compound 3 of Table IV gave only 1,2-addition, but both 1,2- and 1,4-addition resulted with ethyl- and \( n \)-butylmagnesium bromides. (d) Compound 7 of Table VI gave only a trace of saturated ester (the 1,4-product), but good yields were obtained from \( \alpha \)-naphthyl-,
α-tolyl- and phenylmagnesium bromides. (e) The reactions of two amides (Compounds 1 and 7, Table VIII) gave more 1,2-addition than with phenyl- and ethylmagnesium halides.

It has been pointed out by Kohler (7) that arylmagnesium compounds often give more 1,2-addition than the alkyl derivatives and several reactions support this view. The reactions of compounds 1, 3, 4, 5, 7 and 8 of Table III gave a greater amount of the 1,2-product with phenylmagnesium bromide than with the ethyl derivative. The same tendency is illustrated by the reactions of compounds 7 of Table V and 2 of Table VII. Table XI summarizes the results of a series of comparable experiments in which ethyl styryl ketone was added to several organomagnesium bromides (7). Phenylmagnesium bromide

### TABLE XI

<table>
<thead>
<tr>
<th>Grignard Reagent</th>
<th>Per Cent 1,4-Addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_6\text{H}_5\text{MgBr} )</td>
<td>40</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5\text{CH}_2\text{MgBr} )</td>
<td>68</td>
</tr>
<tr>
<td>( \text{iso-C}_6\text{H}_5\text{MgBr} )</td>
<td>69</td>
</tr>
<tr>
<td>( \text{CH}_3\text{MgBr} )</td>
<td>70</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5\text{MgBr} )</td>
<td>71</td>
</tr>
</tbody>
</table>

obviously favored 1,2-addition, but differences were not
compound than with ethyltrimethylamine bromide. However, compounds

molecular than with ethyltrimethylamine bromide, however, according to unexpected results were greater with terti-ethyltrimethylamine.

and round that the ratio of the amount of saturated ketone

Table 2, Table 3, Table 4, Table 5, Table 6, and Table 7. (Table 6) the product (Table 5) the product of the con-

the outermost bonding of the tert-amy and tert-butyl

The work of Stegenga (6) summarized in Table 1 illustrates the
tendency for 1,2-addition than the ethyl and phenyl compounds

stoppel derivatives are shown in series 1 to have less

products. Upon this evidence alone, the oxidation and

benzyl ethyl, tert-butyl, and methyl of ethylated reactants with the

compound of Table A gave only the 1,2-products with the

products than ethyl- or phenyltrimethylammonium bromide with com-

of ethyltrimethylamine bromide gave neither products of tert-

and 1,4-addition is discussed on page 67 of this thesis.

heterogen among of ethylated reactants upon the amount of 1,2-

the influence of the different

other effect on the phenyl derivatives (cf. also the reaction

methacrylamid bromide did not give more 1,2-addition than the

of persulfate. Interest that with ethyl ethyl ketone, method-

found in the behavior of the other ethylated reactants. It is

- 80 -
11 of Table X gave 1,2-addition with tert.-butylmagnesium chloride and 1,4-addition with other Grignard reagents. The apparent abnormality of the later reaction may be attributed to the low yield (20 per cent) of 1,2-product from the tert.-butyl reagent or the peculiarities of the partially aromatic conjugated system.

The organic radicals have been arranged in several series to express their behavior in various reactions and it is possible that some correlation exists between such orders and Series I from the addition reactions of conjugated systems. Evans and co-workers (171) found that the decomposition voltages of organomagnesium bromides increased as given in Series II, but Stevens (5) has pointed out that any relation between Series II

\[
\text{CH}_2=\text{CHCH}_2\left\langle \text{tert.-C}_4\text{H}_9 \right\rangle \left\langle \text{iso-C}_8\text{H}_7 \right\rangle \left\langle \text{iso-C}_4\text{H}_9 \right\rangle \left\langle \text{C}_2\text{H}_5 \right\rangle \left\langle \text{n-C}_4\text{H}_9 \right\rangle \left\langle \text{n-C}_3\text{H}_7 \right\rangle \left\langle \text{CH}_3 \right\rangle \left\langle \text{C}_6\text{H}_5 \right\rangle
\]

this series and the reactions of crotonaldehyde (Table I) is as yet "problematical" for allylmagnesium bromide reacted with the aldehyde in a manner similar to the ethyl and phenyl Grignard reagents rather than the tert.-butyl compounds. Further, the position of the methyl group in Series II does (171) Evans, Lee and Lee, J. Am. Chem. Soc., 57, 489 (1935).
not correspond with that given in Series I.

A difference in the reaction velocities of 1,2- and 1,4-addition undoubtedly accounts for the products formed, and some correlation with the reactivities of Grignard reagents, as determined by other reactions, should be possible. Several methods have been used in studies of relative reactivities and, as would be expected, absolute agreement was not found. Kharasch and Weinhouse (172) added one equivalent of benzophenone to equimolar mixtures of two Grignard reagents and, from an examination of the products of the reactions, determined which magnesium compound reacted more rapidly. Their order of increasing reactivity is given in Series IIIa

SERIES IIIa

\[ \alpha-C_{10}H_7MgBr \prec C_6H_5MgBr \prec n-C_4H_9MgBr \prec C_6H_5CH_2MgCl \prec \text{tert.}-C_4H_9MgCl \]

and follows exactly the well known electronegativity series determined from the scission of unsymmetrical mercurials by hydrogen chloride (173). Series IV gives a part of the organic radicals in order of increasing electronegativity

and a comparison with Series IIIa indicates that the more
electron-negative groups gave the less reactive Grignard re-
agents. Unfortunately, the correlation is not a general one
and competitive reactions of mixtures of phenylmagnesium bro-
mide and several other organomagnesium bromides with benzo-
phenone gave the increasing order of reactivity shown in
Series IIIb (174). Further, competitive reactions of mixtures

of Grignard reagents with benzaldehyde, carbon dioxide, 2,4,6-
trimethylbenzoyl chloride, phenylacetylene, benzonitrile and
allyl bromide gave good agreement with the increasing order of

(174) Unpublished studies by Dr. M. W. Van Ess in this
laboratory.
reactivity given in Series V (175). Series IIIb, with the exception of methylmagnesium bromide, and Series V, with the

SERIES V

\[
\begin{align*}
C_6H_5CH_2MgCl & \quad n-C_6H_5MgBr \quad C_6H_5MgBr \quad \text{(isomer)} \\
\text{[isomer]} & \quad \text{[isomer]} \quad \text{[isomer]} \\
\alpha-C_10H_7MgBr & \quad \text{CH}_3=\text{CHCH}_2MgBr \\
\text{(C}_6\text{H}_5\text{)}_3\text{CMgCl} & \quad \text{[isomer]}
\end{align*}
\]

exceptions of the benzohydryl and allyl compounds, are in good agreement with Series IV, but the more electronegative groups gave the more reactive Grignard reagents. An increasing order of electronegativities determined by the cleavage of unsymmetrical organolead compounds was found to be, alkyl, aryl, allyl (176), and the position of the allyl radical in Series V appears in better agreement with this order than with Series IV.

Comparisons of the increasing ability of Grignard reagents to add to the 1- and 2-positions of conjugated systems (Series I) with Series IIIa, IIIb, IV and V, determined by competitive reactions, are not entirely satisfactory. In

(175) Unpublished studies by several workers in this laboratory.

Series I and IIIa the positions of benzylmagnesium chloride may not be in agreement, but the order, tert.-butyl, n-alkyl, aryl, follows exactly. Series IIIb cannot be compared independently, for the aromatic groups are not differentiated in Series I. In Series IV the order, tert.-butyl, n-alkyl, aryl, again follows Series I, the more electronegative groups favoring 1,2-addition, but the positions of the benzyl, methyl and allyl radicals are in disagreement. Series V does not include several Grignard reagents desirable for comparison with Series I, but benzylmagnesium chloride appears anomalous.

A rather comprehensive series of relative reactivities was determined by measuring the time required by individual Grignard reagents to react with benzonitrile (177). The aromatic and allyl compounds were found more reactive than the alkyl Grignard reagents, and tert.-butylmagnesium chloride was shown even less reactive than the simple alkyl derivatives (Series VI). This arrangement agrees well with Series I,

SERIES VI

\[ \text{tert.-C}_2\text{H}_5\text{Hg} < \text{alkyl} < \text{aryl} \]

increasing reactivity favoring 1,2-addition. However, methyl-

(177) Gilman and co-workers, Rec. trav. chim., 55, 577 (1936).
magnesium iodide with benzonitrile was found less reactive than the phenyl and ethyl derivatives (177) and the position of the methyl group in Series I is not in harmony with this result.

An increasing order of rates of reaction for alkyl Grignard reagents with active hydrogen compounds is given in Series VII (178). The arrangement, CH₃, n-C₄H₉, C₂H₅, iso-C₃H₇, follows Series I, the less reactive Grignard reagents

SERIES VII

iso-C₃H₇ < CH₃ < n-C₄H₉ < sec-C₄H₉ < n-C₃H₇ < C₂H₅ < iso-C₃H₇

favoring 1,2-addition, but the reactions of compound 32 of Table IV, 4 of Table VII and ethyl styryl ketone (Table XI) certainly do not indicate that isobutylmagnesium halides give more 1,2-addition than the methyl derivatives.

Yet another order of increasing reactivity of Grignard reagents has been found with esters (Series VIII) (179),

SERIES VIII

tert.-C₄H₉MgCl < C₆H₅MgBr < n-C₄H₉MgBr < iso-C₃H₇MgBr < C₆H₅MgBr

(178) Ivanoff and co-workers, Compt. rend., 196, 491 (1933); Bull. soc. chim., 51, 619 (1932).
(179) Vayon, Barbier and Thiebault, Bull. soc. chim., 1, 806 (1934).
but attempted correlations of Series I with this series fail rather completely.

Although the several series are far from harmonious, and Series II and VIII are in complete discord with Series I, the conclusion that the more reactive Grignard reagents favor 1,2-addition may serve at least as a working hypothesis. Series IIIa and VII obviously do not support such a contention, but Series V and VI, and the high reactivity of methylmagnesium bromide with benzophenone (Series IIIb) are in fair agreement.

The influence of the halogen atom of the Grignard reagent upon the amounts of 1,2- and 1,4-addition does not appear of major importance. The several tables in the Historical part of this thesis do not reveal differences of this nature and Stevens (5) has pointed out that tert.-butylmagnesium bromide and chloride gave about the same amounts of 1,4-addition with crotonaldehyde (Table I). In Stevens' investigation, however, the amount of 1,4-addition was slightly greater with the chloride, and Gilman and co-workers (177) have shown that with benzonitrile the bromides are generally more reactive than the chlorides and iodides. These results can be interpreted as indicating that tert.-butylmagnesium bromide favored 1,2-addition because of greater reactivity, but with butyl benzoate a reversed, increasing order of reactivity, \( n-C_8H_9MgI \)
\( \langle n-C_6H_{13}MgBr \rangle \langle n-C_7H_{15}MgCl \rangle \), was found (179). It is unlikely that the tendency of methylmagnesium iodide to favor 1,2-addition can be explained by increased reactivity caused by the iodine atom, for the organomagnesium iodides were found less reactive than the corresponding bromides and chlorides (177, 179). A valuable procedure for obtaining comparable addition reactions might be found in the use of simple magnesium compounds \( R_2Mg \), for the uncertainties of the influence of various halogen atoms and the varying reactivities of \( RMgX \) and \( R_2Mg \) are eliminated. As yet the reactions of conjugated systems with diaryl- or dialkylmagnesium compounds have not been investigated.

Stevens (5) has stated that two factors, steric hindrance and percentages of \( R_2Mg \) and \( RMgX \) of Grignard reagents, are inadequate in explaining the reactions of conjugated systems. The steric effect of phenylmagnesium bromide in 1,2-addition should not be greater than that of methylmagnesium iodide and less than that of ethylmagnesium bromide (Cf. Series I), if increasing steric hindrance is expressed by the order, methyl, ethyl, phenyl (determined from the reactions of carbonyl compounds). Such an order may not be applicable to Grignard reagents and certainly cannot be extended to include the mesityl group, for 2,4,6-trimethylphenylmagnesium bromide was found highly reactive (175). Grignard reagents with
different percentages of $\text{RMg}$ and $\text{RMgX}$ may react in a similar manner, for Series I indicates that ethyl- and $n$-butylmagnesium bromides (having approximately 42 and 82 per cent of $\text{RMg}$, respectively) (177a) gave the same type of addition with unsaturated ketones. Also, phenylmagnesium bromide and tert.-butylmagnesium chloride which have about the same amounts of $\text{RMg}$ and $\text{RMgX}$ (75-81 and 62-75 per cent, respectively) (180), added differently to crotonaldehyde (Table I).

The metal of the organometallic compound may or may not determine the amounts of 1,2- and 1,4-addition of conjugated systems. Organometallic compounds with various metals and the same R-group show no difference in behavior with several reactants. Acrolein (Compound 1, Table II) gave the same product with diethylzinc and ethylmagnesium bromide. Chalcone (Compound 16, Table IV) gave 1,4-addition with benzohydrylsodium (34) and the benzohydryl derivatives of magnesium, lithium and potassium (181). Phenyl phenylethynyl ketone gave 1,2-addition with the phenylethynyl derivatives of magnesium and sodium (117), and pyridine and its derivatives (Compounds 5, 6 and 7, Table X), gave the same type of

(181) Studies in progress by Dr. H. Gilman and the author of this thesis in this laboratory.
addition with Grignard reagents and organolithium compounds. Finally, Reformatsky's reaction between chalcone or α-methylchalcone and methyl bromoacetate gave the same product (1,2-
\[ \text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{H}_3 + \text{BrCH}_2\text{CO}_2\text{CH}_3 + \text{Zn(Mg)} \rightarrow \text{C}_6\text{H}_5\text{CH}=\text{CH(COH)}\text{C}_6\text{H}_3 \]
\[ \text{CH}_2\text{CO}_2\text{CH}_3 \]
addition) when magnesium was substituted for zinc (182).

In two reactions the metal of the organometallic compound has been found influential in directing the course of addition. Luttringhaus (164) found that chalcone gave 1,2-addition with phenyllithium and Kohler (19) in one of his earlier publications established 1,4-addition with phenylmagnesium bromide. Benzophenone-anil (Compound 1, Table X) with phenylmagnesium bromide gave 1,4-addition and, with phenyllithium, 1,2-addition (183). The work given in the
\[ (\text{C}_6\text{H}_5)_2\text{C}=\text{NC}_6\text{H}_5 + \text{C}_6\text{H}_5\text{Li} + \text{H}_2\text{O} \rightarrow (\text{C}_6\text{H}_5)_3\text{CNHC}_6\text{H}_3 \]
experimental part of this thesis extends such differences to the reactions of the phenylmetallic compounds of several

(182) Kohler and Heritage, Am. Chem. J., 43, 475 (1910). See also Kohler, Heritage and Macleod, ibid., 46, 217 (1911) who determined the amounts of 1,2- and 1,4-addition of various esters in Reformatsky reactions.
metals with chalcone, 4-dimethylaminochalcone and benzophenone-anil, and is summarized in Table XII. The phenyl-metallic derivatives of Zn, Al, Mn, Be and Mg with chalcone gave β,β-diphenylpropiophenone (the 1,4-product) and those of Li, Ca, Na and K gave largely diphenylstyrylcarbinol (the 1,2-product). Phenyllithium, p-dimethylaminophenyl-lithium and phenylsodium with chalcone gave, in addition to the 1,2-products, low yields of 1,4-products. 4-Dimethylaminochalcone with the phenyl derivatives of Be, Mg, Li and Ca gave products corresponding to those isolated from the reactions of chalcone, and when benzophenone-anil was added to phenylsodium and -potassium, triphenylmethylaniline was formed.

The data recorded in Table XII divide the organometallic compounds into two groups, the derivatives of Zn, Al, Mn, Be and Mg which gave 1,4-addition, and the derivatives of Li, Ca, Na and K which gave largely 1,2-addition. An explanation of these results lies in the reactivity of the organometallic compounds in question. Investigations of the reactivities of organometallic compounds of various metals have been summarized and rules given helpful in predicting the reactivities of the lesser known derivatives (184).

### TABLE XII
**ADDITION REACTIONS OF CHALCONE, 4-DIMETHYLAMINOCHALCONE AND BENZOPHENONE-ANIL WITH PHENYLMETALLIC COMPOUNDS.**

Types of Addition and Yields in Per Cent

<table>
<thead>
<tr>
<th>Organometallic</th>
<th>( \text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{H}_5 )</th>
<th>( \text{p}-(\text{CH}_3)\text{C}_9\text{H}_4\text{CH}=\text{CHCO}_2\text{H}_5 )</th>
<th>( \text{C}_6\text{H}_5\text{C}^-=\text{NC}_9\text{H}_4\text{H}_5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{C}_6\text{H}_5)\text{Zn})</td>
<td>91</td>
<td>1 - 4</td>
<td>1 - 4</td>
</tr>
<tr>
<td>((\text{C}_6\text{H}_5)\text{Al})</td>
<td>94</td>
<td>1 - 2</td>
<td>1 - 2</td>
</tr>
<tr>
<td>\text{C}_6\text{H}_5\text{MnI})</td>
<td>77</td>
<td>1 - 4</td>
<td>1 - 2</td>
</tr>
<tr>
<td>((\text{C}_6\text{H}_5)\text{Be})</td>
<td>90</td>
<td>71</td>
<td>(a)</td>
</tr>
<tr>
<td>\text{C}_6\text{H}_5\text{MgBr})</td>
<td>96(19)</td>
<td>52</td>
<td>(a)</td>
</tr>
<tr>
<td>(\text{p}-(\text{CH}_3)\text{C}_9\text{H}_4\text{MgI})</td>
<td>71</td>
<td>(a)</td>
<td>42(157)</td>
</tr>
<tr>
<td>\text{C}_6\text{H}_5\text{Li})</td>
<td>13</td>
<td>69</td>
<td>67</td>
</tr>
<tr>
<td>(\text{p}-(\text{CH}_3)\text{C}_9\text{H}_4\text{Li})</td>
<td>12</td>
<td>76</td>
<td>80(183)</td>
</tr>
<tr>
<td>\text{C}_6\text{H}_5\text{CaI})</td>
<td>45</td>
<td>64</td>
<td>78(165)</td>
</tr>
<tr>
<td>\text{C}_6\text{H}_5\text{Na})</td>
<td>3.5</td>
<td>39</td>
<td>1.5</td>
</tr>
<tr>
<td>\text{C}_6\text{H}_5\text{K})</td>
<td>52</td>
<td>73</td>
<td></td>
</tr>
</tbody>
</table>

(a) The unsaturated carbinol was not isolated, but the crude reaction product gave a red solution with alcoholic hydrogen chloride indicating the presence of the 1,2-product.
The increasing order of reactivity is given in the following series and the organometallic compounds are designated by the chemical symbols for their metallic components. The positions of Mn and Ca are somewhat uncertain, but are approximately as indicated. The group of phenylmetallic compounds which gave 1,4-addition with conjugated systems (Zn, Al, Mn, Be, Mg) are definitely less reactive than the group which gave 1,2-addition (Li, Ca, Na, K). Other conjugated systems and other organometallic compounds than those given in Table XII may not give the transition from 1,4- to 1,2-addition when lithium is substituted for magnesium. Further, organometallic compounds closely related in reactivity would not be expected to give large differences in the amounts of 1,2- and 1,4-addition. One might predict, however, that a relatively unreactive reagent such as a phenylethynylzinc compound would add (unless condensations occurred) to the 1- and 4-positions of the conjugated system of phenyl phenylethynyl ketone (Cf. page 45 of this thesis), and that a highly reactive compound such as phenylpotassium would add to the potential anil linkage of benzalquininaldine (Compound 4, Table X).

Another explanation for the influence of the metal of organometallic compounds in directing addition reactions
may lie in the ability of the metal to form transitory ring

\[ \text{C}_6\text{H}_5\text{CH} = \text{CHC}_6\text{H}_5 \]

compounds. The chelates of Morgan and Drew (185) have been suggested to explain the mechanisms of the reactions of other organic compounds (186).

The product of the reaction of phenylmagnesium bromide with 4-dimethylaminochalcone was originally reported as \( \beta \)-dimethylaminostyryldiphenylcarbinol (the 1,2-product) (46). In view of the many similar reactions which gave 1,4-addition this result was not to have been expected, but it was hoped that the less reactive diphenylberyllium would give the 1,4-product. The reaction of phenylmagnesium bromide was reinvestigated and the supposed "carbinol" melting at 100° was characterized as \( \beta \)-(\( \beta \)-dimethylaminophenyl)-\( \beta \)-phenylpropio-phenone (the 1,4-product). The compound failed to show an active hydrogen when analyzed by the Zerewitinoff method and was synthesized by an independent reaction which left no doubt

(186) Carothers and Berchet, J. Am. Chem. Soc., 55, 2807 (1933); Johnson, ibid., 55, 3029 (1933).
of the structure. Further, \( p \)-dimethylaminostyryldiphenyl-carbinol was synthesized from 4-dimethylaminochalcone and phenyllithium and gave reactions in accord with unsaturated carbinols.

Chalcone was found a valuable reagent for the identification of certain organometallic compounds. In the preparation of diphenylberyllium from phenyllithium and beryllium chloride, a convenient method was needed for establishing that the reaction had actually occurred. The phenyl derivatives of beryllium and lithium add to many of the common reactants in a similar manner although at different velocities. However, chalcone gave the 1,4-product in good yield and the 1,2-product, which would have resulted from phenyllithium, was not isolated. The same reactant was used to characterize phenylmanganese iodide and \( p \)-dimethylaminophenylmagnesium iodide which were prepared from manganese iodide and phenyllithium, and from magnesium iodide and \( p \)-dimethylaminophenyl-lithium, respectively.
SUMMARY

The addition reactions of organometallic derivatives with compounds having conjugated systems have been correlated and their mechanism discussed.

The influence of the groups in conjunction with the conjugated system upon the amounts of 1,2- and 1,4-addition has been defined by rules helpful in predicting the course of untried reactions.

The influence of organometallic compounds in directing addition has been discussed and attempts were made to establish a relationship with relative reactivity data.

The reactions of a series of phenylmetallic compounds with chalcone, 4-dimethylaminochalcone and benzophenone-anil were investigated. The phenyl derivatives of Al, Zn, Mn, Be and Mg (the less reactive types) gave 1,4-addition and those of Li, Ca, Na and K (the more reactive types) gave largely 1,2-addition.

The product of the reaction of 4-dimethylaminochalcone and phenylmagnesium bromide has been characterized as β-(p-dimethylaminophenyl)-β-phenylpropiophenone and not the carbinol originally reported (46).

Chalcone has been used as a reagent for the identification of certain organometallic derivatives prepared from organolithium compounds.