Nearly thirty years ago Tiffeneau and Delange\textsuperscript{2} observed that the action of formaldehyde on benzylmagnesium chloride produced \( o \)-tolylcarbinol instead of the expected benzylcarbinol. Since that time, owing to the widespread development of the use of organomagnesium halides in synthesis, the action of a variety of substances on benzylmagnesium chloride has been reported. Although many reactants (carbon dioxide, acetone and many ketones, acetics and esters) have been shown to produce the normal products, another group of reactants (benzaldehyde, ethyl formate, ethyl chlorocarbonate, halogen methyl alkyl ethers and ethylene oxide) has been found to yield products of rearrangement, usually \( o \)-tolyl derivatives. It has also been observed that rearrangement occurs with other Grignard reagents that show a structural resemblance to benzylmagnesium chloride.\textsuperscript{3} The present investigation, dealing with the action of various reagents upon benzylmagnesium chloride, was undertaken with the object of developing certain generalizations concerning the nature of the reactants that lead to products of rearrangement and of elucidating the mechanism of the reaction.

An important feature of the previously reported reactions of benzylmagnesium chloride is that certain reagents produce both the normal and abnormal products, while with others only one type of product has been observed.\textsuperscript{4} Superficially, this behavior is similar to that of the sodium derivatives of certain enols, which may react to produce substances in which substituents are introduced on the \( \alpha \)-carbon atom or the oxygen atom, or both of these.

Several of the earlier investigators who worked with benzylmagnesium chloride, not anticipating an unusual reaction, reported results that have

\textsuperscript{1} This paper is an abstract of a portion of a thesis submitted by Paul R. Austin to the Graduate Faculty of Cornell University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1930.

\textsuperscript{2} Tiffeneau and Delange, Compt. rend., 137, 573 (1903).

\textsuperscript{3} (a) Carré, Bull. soc. chim., [4] 5, 487 (1909); [4] 7, 841 (1910); (b) Chelintzev and Karmanov, J. Russ. Phys.-Chem. Soc., 47, 161 (1915); Chem. Abstracts, 9, 1472 (1915); (c) Gilman and Harris, This Journal, 49, 1825 (1927); (d) Gilman and Kirby, \textit{ibid.}, 51, 3475 (1929); (e) Gilman and Harris, \textit{ibid.}, 53, 3541 (1931).

\textsuperscript{4} A serious obstacle in studying the reaction mechanism is the difficulty of isolating all of the products of any reaction. It is almost impossible to state with certainty that none of a particular product is formed in a reaction. In many instances complications arise from the reaction of the initial products with a second or third molecule of the organomagnesium halide. This situation obtains in the case of esters, acid halides and anhydrides.
proved to be erroneous or have left some doubt as to the structure of the products. The case of ethyl chlorocarbonate is a striking example of this. Houben\(^6\) reported that benzylmagnesium chloride acted upon ethyl chloro-
carbonate to produce ethyl phenylacetate (43\% yield) and tribenzyl-
carbinol (10\% yield). Recently, Gilman and his collaborators\(^6\) have shown that ethyl o-toluate is produced in this reaction together with a relatively small amount of ethyl phenylacetate. The latter result throws doubt on the structure of the alcohol reported by Houben as tribenzylcarbinol, since one might expect o-tolyldibenzylcarbinol to be produced by the action of benzylmagnesium chloride on ethyl o-toluate.

The present study confirmed completely the findings of Gilman and Kirby, that ethyl o-toluate and ethyl phenylacetate are formed in this reaction, and showed that the alcohol described by Houben is actually tri-
benzylcarbinol. This result indicated that the initial products, ethyl o-
toluate and ethyl phenylacetate, differ greatly in their tendency to react further with benzylmagnesium chloride. Ethyl phenylacetate, the normal product, evidently reacts with benzylmagnesium chloride much more readily than ethyl o-toluate, the product of rearrangement. This difference in reactivity explains similar observations in other cases where the initial products can react further with the Grignard reagent. The following experiment confirmed the predicted difference in reactivity of the initial products. An ethereal solution of equimolar quantities of ethyl o-toluate and ethyl phenylacetate was treated with a dimolar quantity of benzylmagnesium chloride. A large part of the ethyl o-toluate was re-
covered unchanged (72\%), together with a small amount of ethyl phenyl-
acetate (7\%), and tribenzylcarbinol was produced in large quantity (71\% of the theoretical).\(^7\)

In the course of a study of the preparation of ketones by the action of organomagnesium halides on acid chlorides,\(^8\) it was observed that acetyl chloride reacts with benzylmagnesium chloride to produce an o-tolyl ketone (o-methylacetophenone) instead of the expected benzyl ketone. Subse-
sequently, it was found that acetic anhydride and benzoyl chloride react with benzylmagnesium chloride in similar fashion to produce o-tolyl

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\(^6\) Houben, *Ber.*, 36, 3087 (1903).


\(^7\) It seems likely that the action of benzylmagnesium chloride upon ethyl o-toluate does not proceed beyond the formation of the ketone, o-tolyl benzyl ketone. This result, as well as the preferential reaction of ethyl phenylacetate, is in agreement with observations of Conant and Blatt [*This Journal*, 51, 1227 (1929)] on the action of Grignard reagents upon branched chain compounds.

\(^8\) Johnson and Dawson, a preliminary paper presented at the Seventh Midwest Regional Meeting of the American Chemical Society, University of Chicago, May 28, 1927.
derivatives. The case of benzoyl chloride is strictly analogous to that of ethyl chlorocarbonate; the principal products of the reaction are o-methylbenzophenone and phenyldibenzylcarbinol. Evidently in this instance also, the initial products (o-tolyl phenyl ketone and benzyl phenyl ketone) differ greatly in their tendency to react with benzylmagnesium chloride. Only the benzyl derivative reacts further, and produces phenyldibenzylcarbinol.

The results mentioned above, together with a number of other experimental results observed with benzylmagnesium chloride, are summarized in Table I. Nearly all of the reactants listed as abnormal, lead to the production of o-tolyl and benzyl derivatives. The list of normal reactants is not a complete compilation but a general summary of the normal reactions of benzylmagnesium chloride.

<table>
<thead>
<tr>
<th>Abnormal reactants</th>
<th>Normal reactants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>Paraldehyde</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>Alkyl and aryl ketones</td>
</tr>
<tr>
<td>p-Methoxybenzaldehyde</td>
<td>Acetals and ethyl orthoformate</td>
</tr>
<tr>
<td>Ethylene oxide</td>
<td>Ethyl acetate, benzoate and carbonate</td>
</tr>
<tr>
<td>Alkyl chloromethyl ethers</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>Ethyl and methyl chlorocarbonate</td>
<td>Epichlorohydrin and chloroacetone</td>
</tr>
<tr>
<td>Ethyl formate</td>
<td>Allyl iodide</td>
</tr>
<tr>
<td>Acetyl and benzyl chloride</td>
<td>Mercuric chloride</td>
</tr>
<tr>
<td>Acetic and chloroacetic anhydride</td>
<td>Phenyl isocyanate</td>
</tr>
<tr>
<td></td>
<td>Alkyl p-toluene sulfonates</td>
</tr>
</tbody>
</table>

An inspection of this summary shows that the abnormal reactants do not form a homogeneous group. While it is unwise to draw broad generalizations from the limited experimental data, one is led to the conclusion that acid chlorides and anhydrides favor an abnormal reaction, as do formaldehyde and its derivatives (R—O—CH2X), and esters of formic acid. The anomalous behavior of aromatic aldehydes is striking; Schmidlin and García-Banús found that the slow addition of benzaldehyde to benzylmagnesium chloride gave as much as 95% of the normal product (phenylbenzylcarbinol), whereas the reverse addition gave only 30% of the normal product and 70% of diphenylisochromane. In the present study the organomagnesium halide was always added slowly to an excess of the reactant.

Abnormal reactions similar to those of benzylmagnesium chloride have been observed with 3,5-dimethylbenzylmagnesium chloride and α-naphthylmethylmagnesium chloride. Gilman and Harris have shown

\* Some of the p-tolyl derivative is stated to be formed from benzaldehyde, alkyl chloromethyl ethers, ethyl formate and ethylene oxide Ref. 3 (d).

that the reaction between cinnamyl chloride, magnesium and carbon dioxide gives rise, likewise, to a product of rearrangement. Since the abnormal reaction involves the ortho positions of the benzyl group, it seemed of interest to investigate the behavior of substituted benzylmagnesium halides with groups in the ortho position. For this purpose 2-chloro- and 2,6-dichlorobenzylmagnesium chloride were chosen, and their behavior toward carbon dioxide, methyl chlorocarbonate, acetic anhydride and acetyl chloride was observed. The results are shown in Table II, together with the corresponding observations on benzylmagnesium chloride. From these and other available data, it is clear that the rearrangement (abnormal reaction) depends upon the nature of the reactant and of the organomagnesium halide. From the standpoint of the reactants, it appears that the tendency to produce rearrangement decreases in the order: acetyl chloride > acetic anhydride > methyl chlorocarbonate > carbon dioxide. In the Grignard reagents, the tendency to undergo rearrangement appears to decrease to some extent with the introduction of one ortho substituent and decreases further by the introduction of two ortho substituents. In the latter, the rearrangement necessarily leads to a 3-tolyl derivative.

**Table II**

**Reactions of Benzyl- and Ortho-Substituted Benzylmagnesium Chlorides**

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Benzyl-</th>
<th>Organomagnesium chloride</th>
<th>2-Chlorobenzyl</th>
<th>2,6-Dichlorobenzyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>Normal</td>
<td>Normal</td>
<td>2-ClC₆H₄CH₂COOH</td>
<td>2,6-Cl₂C₆H₄CH₂COOH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Normal</td>
<td>2-Chlorophenylacetic acid</td>
<td>2,6-Dichlorophenylacetic acid</td>
</tr>
<tr>
<td>CH₃COCl</td>
<td>Rearrangement</td>
<td>Normal</td>
<td>2-ClC₆H₄CH₂COOH</td>
<td>2,6-Cl₂C₆H₄CH₂COOH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methyl o-toluate</td>
<td>2-Chlorophenylacetic acid</td>
<td>Methyl 2,6-dichlorophenylacetic acid</td>
</tr>
<tr>
<td>(CH₃CO)₂O</td>
<td>Rearrangement</td>
<td>Rearrangement</td>
<td>2,3-(CH₃)ClC₆H₄COCH₃</td>
<td>2,6-Cl₂C₆H₄CH₂COCH₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methylacetophenone</td>
<td>2-Methyl-3-chloroacetophenone</td>
<td>4-Methyl-3,5-dichloracetophenone</td>
</tr>
</tbody>
</table>

In the organomagnesium halides that undergo abnormal reaction, a triad system $H-C=C-CH₃-MgX$ is present; the rearrangements result in the introduction of the entering group in the $\gamma$-position instead of the $\alpha$-position, and a migration of hydrogen in the reverse direction, from the $\gamma$-position to the $\alpha$-position. With an acid chloride, for example, the following reactions can be written.
The formulation of the intermediate product I, resolves the rearrangement into two steps. The plausibility of this point of view is enhanced by experimental evidence from studies by Prévost,\textsuperscript{11} who showed that the action of Grignard reagents upon halides of the type $R-CH=CH-CH_2Br$, produced compounds corresponding in structure to the intermediate compound I.

\[
C_2H_6CH=CHCH_2Br + C_6H_5MgBr \rightarrow C_7H_8CHOHCH_2C_6H_5
\]

In the examples cited, 3-phenylpentene-1 (II) appears as the abnormal product and represents the first step in the mechanism formulated above. In this compound, the phenyl group does not sufficiently activate the hydrogen on the $\gamma$-carbon atom to cause a migration to the $\alpha$-position. An acyl group, in the structure I, causes the $\gamma,\alpha$-migration of hydrogen to occur easily and in the final product the double bond forms a conjugated system with the carbonyl group. The second step of the abnormal reaction ($\gamma,\alpha$-migration of hydrogen) appears to be analogous to the well known keto $\rightarrow$ enol transformations. The effect of variations of $R$ in the system $RCHCO-$ is parallel to the effect in the system $RCHCH=CH_2$; in both systems the activating effect of the $R$ group diminishes in the order: acyl $>$ phenyl $>$ alkyl.

The effect of substituents in the triad system upon the first step of the rearrangement ($\alpha,\gamma$-migration of the entering group) is more obscure. In the system $A-C=C-CH_2-B$, the nature of the substituents $A$ and $B$, as well as that of the reactant, have an important effect on the inherent tendency to undergo abnormal reaction. In certain triad systems (cinnamyl bromide) abnormal reactions occur when $B$ is a halogen atom, or the MgX residue; in others (benzyl chloride and iodide) abnormal reactions do not occur when $B$ is a halogen atom,\textsuperscript{12} but do occur when $B$ is the MgX residue.\textsuperscript{10}


\textsuperscript{12} We have not been able to observe the formation of o- or p-tolyl derivatives in reactions of benzyl chloride and benzyl iodide. Mr. E. W. Scott in this Laboratory has...
residue. From these comparisons it appears that an MgX residue in the 
$\alpha$-position produces a greater inherent tendency to undergo abnormal reac-
tion than a halogen atom, and that a system containing a phenyl group in
the $\gamma$-position is more prone to undergo rearrangement than one in which
the $\beta$- and $\gamma$- atoms form part of a benzene ring.

Of the theories that have been proposed for the mechanism of the
formation of abnormal products from benzylmagnesium chloride, the hy-
pothesis of Schmidlin and Garcia-Banús\textsuperscript{10} appears to be the most satis-
factory. They assume a dynamic isomerism between the normal form and
an $o$-quinonoid form (III)\textsuperscript{18}

$$\begin{align*}
\text{Normal form} & \quad \xrightarrow{\text{CH$_2$-MgX}} \quad \text{o-Quinonoid form} \\
\text{Benzyl group} & \quad \text{Phenoxy1 group}
\end{align*}$$

The suggestion of a transformation to $o$-tolylmagnesium chloride appears
to be untenable, since this condition would require the formation of $o$
tolyl derivatives with all reactants or a dynamic isomerism between benzyl
and $o$-tolyl magnesium halides. In order to test this point, a careful
examination was made of the action of carbon dioxide on benzylmagnesium
chloride and on $o$-tolylmagnesium bromide. All of the fractions and all
of the filtrates were examined minutely in each case, and it was found that
no $o$-toluic acid was produced from benzylmagnesium chloride nor was any
phenylacetic acid produced from $o$-tolylmagnesium bromide.

Tiffeneau and Delange\textsuperscript{2} have compared this rearrangement with certain
abnormal reactions of sodium phenolate. In the phenoxy1 group, there
is present a triad system similar to that of the benzyl group, except that
an oxygen atom takes the place of the $\alpha$-methylenegroup.

The C-alkylation of phenols as well as many aliphatic enols may be ac-
counted for on the basis of addition of the reactant at the $\beta,\gamma$-double
bond,\textsuperscript{14} a mechanism that does not require the postulation of a tautomeric
form of the enol. Although the addition theory of Michael\textsuperscript{16} has been
effected reactions between benzyl iodide and sodium cyanide under the same conditions
that give rise to an abnormal reaction with $\alpha$-furfuryl chloride (This Journal, 52,
1284 (1930)), but was unable to detect any $o$- or $p$-tolunitrile in the product.

\textsuperscript{13} Stewart, "Recent Advances in Organic Chemistry," Longmans Green and Co.,
London, 5th ed., 1927, Vol. II, p. 295, suggests a similar $p$-quinonoid structure to ac-
count for the red color of sodium benzyl.

\textsuperscript{14} Claisen, Ann., 442, 222 (1925).

\textsuperscript{16} Michael, J. prakt. Chem., [2] 37, 486 (1888); 46, 189 (1892)
widely adopted, the experimental evidence does not appear to exclude the possibility of electropy of the enol ion or radical nor of 1,4-addition (when conjugated systems are involved).

Although the conventional theory of addition to the double bond can be used to explain the abnormal behavior of benzylmagnesium chloride and its analogs, this theory does not satisfactorily account for the formation of 3-phenylpentene-1 (II) observed by Prévost. In view of the comprehensive studies of Gilman and his collaborators, it appears unlikely that the Grignard reagent can be assumed to add to the ethylenic bond in the system, RCH=CHCH₂Br.

The observation that products arising from the o-quinonoid structure are not observed in all reactions of benzylmagnesium chloride is our principal objection to accepting the hypothesis of Schmidlin and Garcia-Banh as a complete elucidation of the mechanism of this transformation. The postulation of a rearrangement before the introduction of the reactant does not appear to suffice, since it does not account for the important effect of the nature of the reactant and does not allow a prediction of the result. It is obvious that certain structural features of the triad systems are prerequisite for the abnormal reaction, but the experimental evidence indicates clearly that the reactant must likewise possess some structural characteristic that is also requisite for the abnormal reaction. It would seem more reasonable to assume that the change of structure occurs in the course of the reaction, through rearrangement of electrons in a free benzyl radical or a benzyl ion.

**Experimental**

**Preparation of Grignard Reagents.**—All of the organomagnesium halides used in this study were prepared in the conventional manner; the few reactions that did not start spontaneously were initiated by the addition of a small quantity of ethylmagnesium bromide solution. The R-MgX content and the yields were determined by titration, using methyl red as indicator. Benzylmagnesium chloride was usually prepared in one mole runs, using one mole of halide to ten moles of ether. The yields were over 90% of the theoretical.

**Benzylmagnesium Chloride and Ethyl Chlorocarbonate.**—A repetition of the procedure used by Houben led to the isolation of an ester fraction and a solid alcohol. In this experiment, as in other typical experiments, a solution of one equivalent of the organomagnesium halide was allowed to drop slowly into a well-cooled solution of slightly more than one equivalent of the reactant. The ester fraction proved to consist largely of ethyl o-toluate, as shown by saponification to o-toluic acid; m. p. 103-104°. This acid proved to be identical with o-toluic acid prepared from o-toluidine by way of o-tolunitrile. A small amount of phenylacetic acid was present in the mother liquors. This result agrees with previous observations of Gilman.


17 A discussion of the application of electronics to isomeric change, with references to the original literature, is given by Stewart, Ref. 13, pp. 344-351. For references to the rearrangement of free radicals see Ref. 3(e).

The solid alcohol was recrystallized twice from ligroin, once from aqueous methyl alcohol and once from aqueous ethyl alcohol; m. p. 115-116°. The lower melting point, 108-111°, reported by Houben is probably due to the presence of dibenzyl as an impurity; Klages and Heilmann report that tribenzylcarbinol melts at 114-115°. That this alcohol is the normal product, tribenzylcarbinol, was shown by its identity with the solid alcohol obtained by the action of benzylmagnesium chloride on ethyl phenylacetate, diethyl carbonate and dibenzyl ketone. Since we were unable to obtain dibenzyl o-tolylcarbinol by the action of benzylmagnesium chloride on ethyl o-toluate, it seems unlikely that this carbinol is formed in the reaction between benzylmagnesium chloride and ethyl chlorocarbonate.

When benzylmagnesium chloride (3 moles) is added to an ethereal solution of ethyl chlorocarbonate (1 mole), the principal product is tribenzylcarbinol and only a very small amount of an ester fraction is obtained. It seems likely under these conditions that ethyl o-toluate is largely converted to benzyl o-tolyl ketone. Tribenzylcarbinol is also produced by the action of benzylmagnesium chloride on phenylacetetyl chloride.

**Benzylmagnesium Chloride and Methyl Chlorocarbonate.**—The addition of 0.07 mole of benzylmagnesium chloride to an ice-cold solution of 10 g. of methyl chlorocarbonate in 25 cc. of ether gave an ester fraction from which 1.0 g. of o-toluic acid, m. p. 103-104°, was obtained. The melting point of this acid remained unchanged after mixture with an equal quantity of authentic o-toluic acid, m. p. 103-104°. An attempt to isolate phenylacetic acid from the reaction products was unsuccessful, but a microscopical examination of the crude o-toluic acid showed the presence of some phenylacetic acid.

**Benzylmagnesium Chloride and Diethyl Carbonate.**—The principal product of this reaction is tribenzylcarbinol; after purification the crystals melted at 115-115.5°, and were identical with the specimens obtained by other methods. Only a trace of a low-boiling liquid fraction was obtained.

**Benzylmagnesium Chloride and Ethyl o-Toluate.**—Ethyl o-toluate was allowed to react with an excess of benzylmagnesium chloride, in an effort to prepare dibenzyl-o-tolylcarbinol. Although a reaction occurred, the desired alcohol could not be isolated. From 16 g. of ethyl o-toluate there was obtained 12 g. of a liquid, b. p. 225-227° at 7 mm., which was probably benzyl o-tolyl ketone. We did not succeed in identifying and characterizing this compound.

**Competition of Ethyl Phenylacetate and Ethyl o-Toluate for Benzylmagnesium Chloride.**—To a solution of 16 g. (0.1 mole) of ethyl phenylacetate and 16 g. (0.1 mole) of ethyl o-toluate in 100 cc. of dry ether, an ethereal solution of benzylmagnesium chloride (0.2 mole) was added slowly with stirring, during about four hours. The reaction mixture was decomposed with ice and diluted sulfuric acid and the ether layer separated. Ether extracts of the aqueous layer were combined with the original ether layer and dried over magnesium sulfate. After removal of the ether, there remained 46 g. of a liquid that yielded 15.5 g. of an ester fraction; b. p. 100-103° at 8 mm. Upon saponification this fraction gave 10 g. of crude o-toluic acid, m. p. 98-100°, which corresponds to a 72% recovery of ethyl o-toluate. The filtrates from the crystallization of the crude o-toluic acid were concentrated and yielded less than 1 g. of phenylacetic acid, which after crystallization from ligroin melted at 75-78°.

The residue from the distillation of the ester fraction solidified on cooling; the weight of this solid (21.5 g.), calculated as tribenzylcarbinol, represents a 71% conversion of the

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10 Klages and Heilmann, *Ber.*, 37, 1456 (1904).
11 Sachs and Loeyv, *ibid.*, 36, 1589 (1903).
12 It was found that small amounts of either phenylacetic or o-toluic acid, in the presence of a large amount of the other, could be detected by this method.
ethyl phenylacetate. After recrystallization from alcohol, 8 g. of tribenzylcarbinol, m. p. 114–115°, was obtained. A mixed melting point with the tribenzylcarbinol prepared from benzylmagnesium chloride and ethyl chlorocarbonate was 115–116°.

**Benzylmagnesium Chloride and Carbon Dioxide (Solid).—**A solution of benzylmagnesium chloride (0.1 mole) was added to a slush of solid carbon dioxide and ether, with frequent shaking to avoid the formation of lumps. The reaction mixture was allowed to warm to 15° and was decomposed with dilute sulfuric acid in the customary manner. The crude acid weighed 5.4 g. (40% yield) and after crystallization from water melted at 76–77°. A mixed melting point with an authentic specimen of phenylacetic acid, prepared from benzyl cyanide, was 76–77°. Microscopical examination of all portions of the product indicated no trace of o-toluic acid.

**o-Tolylmagnesium Bromide and Carbon Dioxide (Solid).—**The Grignard reagent was prepared in the usual manner from o-bromotoluene, in yields of over 90% of the theoretical. A solution of o-tolylmagnesium bromide (0.1 mole) was added to a slush of solid carbon dioxide and ether, as described above. There resulted 8.5 g. (62% yield) of crude acid, which after crystallization from ligroin and from water melted at 103–104°. A mixed melting point with an authentic specimen of o-toluic acid was 103–104°. All of the filtrates of precipitation and crystallization were evaporated and examined microscopically; no phenylacetic acid could be detected.

**o-Tolylmagnesium Chloride and Dibenzyl Ketone.**—This reaction was carried out in an attempt to synthesize dibenzyl-o-tolylcarbinol. Dibenzyl ketone for this purpose was prepared in 65% yields by the distillation of calcium phenylacetate. A solution of o-tolylmagnesium bromide (0.17 mole) was added to 31 g. (0.15 mole) of dibenzyl ketone in 100 cc. of ether. The reaction mixture was treated in the usual manner and was subjected to steam distillation. The non-volatile portion was extracted with ether and gave 35 g. of an oil; on standing for five days a crystalline precipitate separated from this oil. The solid was separated by adding ligroin and filtering; from the filtrate 20 g. of unchanged dibenzyl ketone was recovered.

The crystalline solid was crystallized twice from alcohol and twice from acetone; it formed fine white needles which melted at 157–158° when heated rapidly, or at 154° in a slowly heated bath. Analyses indicate that the compound is not dibenzyl-o-tolylcarbinol (C_{12}H_{10}O); its composition corresponds more closely to that of tetra-benzyl ethylene glycol (C_{16}H_{26}O_2).

*Anal.* Calcd. for C_{12}H_{10}O: C, 87.4; H, 7.4. For C_{16}H_{26}O_2: C, 85.3; H, 7.1. Found: C, 85.82; H, 8.83.

**Benzylmagnesium Chloride and Acetic Anhydride.**—A solution of benzylmagnesium chloride (0.55 mole) was added slowly, with stirring, to a solution of 100 g. (1.65 moles) of acetic anhydride in 100 cc. of ether. After working up the product in the usual way there was obtained 23 g. (30% yield) of a liquid, b. p. 205–230°, that proved to be 2-methylacetophenone. The remainder of the reaction product, which probably contained dibenzylmethylenecarbinal, was not investigated. The structure of the ketone was established by oxidation with sodium hypobromite solution. From 13.5 g. of the ketone there resulted 6 g. of an acid which, after crystallization from ligroin and from water, melted at 104–105°. A mixed melting point with an authentic specimen of o-toluic acid was 104°. No trace of phenylacetic acid was found in the oxidation products from this ketone.

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23 We are indebted to Dr. Wallace H. Carothers of the Experimental Station of E. I. du Pont de Nemours and Co., for these microanalyses. The values reported are the mean results of five concordant analyses.

Benzylmagnesium Chloride and Chloroacetic Anhydride.—A solution of benzylmagnesium chloride (0.5 mole) was added slowly, during the course of two hours, to a well-stirred solution of 105 g. (0.6 mole) of chloroacetic anhydride in 600 cc. of ether at 0°. During the course of the reaction a white crystalline solid precipitated. The reaction mixture was decomposed with ice-cold dilute hydrochloric acid and the ether layer and extracts were dried over magnesium sulfate. On fractionating the product there was obtained 36 g. (42% yield) of a halogenated ketone, b. p. 125–135° at 14 mm., with strong lachrymatory properties. On redistillation there was obtained a clear pale yellow liquid, b. p. 129–130° at 11 mm., which proved to be chloromethyl o-tolyl ketone.


The semicarbazone of chloromethyl o-tolyl ketone was found to melt at 103–105°. The structure of the ketone was established by oxidation with sodium hypochlorite; 10 g. of the ketone gave 4.5 g. (56% yield) of o-tolyllic acid which melted at 104°. This was checked by a mixed melting point with an authentic specimen.

Benzylmagnesium Chloride and Acetyl Chloride.—A solution of the Grignard reagent (0.37 mole) was added slowly to 39 g. (0.5 mole) of acetyl chloride in 400 cc. of ether. During the course of the reaction a white precipitate formed. The reaction mixture was treated in the usual manner and gave 12 g. (24% yield) of a ketone fraction boiling mainly at 102–103° at 22 mm., and 202–206° at 745 mm. This product proved to be almost entirely o-methylacetophenone, as shown by examination of the semicarbazone and by oxidation to o-tolyllic acid.

A sample of 1.5 g. of the ketone, on oxidation with sodium hypobromite solution gave 0.9 g. of crude o-tolyllic acid; after three crystallizations from water this acid melted at 102–103°, and a mixed melting point with authentic o-tolyllic acid was 103–104°.

The semicarbazone of the ketone melted at 202°; since the values 192° and 203° are reported in the literature, comparison was made with the semicarbazone of authentic o-methylacetophenone. For this purpose, the ketone was prepared by the action of methylmagnesium iodide on o-tolunitrile. The synthetic ketone boiled at 204° at 745 mm., and its semicarbazone melted at 205°. A mixed melting point of this semicarbazone with the one obtained above was 204–205°.

Benzylmagnesium Chloride and Benzoyl Chloride.—This reaction was first carried out by adding benzylmagnesium chloride to an excess of benzoyl chloride in ether, cooled in an ice–salt mixture. This procedure led to the formation of a relatively small amount of the ketone fraction and a large amount of the tertiary alcohol. Subsequently, it was found that the yield of the ketone fraction was increased by cooling the ethereal solution of benzoyl chloride in a bath of carbon dioxide snow.

A solution of benzylmagnesium chloride (0.24 mole) was added slowly, with vigorous stirring, to a solution of 70 g. (0.5 mole) of benzoyl chloride in 50 cc. of ether, cooled in carbon dioxide snow. The reaction mixture was decomposed with 30% sulfuric acid and subjected to steam distillation. The oily residue was taken up in ether, washed thoroughly with dilute alkali and dried. After removal of the ether, there remained 37 g. of a liquid which was fractionated under reduced pressure. A fraction collected at 162–184° at 11 mm., on redistillation gave 9 g. of a ketone which distilled almost completely at 164–169° at 9 mm., and proved to be phenyl o-tolyl ketone (2-methylbenzophenone). A sample of 1.4 g. of this ketone on oxidation with aqueous potassium permanganate gave 1.0 g. of a solid which was a mixed melting point of 155–157° with an authentic specimen.

This experiment was carried out by Mr. Tab Nilanidhi, in connection with a study of the preparation of chloromethyl ketones from various Grignard reagents and chloroacetic anhydride.

15 Auwers, Ann., 408, 242 (1915).
permanganate solution gave 0.6 g. of an acid; the latter after several crystallizations
from ligroin and absolute alcohol, melted at 127°. A mixed melting point with an
authentic specimen of o-benzoylbenzoic acid, m. p. 127°, showed no depression.

Fractional distillation of the higher boiling material in the crude reaction product
gave 10 g. of a liquid, distilling almost entirely at 224–235° at 8 mm., that solidified on
cooling. This was recrystallized twice from ligroin, and from aqueous alcohol; m. p.
84–85°. This substance proved to be identical with a specimen of phenyldibenzyl-
carbinol, m. p. 84–85°, prepared from benzylmagnesium chloride and ethyl benzoate.
Klages and Heilmann\(^9\) reported 86–87° for the melting point of this carbinol.

Reactions of 2-Chlorobenzylmagnesium Chloride

Preparation of the Grignard Reagent.—o-Chlorotoluene was chlorinated at the
boiling point, in a quartz flask, in the light of a mercury vapor lamp; it was found ad-
visable to underchlorinate slightly. The purified o-chlorobenzyl chloride had the fol-
lowing boiling points: 84–85° at 3 mm., 96–98° at 14 mm., 110° at 21 mm. The
Grignard reagent was always prepared with the freshly distilled halide, using 10 moles
of ether to one of the halide; the yields varied from 60–75% of the theoretical. Since
this organomagnesium halide appeared to be particularly sensitive to atmospheric
oxidation, it was prepared in small amounts and used at once.

o-Chlorobenzylmagnesium Chloride and Carbon Dioxide (Gas).—This reaction
produced o-chlorophenylacetic acid, which formed white needles melting at 94–98
°. The melting point recorded for this acid in the literature\(^2\) is 95°; the melting point of
2-methyl-3-chlorobenzoic acid is 159°.\(^2\)

o-Chlorobenzylmagnesium Chloride and Methyl Chlorocarbonate.—A solution
of the Grignard reagent (0.032 mole) was added slowly to an excess of methyl chloro-
carbonate in 50 cc. of ether, cooled to 0°. The crude reaction product containing the
ester fraction was saponified by strong potassium hydroxide solution, and upon acidifica-
tion gave 1 g. of an acid. After two crystallizations from alcohol and water, the acid
melted at 95–96° (softening at 93°). A mixed melting point with o-chlorophenylacetic
acid obtained in the preceding experiment was 95–96°. It appears that the abnormal
reaction does not occur to any appreciable extent in this case.

o-Chlorobenzylmagnesium Chloride and Acetic Anhydride.—A solution of the
Grignard reagent (0.07 mole) was added slowly to an ethereal solution of 50 g. (0.83
mole) of acetic anhydride, cooled in an ice–salt bath. The mixture was decomposed in
the usual way but no attempt was made to isolate the pure ketone, due to the small
quantity available. Oxidation with sodium hypobromite solution, and repeated crys-
tallization of the resulting acid gave 0.1 g. of 2-methyl-3-chlorobenzoic acid; m. p.
159–160°. The formation of this acid indicates that the original ketone was 2-methyl-3-
chloroacetophenone.

o-Chlorobenzylmagnesium Chloride and Acetyl Chloride.—A solution of the
Grignard reagent (0.042 mole) was added to an ice-cooled solution of 12 g. of acetyl
chloride in 50 cc. of ether. The procedure outlined in the preceding experiment gave
0.2 g. of crude 2-methyl-3-chlorobenzoic acid. After three crystallizations the acid
melted at 160° (softening at 157°); a mixed melting point with the 2-methyl-3-chloro-
benzoic acid from the previous experiment was 159–161°. This indicates the presence
of 2-methyl-3-chloroacetophenone in the reaction products.

Reactions of 2,6-Dichlorobenzylmagnesium Chloride

2,6-Dichlorotoluene.—This compound was prepared by an adaptation of a method

\(^9\) Klages and Heilmann; \(^2\) Noelting, \textit{Ber.}, 37, 1025 (1904).
previously described, 29 p-toluene sulfonyl chloride was chlorinated and the sulfonic acid
group was removed by hydrolysis. One mole of p-toluene sulfonyl chloride (190 g.)
mixed with 11 g. of antimony pentachloride was chlorinated at 70-80°, in a 500-cc. flask
provided with a mechanical stirrer and reflux condenser. The chlorination was
stopped when the gain in weight attained 69 g.; this required four to five hours. The
 crude 2,6-dichlorotoluene-4-sulfonyl chloride was converted to the sodium salt of the
sulfonic acid by pouring the reaction mixture carefully into a concentrated solution of
sodium hydroxide. The sparingly soluble sodium 2,6-dichlorotoluene-4-sulfonate
was recrystallized from water; the yields were 85-93% of the theoretical. Elimination
of the sulfonic acid group was effected by heating with 85% sulfuric acid.

A mixture of 300 g. of the above salt and 1 liter of 85% sulfuric acid was refluxed
for nine hours; 200 cc. of water was added and the solution was distilled until the aqueous
layer of the distillate amounted to 250 cc. The reaction mixture was again refluxed for
nine hours, 250 cc. of water was added, and the mixture was distilled until fumes started
to appear (250-300 cc. of aqueous distillate had been collected). The heavy layer of
2,6-dichlorotoluene in the distillates was separated and dried over solid sodium hy-
droxide. The yield of crude product was 42-50% of the theoretical; the purified 2,6-
dichlorotoluene boiled at 54-56° at 8 mm., nD 55 1.5510, d4 1.2686. A quantity of 2,3,6-
trichlorotoluene (b. p. 96° at 10 mm., m. p. 41-42°) amounting to about 25% of the
weight of 2,6-dichlorotoluene was isolated from the high-boiling fractions.

2,6-Dichlorobenzyl Chloride.—2,6-Dichlorotoluene was chlorinated in the manner
described for the chlorination of o-chlorotoluene. The initial temperature was 194°,
and the reaction was practically complete when the temperature reached 230°. The
 crude product was subjected to fractional distillation under reduced pressure; the main
fraction, b. p. 107-110° at 9 mm., or 135° at 25 mm., consisted of a mixture of liquid and
solid. After cooling thoroughly the solid was removed by filtration and was recrystal-
lized twice from ligroin; m. p. 39-40°. The material can also be crystallized from al-
cohol and from ether; its lachrymatory properties make all crystallizations troublesome.
For analysis, the 2,6-dichlorobenzyl chloride was recrystallized three times from ether,
at the temperature of carbon dioxide snow, using the technique of Dufraisse.30

Anal. Calcd. for C1H2Cl3:Cl, 54.45. Found: Cl, 54.18, 53.93.

The liquid material separated from the crystals appeared also to consist chiefly of
2,6-dichlorobenzyl chloride; its melting point was probably depressed by the presence
of a small quantity of 2,6-dichlorotoluene. A dichlorobenzyl chloride has been described
by Bellstein and Kuhlberg31 but their product differs in physical properties from the
one described above.

2,6-Dichlorobenzyl chloride is oxidized with difficulty to 2,6-dichlorobenzoic acid.
Heating with dilute nitric acid32 in a sealed tube at 140°, for twenty-four hours, produced
an acid which, after recrystallization from water, melted at 136-137°; neut. equiv.,
191.2. Oxidation with boiling aqueous potassium permanganate solution (fifteen hours)
gave an acid, which was recrystallized twice from water and once from ligroin; m. p.
138-140°, neut. equiv. 191.4. The reported melting point of 2,6-dichlorobenzoic acid
is 143.7°,33 and the calculated neutralization equivalent is 190.9.

Preparation of 2,6-Dichlorobenzylmagnesium Chloride.—This preparation was
carried out using 0.2 mole of the halide, 100 cc. of ether and slightly more than the theo-
retical quantity of magnesium turnings. The yields of RMgX were about 90% of the

29 (a) Geigy and Co., German Patent, 210,856; Friedländer, 9, 104 (1908-1910);
31 Bellstein and Kuhlberg, Ann., 146, 317 (1868); 150, 313 (1869).
theoretical, when highly purified specimens of the halide were used. The yields were somewhat lower with less pure samples.

2,6-Dichlorobenzylmagnesium Chloride and Carbon Dioxide (Gas).—The acid obtained from 0.02 mole of the Grignard reagent after two crystallizations from dilute alcohol weighed 0.1 g.; m. p. 156-157° (softening at 150°). This acid is 2,6-dichlorophenylacetic acid and is identical with the acid obtained in the following experiment. Analyses and determinations of the neutralization equivalent are described below.

2,6-Dichlorobenzylmagnesium Chloride and Methyl Chlorocarbonate.—A solution of the Grignard reagent (0.047 mole) was added slowly to 10 g. of methyl chlorocarbonate in 25 cc. of ether. After decomposing in the usual way, the product was saponified with 30% potassium hydroxide solution. The alkaline solution was filtered from an unsaponifiable residue (see below) and gave 6 g. of a crude acid upon acidification. After three crystallizations from dilute alcohol the 2,6-dichlorophenylacetic acid melted at 157-158° (softening at 152°); neut. equiv.: calcd., 205.0; found, 206.5, 207.1.

Anal. Calcd. for C₈H₇Cl₁₁O₂: Cl, 34.60. Found: Cl, 34.83, 34.81.

A mixed melting point with the acid obtained from the reaction of carbon dioxide and 2,6-dichlorobenzylmagnesium chloride was 157-158° (softening at 152°). An attempt to oxidize this acid to 2,6-dichlorobenzoic acid, by means of aqueous potassium permanganate, was unsuccessful; the original acid was recovered unchanged.

The unsaponifiable residue separated from the alkaline solution of the acid crystallized from ethyl acetate in fine white needles, m. p. 165-166°. The molecular weight as determined by the depression of the melting point of camphor (Rast) was 339. This value indicates the presence of two dichlorobenzyl groups, and suggests the possibility that the compound may be 2,6,2',6'-tetrachlorodibenzyl ketone (mol. wt. 348), or 2,6,2',6'-tetrachlorodibenzyl. The quantity of material was insufficient for further investigation.

2,6-Dichlorobenzylmagnesium Chloride and Acetic Anhydride.—A solution of the Grignard reagent (0.056 mole) was added to a solution of 25 g. of acetic anhydride in 25 cc. of ether. After decomposition with dilute sulfuric acid and evaporation of the ether layer, an oily liquid remained. The crude product upon oxidation with sodium hypobromite solution gave an acid that was purified only with difficulty. After numerous precipitations and crystallization there was obtained 0.1 g. of a pure product, m. p. 157-158°, which proved to be identical with the 2,6-dichlorophenylacetic acid described above (mixed melting point, 157-158°). The formation of this acid indicates the presence of 2,6-dichlorophenylacetone in the reaction product.

2,6-Dichlorobenzylmagnesium Chloride and Acetyl Chloride.—The product of this reaction was oxidized with sodium hypobromite solution in the usual way. After repeated fractional precipitations and crystallizations there resulted about 0.1 g. of an acid, m. p. 188-189°, which was presumably 3,5-dichloro-4-methylbenzoic acid. Claus and Beysen reported a melting point of 187-188° (uncorr.) for this acid. The isolation of 3,5-dichloro-4-methylbenzoic acid indicates the presence in the reaction product of 3,5-dichloro-4-methylacetophenone, a product of para rearrangement.

Summary

Acetyl chloride, benzoyl chloride, acetic anhydride and chloroacetic anhydride have been found to react with benzylmagnesium chloride to produce o-tolyl ketones instead of the expected benzyl ketones.

The action of benzylmagnesium chloride on ethyl chlorocarbonate was found to give principally ethyl o-toluate and tribenzylcarbinol. It is

suggested that the formation of these products depends upon a selective action of the Grignard reagent on the initial products of the reaction.

2-Chlorobenzylmagnesium chloride and 2,6-dichlorobenzylmagnesium chloride have been prepared and their behavior toward certain reactants has been investigated. The tendency of these reactants to yield products of rearrangement appears to decrease in the following order: acetyl chloride > acetic anhydride > methyl chlorocarbonate > carbon dioxide.

The mechanism of the rearrangement process in abnormal reactions of benzylmagnesium chloride is discussed.

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[Contribution from the John Harrison Laboratory of Chemistry of the University of Pennsylvania]

REDUCTION STUDIES OF SCHIFF BASES. I. THE REDUCTION OF METHYLENE-PARA-AMINOPHENOL AND ITS PROBABLE STRUCTURE

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Schiff bases of the simple type RCH=NR', when of relatively high molecular weight, are apparently not polymerized, and can in many cases be hydrogenated to the corresponding secondary amines. With bases obtained from aldehydes of low molecular weight, notably formaldehyde, polymerization occurs, and may be the cause of difficulties in reduction. Polymerization has been demonstrated for compounds such as methylene-aniline, methylene-toluidines, and ethylidine-aniline. That a reversible relationship may exist among monomeric and polymeric forms was suggested by early investigators, and was made to appear very probable by the work of Ingold and Piggott. No account of the polymerization of these bases appears in the recent review by Carothers.

Cyclic structures of the type (A) were assigned to certain polymeric

1 These and the corresponding ketone derivatives may be called the azomethines: Möhlau, Ber., 31, 2250 (1898).

2 See, e.g., German Patent 211,869; Wheeler, This Journal, 35, 976 (1913); Shepard and Ticknor, ibid., 38, 381 (1916); Kaufmann and Müller, Ber., 51, 126 (1918); Skita and Keil, ibid., 61, 1452 (1928); Zechmeister and Truka, ibid., 63, 2883 (1930); Buck, This Journal, 53, 2192 (1931).

3 Tollens, Ber., 18, 3309 (1885); Miller and Plochl, ibid., 25, 2020 (1892); 29, 1462 (1896); Pulvermacher, ibid., 25, 2762 (1892); Bischoff, ibid., 31, 3248 (1899).

(a) Tollens, ibid., 17, 653 (1884), and Ref. 3; (b) Wellington and Tollens, ibid., 18, 3298 (1885).

4 Ingold and Piggott, J. Chem. Soc., (a) 121, 2381, 2793 (1922); (b) 123, 2745 (1923).

5 Carothers, Chem. Reviews, 8, 353-428 (1931).