1929

A Some rearrangement reactions of organomagnesium halides B New organolead compound in anti-knock studies

James Emory Kirby

Iowa State College

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A. SOME REARRANGEMENT REACTIONS OF ORGANOMAGNESIUM HALIDES.

B. NEW ORGANO-LEAD COMPOUND IN ANTI-KNOCK STUDIES.

BY

James E. Kirby

A Thesis Submitted to the Graduate Faculty
for the Degree of

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Approved

In charge of Major work

Head of Major Department

Dean of Graduate College

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Part A

The writer wishes to express his appreciation to Dr. Henry Gilman for the suggestion of these problems and for the generous advice and encouragement given during this work.

Part B

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A. SOME REARRANGEMENT REACTIONS OF ORGANOMAGNESIUM HALIDES.

1. Studies on Benzylmagnesium Chloride.

I. Introduction

The Grignard reagents have, since their discovery in 1900 by the French chemist whose name they bear, attained a position of importance in the field of synthetic organic chemistry perhaps unapproached by any other single group of compounds. They are convenient to prepare and handle, and may be employed in the synthesis of compounds of many widely different types.

Any reagent, to be of great value in synthetic chemistry, must be "reliable", that is, it must lead to derivatives whose structure may be definitely predicted by comparison with the known behavior of the reagent in question. Twenty-eight years of ever-increasing use have demonstrated quite clearly the reliability of the organomagnesium halides discovered by Grignard. Further, many careful studies have been carried out during this period which were undertaken for the purpose of establishing or refuting the dependability of these reagents. A few of these studies are mentioned here. The problem is one of determining the exact location of an -MgX group, whether it be attached to carbon, or to some other element such as sulfur, oxygen, or nitrogen, by replacing that group with some other group of atoms, the final product being a molecule which permits of ready and certain identification. Studies of this nature thus not only establish the reliability of the reactant, but also of the Grignard reagent itself.

Alkyl sulfates have been suggested by Gilman and Hoyle (1) as reagents for characterizing the -MgX group attached to carbon as well as to some other elements. These reagents introduce an alkyl radical into the molecule in the position originally held by the -MgX group. In accordance with a recent suggestion by Gilman and Heck (2) the reaction may be formulated as follows:

$$(\text{Alkyl-O})_2SO_2 + RMgX \longrightarrow R\text{-Alkyl} + \text{Alkyl-X} + MgSO_4$$
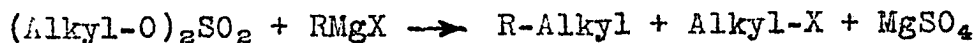
Methyl sulfate has been shown by Gilman and Kirby (3) to give a normal reaction with the difficulty prepared benzhydrylmagnesium chloride. Further, phenyl- and α-naphthyl-isocyanates (4) are reagents for characterizing the -MgX group by the formation of crystalline anilides and α-naphthalides in very good yields.

$$RMgX + R'NCO \longrightarrow R\text{-N=}\overset{OMgX}{C}\text{-R'} \xrightarrow{HOH} R\text{-N=}\overset{OH}{C}\text{-R} \longrightarrow R\text{-NH-CO-R'}$$
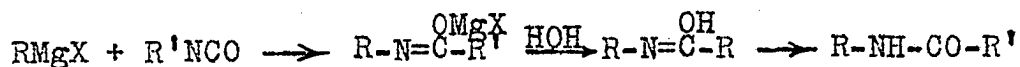
The reliability of phenylisocyanate, diphenylcarbamine chloride, and benzoyl chloride for the characterization of the -MgX group attached to nitrogen was demonstrated by Gilman and Kirby (5).

(1) Gilman and Hoyle, J. Am. Chem. Soc., 44,2621(1922). This reaction was studied earlier by others. References to former work are given in a paper by Gilman and Beaber (ibid., 46,518 (1925)). Subsequent work on alkyl sulfates and the Grignard reagent has been done by Bert (Bull. soc. chim., 37,1252(1925)).
(2) Gilman and Heck, J. Am. Chem. Soc., 50,2223(1928).
(3) Gilman and Kirby, ibid., 48,1733(1926).
(4) Gilman and Furry, ibid., 50,1214(1928). This paper contains references to the earlier work on the reaction between isocyanates and the Grignard reagent.
(5) Kirby, J.E., Some reliable reagents for characterizing the -MgX group. Unpublished thesis. Library, Iowa State College, Ames, Iowa, 1926.

A few instances are, however, recorded in the literature in which the Grignard reagent gives rise to an unexpected product. In 1903 Grignard (6) treated benzylmagnesium chloride with trioxymethylene, the solid polymer of formaldehyde, and obtained a product which he described as the expected phenylethyl alcohol.

$$C_6H_5\text{-}CH_2\text{-}MgCL + HCHO \longrightarrow C_6H_5\text{-}CH_2\text{-}CH_2\text{-}OMgCl \overset{HOH}{\longrightarrow} C_6H_5\text{-}CH_2\text{-}CH_2\text{-}OH$$
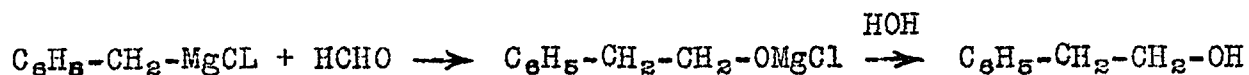
Very shortly after the appearance of Grignard's paper, Tiffeneau and Delange (7) repeated the work of Grignard and definitely proved that the reaction product is not phenylethyl alcohol, but an isomer, o-tolyl carbinol. The appearance of this isomer was first indicated by the fact that the substance obtained can be easily crystallized and melts at 33°, while phenylethyl alcohol remains liquid even at -20°. Further proof was supplied by oxidation of the compound to o-toluic acid under conditions which yield benzoic acid when phenylethyl alcohol is oxidized. The phenylurethanes of both alcohols were also prepared and while their melting points are almost exactly the same, a mixed melting point determination proved them to be different bodies.

Tiffeneau and Delange (7) explained this remarkable reaction by drawing an analogy with the synthetic method first employed by Manasse (8) for the preparation of phenolalcohols.

(6) Grignard, Bull. soc. chim., 29,953(1903).
(7) Tiffeneau and Delange, Compt. rend., 137,573(1903).
(8) Manasse, Ber., 27,2411(1894).
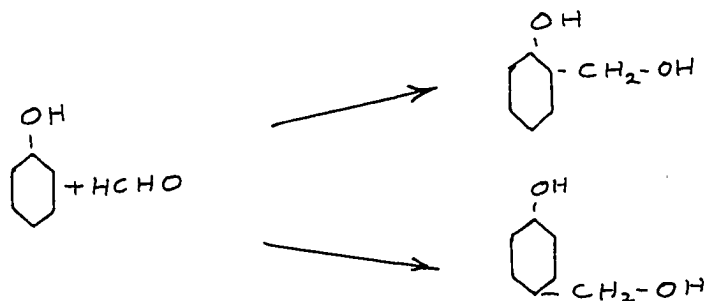
The reaction of benzylmagnesium chloride and formaldehyde is then written as follows:
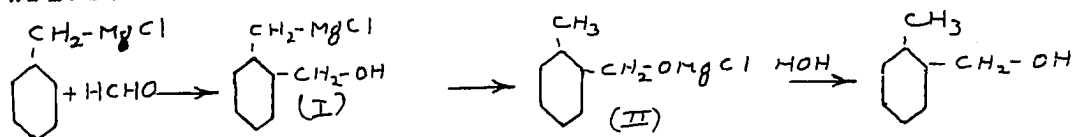
The reasons put forward by Tiffeneau and Delange (7) for assuming formula (II), $\underline{O}$-CH_3-C_6H_4-CH_2-$OMgCl$, to represent correctly the intermediate complex magnesium compound are, in view of recent work of Gilman and Schulze (9), partially invalidated. The intermediate compound did not react with carbon dioxide as would be expected of compound (I). Further, the compound did not form an ester when treated with acetic anhydride and on these grounds formula (I) was discarded. Gilman and Schulze (9) showed that -OMgX compounds yield esters with acetic anhydride. The failure to obtain an ester is difficult to explain. Its formation would have confirmed formula (II) for a compound such as (I), obviously incapable of existence, contains a C-MgX group and should yield a tertiary alcohol with acetic anhydride. Further, two molecules of a compound like (I) would interact and yield compound (II).

(9) Gilman and Schulze, Rec. trav. chim., $\underline{47}$(1928).
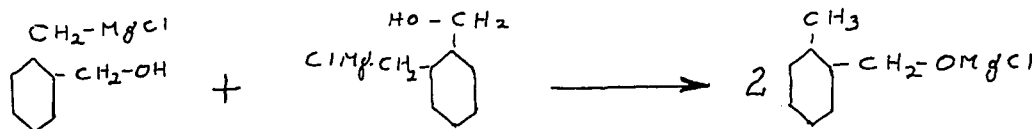
In 1909 Carré (10) studied the reaction of some substituted benzylmagnesium halides with trioxymethylene. He was able to show that m-xylylmagnesium bromide reacts in a normal manner yielding m-xylyl carbinol. The yields obtained with o-xylyl- and p-xylyl- magnesium bromide were too meagre to be conclusive but he was able to show that o-xylylmagnesium bromide reacts with acetone in a wholly normal manner.

A second anomalous behavior of benzylmagnesium chloride was discovered in 1909 by Chichibabin (11). Previously Hell (12) had prepared phenylbenzyl carbinol by the action of benzylmagnesium chloride on benzaldehyde.
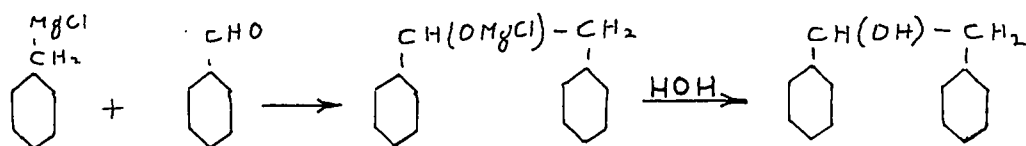
Chichibabin (11) repeated this work and showed that the residues remaining after the crystallization of the phenylbenzyl carbinol yield o-benzoylbenzoic acid, and traces of p-benzoylbenzoic acid, on oxidation. The oxidation products indicated that the reaction proceeded in part abnormally producing an ortho-substituted

(10) Carré, Compt. rend., 148,1108(1909).
(11) Chichibabin, Ber., 42,3474(1909).
(12) Hell, Ber., 37,453(1904).

product. Chichibabin believed this abnormal product to be phenyl o-tolyl carbinol.

Schmidlin and Banús (13) resumed the study of this reaction in connection with studies on the related triphenylmethylmagnesium chloride. These latter studies will be discussed in detail further on in this paper. Schmidlin and Banús (13) isolated from the reaction products of benzaldehyde and benzylmagnesium chloride a white, crystalline compound melting at 110°. The analysis of this compound indicated the molecular formula, $C_{21}H_{18}O$. The oxygen atom appeared to be held in an ether-like linkage, since it gave no chloride when treated with hydrogen chloride, and gave no reaction with acetic anhydride or phenylisocyanate. Since the compound does not react with phenylhydrazine or hydroxylamine hydrochloride the oxygen atom is not ketonic in nature. The compound is oxidized by chromic acid, and by permanganate to o-benzoylbenzoic acid and benzoic acid. Small amounts of anthraquinone also are formed, perhaps due to the known ring-closure of o-benzoylbenzoic acid. Based on these observations, and the fact that the body gives a green color with concentrated sulfuric acid, Schmidlin and Banús (13) concluded that the compound was diphenyl-isochromane.
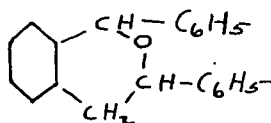
By very slow addition of benzaldehyde to benzylmagnesium

(13) Schmidlin and Banús, Ber., 45, 3193(1912).

chloride a yield of 95% of phenylbenzyl carbinol was obtained by Schmidlin and Banús (13). When the Grignard solution was added to the aldehyde the yield of carbinol dropped to 40% and a 60% yield of diphenyl-isochromane was obtained. That the formation of the isochromane cannot be due to reaction of excess benzaldehyde with the normal intermediate -OMgX compound (I) as formulated below, was experimentally demonstrated by the same workers.

$$C_6H_5-CH_2-MgCl + C_6H_5-CHO = C_6H_5-CH_2-CH(OMgCl)-C_6H_5 \quad (I)$$
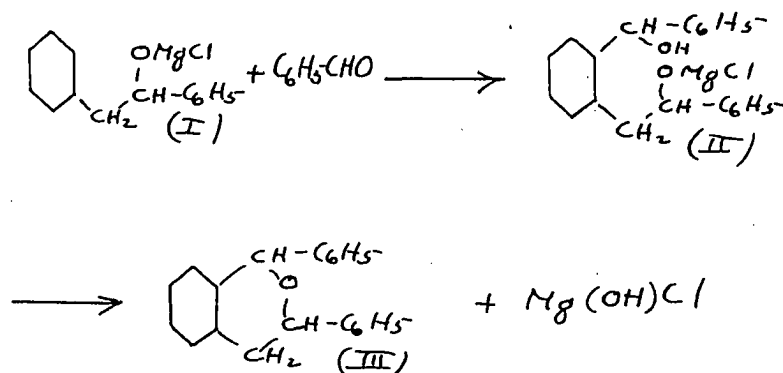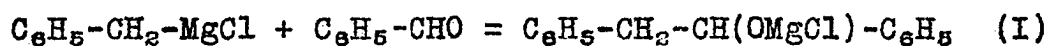
Benzaldehyde was shown to be wholly without action on the -OMgX compound represented by formula (I). These reactions, then, evidently are not the source of the isochromane.

In some experiments Schmidlin and Banús (13) obtained also a compound melting at 123-124°, having the formula $C_{21}H_{16}O$, and capable of being reduced to diphenylisochromane with the aid of platinum black in glacial acetic acid. This compound was concluded to be diphenylisochromene, and its structure was given as
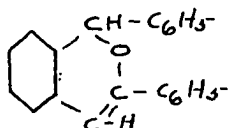
Schmidlin and Banús (13) further demonstrated that benzyl-magnesium chloride is not altered in its mode of reaction by heating at 100° for a considerable period of time. The significance of this experiment will be more apparent in the discussion given below of triphenylmethylmagnesium chloride, which seems to undergo rearrangement when refluxed for several hours in benzene solution. It was, therefore, proposed to represent benzylmagnesium chloride as an equilibrium mixture of two forms, one the normal, the other a quinoidal structure somewhat similar to that proposed for triphenylmethylmagnesium chloride and discussed later.
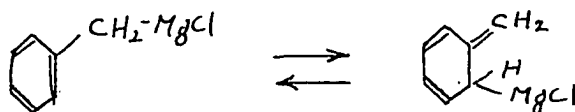
Toward carbon dioxide the equilibrium is shifted completely to the left; toward formaldehyde to the right; and toward benzalde-hyde either form may appear depending upon the concentrations used, and mode of addition of the Grignard solution. These reactions may be represented as follows:
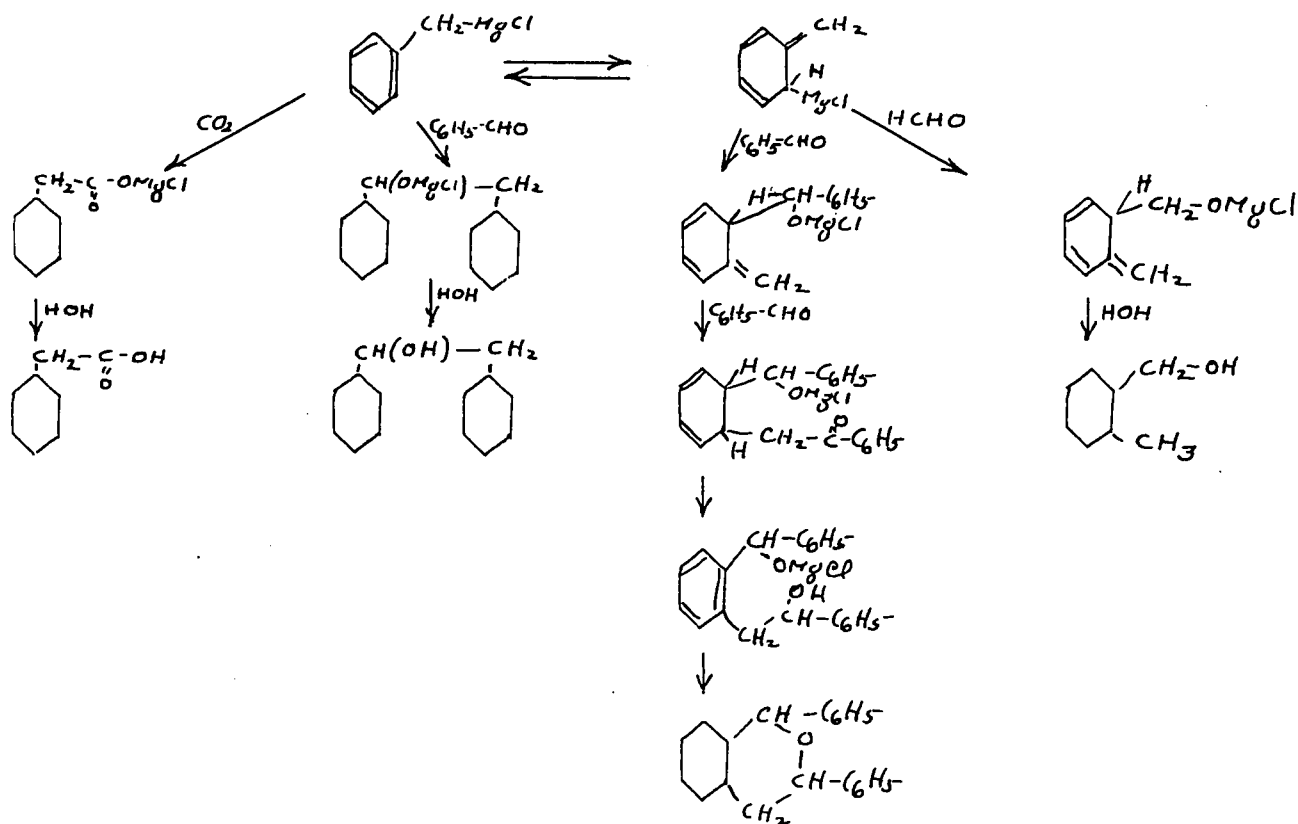
An extended study of the mechanism of the reaction between the Grignard reagent and various aldehydes was carried out by Marshall (14). He showed that the products obtained by the action of two moles of benzaldehyde on one mole of phenylmagnewium bromide are benzophenone and benzyl alcohol. These reactions were expressed by the following equations:

$$C_6H_5\text{-}CHO + C_6H_5\text{-}MgBr = (C_6H_5)_2CH\text{-}OMgBr$$

$$(C_6H_5)_2CHOMgBr + C_6H_5\text{-}CHO + H_2O = (C_6H_5)_2CO + C_6H_5CH_2OH + MgBrOH$$
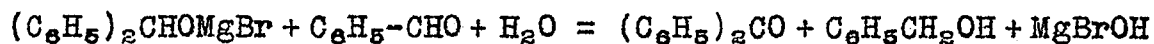
(14) Marshall, J. Chem. Soc., 105, 527(1914); ibid., 107, 509(1915).

Marshall (14) further showed that dibenzoyl phenyl methane
$((C_6H_5CO)_2CH \cdot C_6H_5)$ is among the reaction products of benzyl-
magnesium bromide and benzaldehyde. No mechanism seems to have
been suggested by him for this unusual product.

The most recent studies on the abnormal reactions of benzyl-
magnesium chloride have been carried out by the Spanish chemist,
A. Garcia Banús, and his co-workers. In comparison with the re-
action formulated by Marshall (14) for the reaction between
benzaldehyde and phenylmagnesium bromide, Banús and Vila (15)
suggested that perhaps an excess of benzaldehyde reacts with
benzylmagnesium chloride yielding phenylbenzyl ketone and benzyl
alcohol. The ketone may then condense with benzaldehyde to an
unsaturated ketone (I), which might in turn be reduced to the
saturated ketone, benzoyl diphenylethane (II), by means of hydro-
gen evolved by the action of acid on excess magnesium during
hydrolysis.
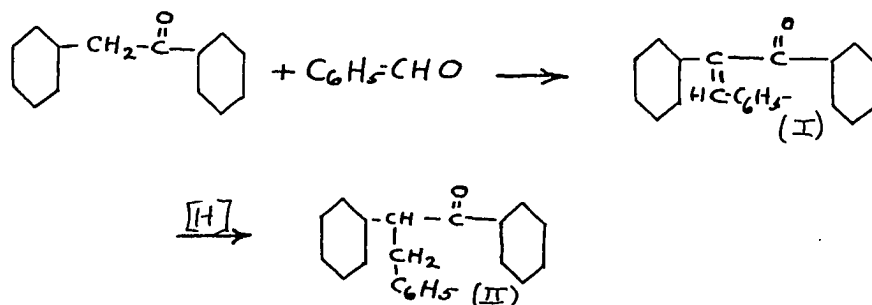
While the empirical formula of (I) corresponds exactly to
that of diphenyl-isochromene, and that of (II) corresponds to
the empirical formula of diphenyl-isochromane, these cannot be

(15) Banús and Vila, Anales soc. españ. fís. quim., 19,326(1921);
C.A., 16,3479(1922).

identical compounds because diphenyl-isochromane shows none of the properties of a ketone, and also because of the oxidation products described above.

Banús and Vila (15) further suggested that if benzylmagnesium chloride has the quinoidal formula as suggested by Schmidlin and Banús (13) that it should be able to combine with one molecule of a compound having two carbonyl groups, such as benzil, by virtue of the two active groups of the rearranged Grignard reagent.
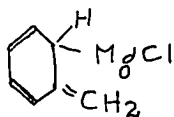
The suggestion was not verified experimentally, since the reaction of benzylmagnesium chloride with benzil, $(C_6H_5\text{-}CO\text{-}CO\text{-}C_6H_5)$, yielded benzoin and dibenzyl. The mechanism of this reduction was thought to be similar to that postulated by Franzen and Diebel (16) for the reduction of azobenzene to hydrazobenzene by means of the Grignard reagent, and was formulated as follows:
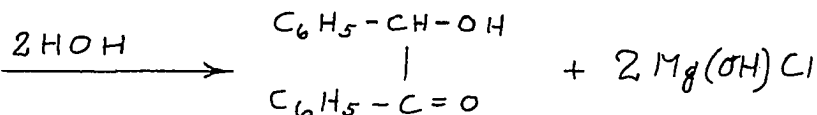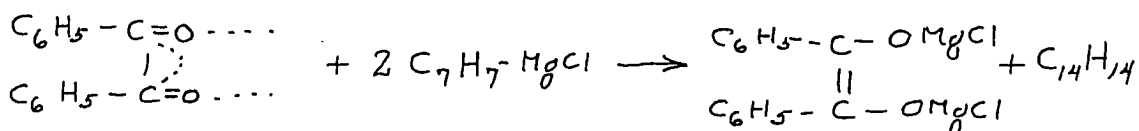
(16) Franzen and Diebel, Ber., 38,2716(1905). The reduction of azobenzene by the Grignard has been recently studied by Gilman and Pickens, (J.Am.Chem.Soc., 47,2406(1925)). This paper contains references to previous work on the reducing action of RMgX compounds.

In a subsequent paper Banús and Medrano (17) showed that while o-chlorotoluene does not react with magnesium, o-tolyl-magnesium bromide and iodide yield with benzaldehyde the normal reaction product, phenyl-o-tolyl carbinol, and no diphenyl-iso-chromane. Thus an equilibrium of the following type probably does not exist.
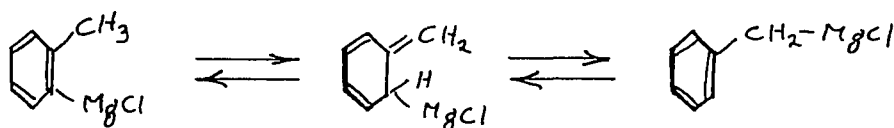
The question of the constitution of diphenyl-isochromane was reopened by Banús and Medrano (17). They showed that the compound does not react with metallic sodium at 100-120° in ligroin. Further, it is not acted upon by thionyl chloride, acetic anhydride in pyridine, or methylmagnesium iodide. It is un-altered by fusion with sodium hydroxide, or magnesium chloride. Hydriodic acid yields a resin. With strong hydrochloric acid in acetic anhydride a hydrocarbon is formed. This hydrocarbon appeared to be diphenylindene (I)

and was converted to diphenylindone (II) by careful oxidation. Compound (II) was conclusively identified by a mixed melting point determination.

(17) Banús and Medrano, Anales soc. españ. fís. quím., 21, 436 (1923); C.A., 18, 2144 (1924).

The fact that diphenyl-isochromane is not formed by the action of excess benzaldehyde on the normal addition product of benzylmagnesium chloride and benzaldehyde was confirmed by Banús and Medrano (17). Pure phenybenzyl carbinol was treated with methylmagnesium iodide and the resulting -OMgX compound, C_6H_5-CH(OMgI)CH_2-C_6H_5, heated with benzaldehyde. No isochromane could be detected among the reaction products. Further, when benzylmagnesium chloride was heated for twenty hours with benzaldehyde, no chromane was obtained. The reaction products were stilbene, the dehydration product of phenybenzyl carbinol, benzal desoxybenzoin,
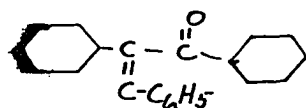
and the dibenzoyl phenylmethane observed by Marshall (14). Following the suggestions of Marshall, Banús and Medrano (17) formulated the reaction as follows:

$$C_6H_5\text{-CHO} + C_6H_5\text{-}CH_2\text{-MgCl} = C_6H_5\text{-CH(OMgCl)-}CH_2\text{-}C_6H_5$$

$$C_6H_5\text{-CH(OMgCl)-}CH_2C_6H_5 + C_6H_5\text{-CHO} = C_6H_5\text{-CO-}CH_2\text{-}C_6H_5 + C_6H_5CH_2\text{-OH}$$

$$C_6H_5\text{-CO-}CH_2\text{-}C_6H_5 + C_6H_5\text{-CHO} = C_6H_5\text{-CO-CH-}C_6H_5$$
$$\text{CH(OH)-}C_6H_5$$

$$C_6H_5\text{-CO-CH-}C_6H_5 \xrightarrow{\text{-HOH}} C_6H_5\text{-CO-C-}C_6H_5$$
$$\text{CH(OH)}C_6H_5 \qquad\qquad \text{CH-}C_6H_5$$

Benzaldesoxybenzoin

$$C_6H_5-CO-\underset{\underset{CH(OH)C_6H_5}{|}}{CH}-C_6H_5 \; + \; C_6H_5CHO \longrightarrow \; C_6H_5-CO-\underset{\underset{CO-C_6H_5}{|}}{CH}-C_6H_5 \; + \; C_6H_5-CH_2OH$$

Dibenzoyl phenyl methane
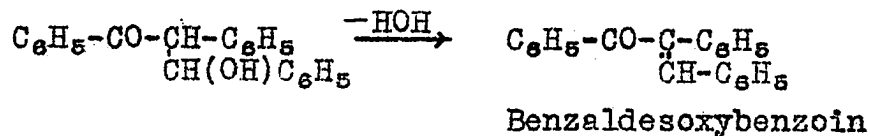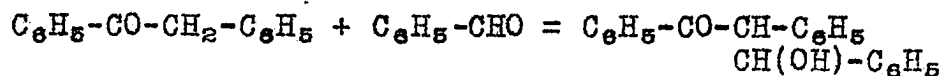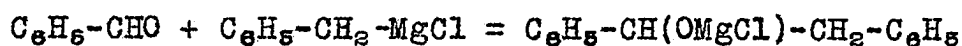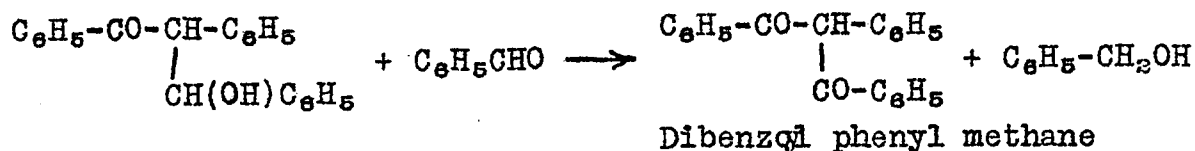
No statement was made by Banús and Medrano in regard to testing out these involved reactions in the laboratory. They were merely submitted as an explanation for the formation of dibenzoyl phenylmethane.

Banús and Medrano (17) further state that p-anisaldehyde, when treated with benzylmagnesium chloride, yields a compound melting at 140-141° and which yields o-phthalic acid on oxidation. Further work on this reaction was promised by these workers but has not appeared as yet.

The reaction of aldehydes with the Grignard reagent is undoubtedly very complex. Chichibabin (18) remarks that they are of little value in demonstrating the constitution of an organo-magnesium halide. He further states (19) that a large amount of high-boiling product (20) is always formed along with o-tolyl carbinol in the reaction between benzylmagnesium chloride and formaldehyde.

A second case in which a Grignard reagent leads to unexpected products is that of triphenylmethyl magnesium chloride.

(18) Chichibabin, Ber., 42,3479(1909).
(19) Chichibabin, loc.cit., footnote, p.3479.
(20) This high-boiling oil has also been observed by us. A trace of di-p-tolyl was obtained from some of this oil (Gilman and Kirby, ref.57). The oil is not a formal since it resists hydrolysis with 10% sulfuric acid.

In 1906 Schmidlin (21) observed that when an ether solution of triphenylchloromethane reacted with magnesium in the absence of air a white, insoluble solid was precipitated, and which seemed to show none of the properties expected of triphenylmethylmagnesium chloride. When treated with carbon dioxide only a very small amount of triphenylacetic acid was formed. Further, when treated with benzaldehyde, this solid yields an entirely unexpected product which Schmidlin proved to be p-benzoyl triphenyl-methane (p-C_6H_5-CO-C_6H_4-(C_6H_5)$_2$-CH). He also found that the magnesium compound was greatly modified in properties when heated for three hours in benzene, in which medium it was readily soluble. The new product, called beta-triphenylmethylmagnesium chloride to distinguish from the first described, or alpha-form, gave high yields of triphenylacetic acid when treated with carbon dioxide; and with benzaldehyde gave beta-benzpinacoline. The benzaldehyde reaction first gave phenyl triphenylmethyl car-binol, which underwent oxidation to beta-benzpinacolone by means of atmospheric oxygen.

$$(C_6H_5)_3CMgCl + C_6H_5\text{-}CHO \longrightarrow (C_6H_5)_3C\text{-}CH(OMgCl)\text{-}C_6H_5 \xrightarrow{HOH}$$

$$(C_6H_5)_3C\text{-}CH(OH)\text{-}C_6H_5 \xrightarrow{O_2} (C_6H_5)_3C\text{-}CO\text{-}C_6H_5$$
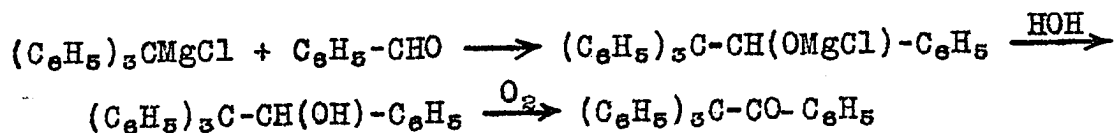
Previously Kehrmann, (22) had suggested that triphenylchlor-omethane exists in two forms, one normal, one quinoidal:

$$(C_6H_5\text{-})_3CCl \quad and \quad (C_6H_5\text{-})_2C=\bigcirc\substack{\text{,H} \\ \text{,Cl}}$$

(21) Schmidlin, Ber., 39,4183(1906).
(22) Kehrmann, Ber., 34,3815(1901).

Analogously triphenylmethylmagnesium chloride can, according to Schmidlin (21), exist in two modifications, a labile, quinoidal, or alpha form; and a stable, normal, beta form:

$$(C_6H_5)_3C-MgCl \quad and \quad (C_6H_5)_2C=\text{⟨⟩}\langle^{H}_{MgCl}$$

$$\text{β-form} \qquad\qquad\qquad \text{α-form}$$
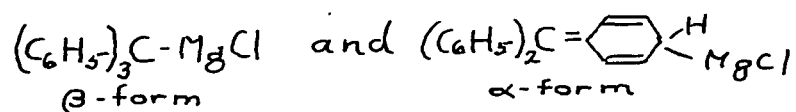
The formation of p-benzoyl triphenylmethane is then expressed as follows:

$$(C_6H_5)_2C=\text{⟨⟩}\langle^{H}_{MgCl} \quad + \quad C_6H_5CHO \rightarrow (C_6H_5)_2C=\text{⟨⟩}\langle^{H}_{CH(OMgCl)C_6H_5}$$

$$\xrightarrow{HOH} (C_6H_5)_2CH\text{⟨⟩}CH(OH)-C_6H_5 \xrightarrow{O_2} (C_6H_5)_2CH\text{⟨⟩}-\underset{O}{\overset{}{C}}-C_6H_5$$
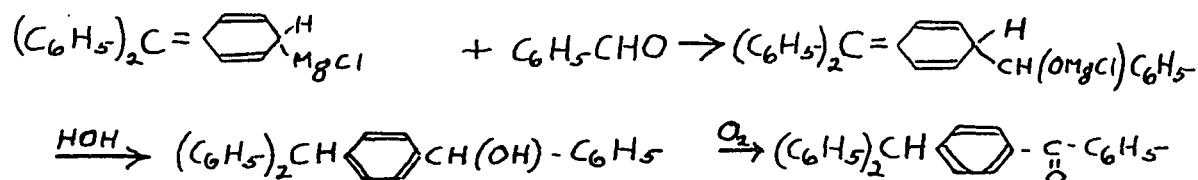
Chichibabin (23) refused to accept the idea of alpha- and beta- forms of triphenylmethylmagnesium chloride as proposed by Schmidlin (21). He expressed a belief that the formation of p-benzoyl triphenylmethane was due to a condensation similar to a Friedel-Craft reaction, and brought about by anhydrous magnesium chloride. He was able to obtain triphenylacetic acid in 90% yield from the so-called alpha form by leading in carbon dioxide for a long period of time. Chichibabin (23) employed an unusually large amount of iodine to start the reaction between the halide and magnesium. In a run employing 10 g. of triphenylchloromethane and 8 g. (excess) of magnesium, 1 g. of iodine was used. The reaction was characterized as "very en-

(23) Chichibabin, Ber., 40,3965(1907).

ergetic".

In a later paper Schmidlin (24) criticized the procedure of Chichibabin (23), stating that due to the very vigorous reaction it was very probable that a rearrangement of the unstable alpha- form occurred even in ether solution. He showed that a solution prepared in the manner used by Chichibabin yields with benzaldehyde both p-benzoyl triphenylmethane and beta-benzpinacoline.

Schmidlin and Hodgson (25) state that both the alpha- and beta- forms yield beta-benzpinacoline when treated with methyl benzoate. While the yield was lower with the alpha- form, still no p-benzoyl triphenylmethane could be isolated. With benzyl chloride the beta- form yields unsym-tetraphenylethane, the alpha- form, the same product in lesser amount. Schmidlin and Hodgson (25) believe that this does not invalidate the existence of the alpha- form. They believe a rearrangement to the stable beta- form occurs during reaction.

When the beta- form was treated with acetone, acetaldehyde, and acetyl chloride no derivatives were obtained. Schmidlin and Hodgson (25) state that while the -MgCl group was broken off by these reagents, no group entered in its place. m-Nitrobenzaldehyde oxidized the beta- form to triphenyl carbinol. They further showed that tri-p-tolylchloromethane yields under the usual conditions no magnesium compound which can be con-

(24) Schmidlin, Ber., 41,426(1908).
(25) Schmidlin and Hodgson, ibid., 41,430(1908).

verted to tri-p-tolylacetic acid, and that special precautions (26) are required for the preparation of that acid.

When treated with cinnamic aldehyde, Schmidlin and Hodgson (26) showed that the alpha- form yields p-cinnamoyl triphenylmethane, $(C_6H_5)_2$-CH-p-C_6H_4-CO-CH=CH-C_6H_5, and the beta- form a-cinnamoyl triphenylmethane, $(C_6H_5)_3$-C-CO-CH=CH-C_6H_5.

Schmidlin and Chichibabin seem to agree that the so-called alpha- form of triphenylmethylmagnesium chloride is exhibited only toward aldehydes. Chichibabin insists that the reaction is merely a condensation reaction, not the manifestation of a rearranged Grignard reagent.

In a search for reliable reagents with which to characterize the -MgX group Gilman and Kirby (5) chose benzylmagnesium chloride as the Grignard reagent for use in their studies. It was thought that, since this particular Grignard reagent was known to exhibit abnormalities in its behavior with aldehydes, it would be reasonable to conclude that substances with which it reacts in a wholly normal manner would probably behave normally with other Grignard reagents. It was shown that benzylmagnesium chloride exhibits no anomalous behavior when treated with phenylisocyanate, benzoyl chloride, acetic anhydride, ethyl acetate, allyl bromide, and phenylcarbamine chloride. The reservation must be made, however, that in no case were the residual tars and oils oxidized in a search for ortho or para

(26) Schmidlin and Hodgson, Ber., 41,438(1908).

substitution products which, it is possible, may have been formed in small amounts and escaped detection. The chief products obtained from the reactions mentioned were, in all cases, normal.

Another interesting reaction of benzylmagnesium chloride is that with methyl iodide. Houben (27) showed that this reaction gives the normal product, ethyl benzene; $C_6H_5-CH_2-MgCl + CH_3I = C_6H_5-C_2H_5 + MgClI$. Later Späth (28) carefully studied this reaction and found that beside the ethyl benzene, there are also formed considerable amounts of dibenzyl and a high-boiling oil. The high-boiling oil was concluded to be 1-2-3 triphenyl propane. Some ethane is evolved in the reaction also. Fuson (29) repeated the work of Houben (27), and Späth (28), and while he obtained ethyl benzene, ethane, and dibenzyl, he did not find the high-boiling oil. He was able to show that either alone or with the aid of zinc powder benzyl chloride condenses with dibenzyl yielding p-benzyl dibenzyl $(\underline{p}-C_6H_5-CH_2-C_6H_4-CH_2-CH_2-C_6H_5)$. This latter compound is isomeric with 1-2-3 triphenylpropane and Fuson concluded that Späth's compound was probably p-benzyl dibenzyl formed by the action of excess benzyl chloride on dibenzyl. In a recent paper Späth (30) contests the conclusion of Fuson and promises a further investigation of the reaction.

(27) Houben, Ber., 36,3083(1903).
(28) Späth, Monatsh., 34,1991(1913).
(29) Fuson, J. Am. Chem. Soc., 48,2681(1926); 48,2937,(1926).
(30) Späth, Ber., 60,702(1927).

II. Reactivity of Benzyl and Related Halides.

A group of halides closely related to benzyl chloride has been repeatedly shown to display unusually great reactivity. The members of this group, comprising allyl-, benzyl, benzhydryl-, triphenylmethyl-, cinnamyl-, and related halides, all contain the grouping, $c'=c'-CH_2-X$, the unsaturated linkage being either an aliphatic double bond, or one of the double-linkages of a benzene ring. Some of the outstanding examples of this increased reactivity are reviewed here.

As long ago as 1890 the greater reactivity of allyl- and benzyl halides toward alcoholic alkali, as compared with the corresponding propyl and ethyl halides, was quantitatively demonstrated by Conrad, Hecht and Brüchner (31). They assembled the following table based on the propyl radical as unity as a comparison of the reactivities of the several halides.

Table I.

Halogen	Propyl	Ethyl	Allyl	Benzyl
Cl	1	--	65.70	126.5
Br	1	3.24	61.30	120.1
I	1	2.85	54.34	93.95

This table has been quoted by Vaubel (32), and recently by Claisen (33). The work of Claisen will be discussed in con-

(31) Conrad, Hecht and Brüchner, Zeit. phys. chem., 3,450,(1889); ibid., 4,631(1890).
(32) Vaubel, Ber., 24,1692(1891).
(33) Claisen, Ann., 442,216(1925).

siderable detail below.

A further evidence of the looseness of attachment of the allyl and benzyl groups was furnished by Collie and Schrywer (34), who showed that when trimethyl allyl ammonium hydroxide is heated the allyl group splits off yielding allyl alcohol.

$$(CH_3)_3C_3H_5-NOH \longrightarrow (CH_3)_3N + C_3H_5OH$$

Trimethyl benzyl ammonium hydroxide yields primarily benzyl alcohol. On the other hand, trimethyl benzyl ammonium chloride yields a mixture of benzyl chloride and methyl chloride.

$$(CH_3)_3(C_7H_7)NCl \begin{array}{c} \nearrow (CH_3)_3N + C_7H_7Cl \\ \searrow (CH_3)_2(C_7H_7)N + CH_3Cl \end{array}$$
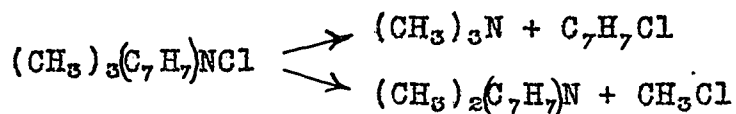
von Braun (35) comments at length on the activity of the allyl group. Among other instances he mentions his own work (36) on the action of allyl bromide and cyanogen bromide, and the work of Tiffeneau (37), who demonstrated that allyl bromide readily reacts with the Grignard reagent.

$$RMgX + C_3H_5Br \longrightarrow R-C_3H_5 + MgXBr$$
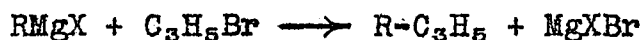
(34) Collie and Schrywer, J. Chem. Soc., 57, 767(1890).
(35) vonBraun, Ber., 51, 79(1918).
(36)   ibid., 33, 2728(1900).
(37) Tiffeneau, Compt. rend., 139, 481(1904).

Shoesmith and co-workers (38) have carried out a series of careful experiments on the rate of hydrolysis of ring-substituted benzyl bromides. They have demonstrated (38a) the ease of hydrolysis of the three methoxybenzyl bromides, the ortho and para exceeding that of the meta. The activity of the side-chain halogen is explained by them on the theory of alternating polarity, the methoxyl oxygen being taken as the "key-atom".
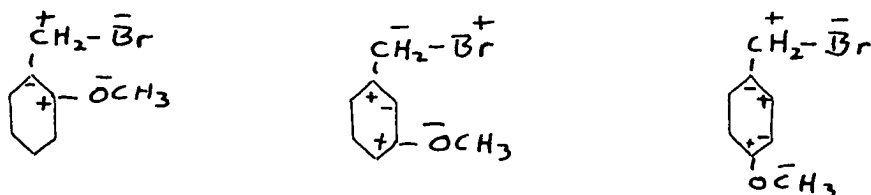
In the case of the ortho and para derivatives the bromine atom is negative and thus should be, and is, more easily removed by hydrolysis than in the case of the meta isomer.
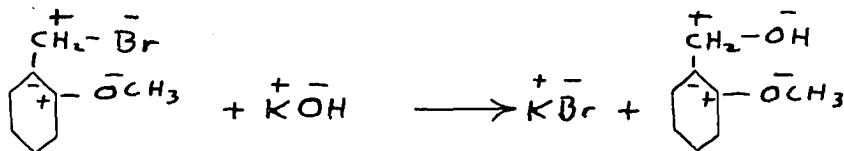
In the case of the meta isomer a greater ease of reduction than in the case of the other two was found (37b).

(38)
(a) Lapworth and Shoesmith, J. Chem. Soc., 121,1391(1922).
(b) Shoesmith, ibid., 123,2828(1923).
(c) ibid., 125,1312(1924).
(d) Shoesmith and Slater, ibid., 125,2278(1924).
(e) ibid., 127,214(1926).
(f) Shoesmith and Taylor, ibid., 127,2832(1926).
(g) Shoesmith and Connor, ibid., 127,1768(1927).
(h) Shoesmith and Rubli , ibid., 127,3098(1928).

$$\overset{-}{C}H_2-\overset{+}{B}r$$

(reaction scheme)

$$\underset{-OCH_3}{\bigcirc} + \overset{+}{H}\overset{-}{I} \longrightarrow \underset{-OCH_3}{\overset{CH_3}{\bigcirc}} + \overset{-}{I}\overset{+}{Br}$$

$$IBr + HI \longrightarrow HBr + I_2$$
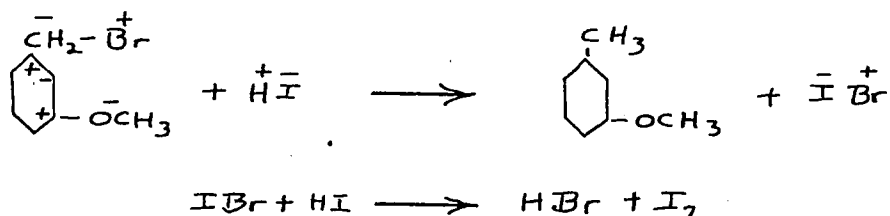
m-Methoxybenzylbromide was completely reduced by hydriodic acid in one hour.

The rate of hydrolysis of the three tolyl-ethyl bromides was shown (38g) to be much less than that of the xylyl bromides (38d) and that the differences between the isomers were far less marked. The tolyl-ethyl bromides, $CH_3-C_6H_4-CH_2-CH_2Br$, do not have the unsaturated grouping, $C'=C'-CH_2X$.

The rearrangement of the allyl ethers of phenol to ring-alkylated phenols has been demonstrated by Claisen and Eisleb (39). On distillation, allyl phenyl ether rearranges to a mixture of ortho- and para- allyl phenol.

$$\underset{}{\overset{OC_3H_5}{\bigcirc}} \longrightarrow \underset{C_3H_5}{\overset{OH}{\bigcirc}} + \underset{C_3H_5}{\overset{OH}{\bigcirc}}$$
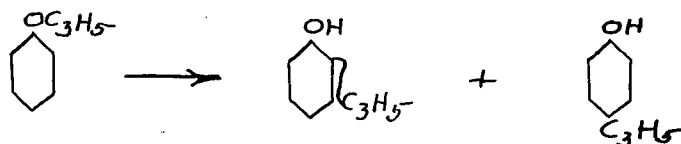
These workers have rearranged a great variety of allyl phenyl ethers in this manner.

Quite recently Adams and Powell (40) have shown that benzyl phenyl ethers do not rearrange in the manner of the allyl ethers. However, Inonor (41) has shown that benzyl ethers are more

(39) Claisen and Eisleb, Ann. 401,21(1913); Claisen, ibid., 418, 69(1919).
(40) Adams and Powell, J. Am. Chem. Soc., 42,648(1920).
(41) Inonor, J. Russ. Phys. Chem. Soc., 59,545(1927); (C.A., 22, 1756(1928)).

easily split than the corresponding methyl-, ethyl-, iso-amyl-, and phenyl- ethers. Gomberg and Kamm (42) showed that tri-phenylmethyl ethyl ether is split by phenylmagnesium bromide at 150-160°. Schorigin (43) was able to rearrange triphenyl-methyl o-tolyl ether to α-α-α triphenyl β2-hydroxyphenyl ethane by heating with metallic sodium at 120°.

$$(C_6H_5)_3C\text{-}O\text{-}\underline{o}\text{-}C_6H_4\text{-}CH_3 \xrightarrow{\ Na\ } (C_6H_5)_3C\text{-}CH_2\text{-}\underline{o}\text{-}C_6H_4\text{-}OH$$
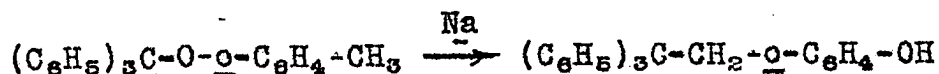
Van Alphen (44) showed that phenyl benzyl ether is rearranged to p-hydroxy diphenylmethane by heating at 160° with anhydrous zinc chloride. The reaction was explained on the basis of an addition of the zinc chloride to the residual valences of the oxygen atom.
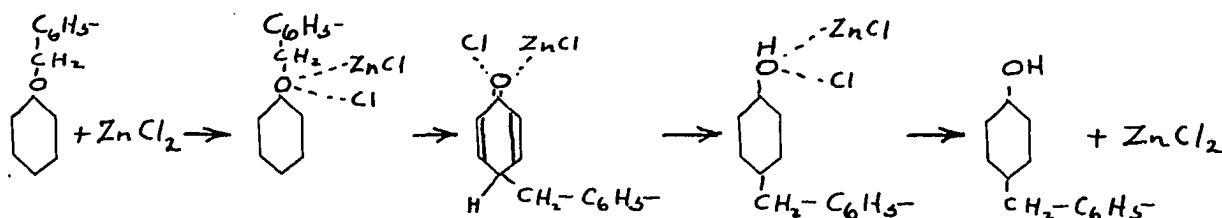
In a recent paper Short (45) has also demonstrated the action of zinc chloride in the rearrangement of benzyl ethers.

Further studies on the splitting of allyl and benzyl

(42) Gomberg and Kamm, J. Am. Chem. Soc., 39,2009(1917).
(43) Schorigin, Ber., 59,2510(1926).
(44) Van Alphen, Rev. trav. chim., 46,799(1928).
(45) Short, J. Chem. Soc., p.528(1928).

ethers are now being carried out by Gilman and McKenna (46).
Another interesting reaction of the allyl group is that recent-
ly discovered by Gilman and Heck (47). Previously Gilman and
Beaber (48) had demonstrated the alkylating action of alkyl
arylsulfonates when treated with the Grignard reagent. Gilman
and Heck (2) have proposed the following reactions to account
for this alkylating reaction.

$$RSO_2O\text{-}Alkyl + R'MgX \longrightarrow R'\text{-}Alkyl + RSO_2OMgX$$

$$RSO_2OMgX + RSO_2O\text{-}Alkyl \longrightarrow AlkylX + (RSO_2O)_2Mg$$
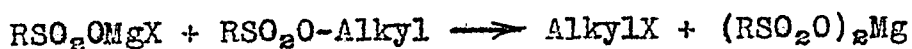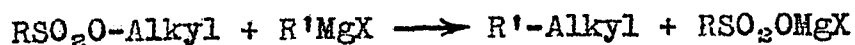
In a continuation of their studies on the alkylating action of
esters Gilman and Heck (47) have now shown that allyl chloro-
acetate, $(Cl\text{-}CH_2\text{-}COOC_3H_5)$, and allyl benzoate, $(C_6H_5\text{-}COOC_3H_5)$,
when treated with phenylmagnesium bromide, give small amounts
of allyl benzene. These are the only cases thus far found in
which carboxylic esters display an alkylating action similar
to the sulfonic esters.

Another reaction of great interest in connection with the
increased reactivity of allyl-, benzyl-, and related halides
is that of the ring-alkylation of phenols. Claisen (49) demon-
strated that when sodium phenolate is heated in benzene suspen-

(46) Gilman and Miss M. H. McKenna, unpublished work.
(47) Gilman and Heck, unpublished work.
(48) Gilman and Beaber, J. Am. Chem. Soc., 47,518(1925); Gilman,
 Robinson and Beaber, ibid., 48,2715(1926).
(49).Claisen, Ann., 442,210(1925).

sion with allyl bromide the product is not phenyl allyl ether, but a mixture of ortho- and para- allyl phenols and smaller amounts of material having two allyl groups in the ring.
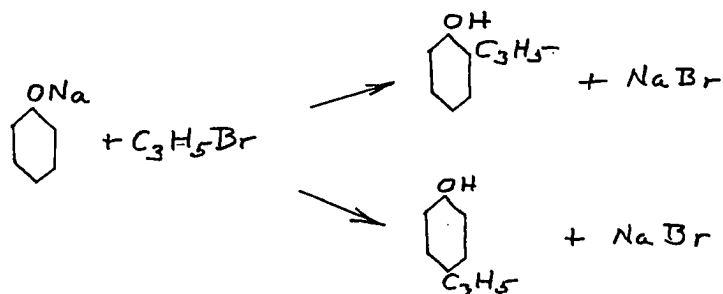
Similar ring-alkylation was found with benzyl chloride and cinnamyl bromide. The C-alkylation takes place in non-dissociating solvents as benzene and toluene. Normal o-alkylation, or ether formation, takes place in dissociating solvents as alcohol and acetone. This reaction is closely analogous to the alkylation of acetoacetic ester, in which the entering group ordinarily is attached to the carbon atom.

$$CH_3-\underset{ONa}{C}=CHCO_2C_2H_5 + RX \longrightarrow CH_3-\underset{O}{C}-CHR-CO_2C_2H_5 + NaX$$
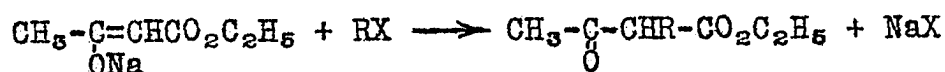
Nevertheless, O-alkylation may also occur here, notably in the case of ethyl chlorocarbonate,

$$CH_3-\underset{ONa}{C}=CH-CO_2C_2H_5 + Cl-CO_2C_2H_5 \longrightarrow CH_3-\underset{O-CO_2-C_2H_5}{C}=CH-CO_2-C_2H_5 + NaCl$$
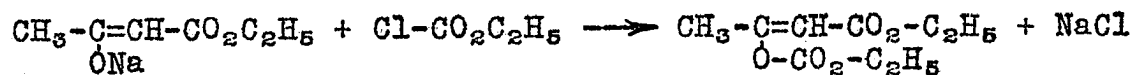
References to these reactions, and the explanations proposed by Wislicenus, Michael, K. H. Meyer, and Michael are found in the paper by Claisen (49). Michael's (50) explanation is given

(50) Michael, J. prakt. chem., 37, 486(1886).

here, as quoted by Claisen.

$$-\underset{-CH}{\overset{C-ONa}{\|}} \; + \; RI \;\longrightarrow\; -\underset{-CHR}{\overset{C-\overset{I}{\diagdown}ONa}{|}} \;\longrightarrow\; -\underset{-CHR}{\overset{C=O}{|}} \;\longrightarrow\; -\underset{-C-R}{\overset{COH}{|}}$$
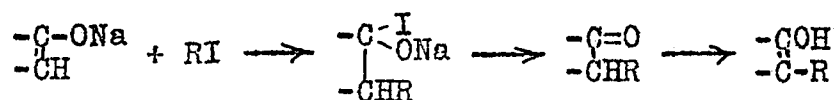
Busch and Knoll (51) showed that the very active benhydryl bromide and triphenylmethyl chloride both alkylate the phenol ring. The mechanism of ring alkylation given by them closely follows that of Michael (50) given above for the alkylation of acetoacetic ester.
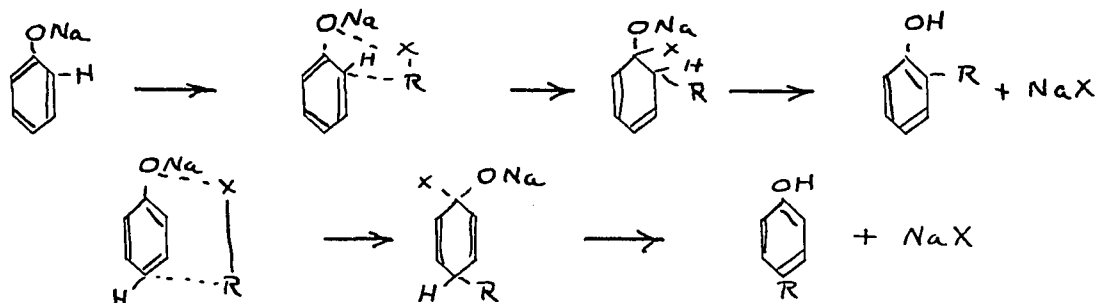
von Auwers (52) has strikingly demonstrated the marked tendency toward C-alkylation exhibited by allyl bromide and benzyl chloride. His results are summarized in the following table.

Table II.

	Halide	C-Deriv	θ-Deriv
[Hydroxy cumarilic acid - ethyl ester structure]	C_2H_5I	22.5%	36%
	CH_3I	53%	42.5%
	C_3H_5Br	73-79%	---
	C H Cl	68.5%	29.5%
[5-Methyl hydroxy cumarilic acid - ethyl ester structure]	C_2H_5I	12-20%	38-48%
	CH_3I	54%	34%
	C_3H_5I	44-55%	---
	C H Cl	65-71.5%	22.5-28%

(51) Busch and Knoll, Ber., 60,2243(1927).
(52) von Auwers, Ber., 61,408(1928).

von Auwers (52), however, does not consider that this apparent
regularity affords a quantitative measure of the affinity re-
quirement of a given radical, although that requirement is a
factor of real significance in determining the location taken
by the entering group.

In a very recent paper Földi (53) has reviewed the work on
direct alkylation of phenols and given a new instance of the
looseness of attachment of a benzyl group. He had previously
shown (54) that benzyl benzenesulfonate on warming splits to
benzenesulfonic acid and the benzylidene radical.

$$C_6H_5SO_3-CH_2-C_6H_5 \longrightarrow C_6H_5SO_3H + C_6H_5CH\mathord{<}$$

The divalent benzylidene radical polymerizes to phenylated
cycloparaffins and an amorphous powder of high molecular weight.
The splitting takes place on warming the ester without applica-
tion of a solvent. The allyl ester also reacts in xylene solu-
tion to give an unknown, unsaturated body. In the more recent
paper (53) he studied the splitting of benzyl benzene sulfonate
in the presence of different bodies such as hydrocarbons,
phenols, phenol ethers, esters and aldehydes. With few ex-
ceptions a benzylation of the ring of the aromatic ring occur-
red. The general procedure consisted of warming the ester with
two to five equivalents of reactant, without other solvent. The
reaction was found to be exothermic at 110-140°. The results

(53) Földi, Ber., 61,1609(1928).
(54)   ibid., 60,656(1927).

are tabulated below.

Table III.

Reactant	Products and Yield	
Benzene	Diphenylmethane	77°
Toluene	Phenyl p-tolylmethane	85°
Nitrobenzene	Polymers of high molecular weight.	
Phenol	p-benzyl phenol	
Anisole	p-benzyl anisole	77%
Benzaldehyde	Polymers	--
Methyl salicylate	3-Benzyl 6-hydroxyl methyl benzoate	56%

Földi also attempted the alkylation of unsaturated aliphatic compounds but met with success only in the case of ethyl cinnamate, which gave a benzyl derivative in 12.5% yield. The reaction is not analogous to the above mentioned ring alkylations, since it is really the benzylidene group which adds. In the case of ethyl cinnamate the following mechanism was postulated.

$$C_6H_5\text{-CH} \quad \quad C_6H_5\text{-CH} \quad \quad C_6H_5\text{-CH}$$
$$\|\quad + C_6H_5\text{-CH}\langle \longrightarrow \quad \| \quad \rangle CH\text{-}C_6H_5 \longrightarrow \quad \|$$
$$C_2H_5O_2C\text{-CH} \quad \quad C_2H_5O_2C\text{-CH}' \quad \quad C_2H_5O_2C\text{-C-CH}_2\text{-}C_6H_5$$
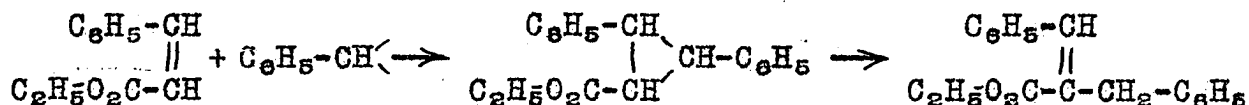
By analogy, the reaction with an aromatic ring is written as follows:
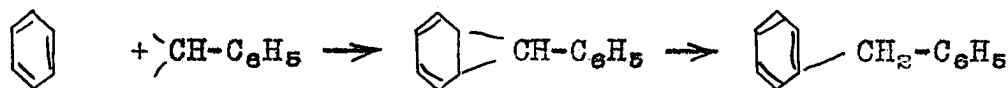
Conant, Kirner and Hussey (55) have carefully measured the "reactivity" of several substituted benzyl chlorides making use of the following reaction: RX + KI = RI + KX. The solvent employed was absolute acetone. Using n-butyl chloride as a standard for comparison, the following values were obtained.

(55) Conant, Kirner and Hussey, J. Am. Chem. Soc., 47,488(1925).

Table IV.

Halide	Reactivity
o-NO$_2$-C$_6$H$_4$CH$_2$Cl	1800
p-NO$_2$-C$_6$H$_4$-CH$_2$Cl	1370
2-4(NO$_2$)$_2$C$_6$H$_3$-CH$_2$Cl	50,800

The reactivity of the o-nitrobenzyl chloride is slightly greater than that of the corresponding p-nitrobenzyl chloride. As stated by Conant, Kirner and Hussey (55), these results are not in accord with those of other workers. Slator (56) showed that the ortho derivative has nearly the same reactivity as benzyl chloride itself, while the para compound is nearly twice (1.8 times) as reactive. Studies of this nature are of questionable value as applied to the problem at hand, the rearrangement reactions of benzylmagnesium halides. The reactivity of a given halide measured by a given process in a given solvent is not a criterion of its behavior toward other reagents in other solvents.

The reaction mentioned above in which Schorigin (57) discovered the wandering of an ether group from the phenolic oxygen to a side chain
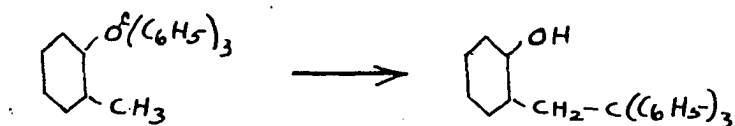
(56) Slator, J. Chem. Soc., 85,1786(1904); 87,481(1905); 95, 93(1909).
(57) Schorigin, Ber., 59,2502(1926).

and the side-chain alkylation of o-cresol

$$\text{(o-cresol-ONa)} + (C_6H_5)_3CCl \longrightarrow \text{(ring)}-OC(C_6H_5)_3,\ CH_3 + NaCl$$
$$\searrow \text{(ring)}-OH,\ CH_2-C(C_6H_5)_3$$
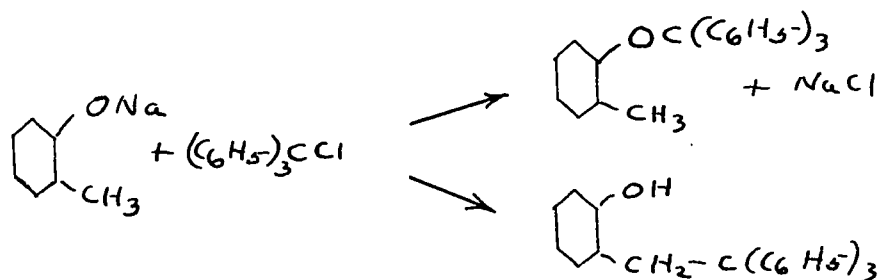
are interpreted by him as evidence that sodium o-cresylate may react as though existing in a tautomeric ortho-quinoidal form.

$$\text{(ring)}\ ONa,\ CH_3 \rightleftharpoons \text{(ring)}\ H-ONa,\ CH_2 + Cl-C(C_6H_5)_3 \longrightarrow \text{(ring)}\ OH,\ CH_2-C(C_6H_5)_3$$
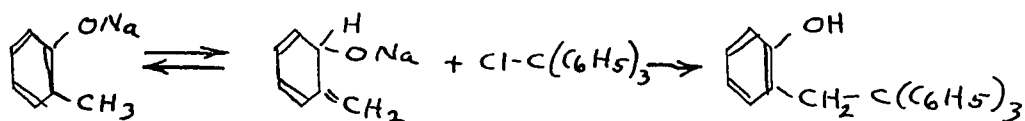
He further assumes that toluene itself may be in equilibrium with such a form.

$$\text{(ring)}-CH_3 \rightleftharpoons \text{(ring)} = CH_2,\ H,\ H$$
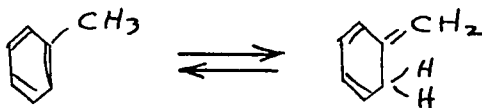
It is known that in sunlight or ultra-violet light the chlorination of toluene leads to benzyl chloride. This reaction is explained by Schorigin (57) as follows:

$$\text{(ring)} = CH_2,\ H,\ H + Cl_2 \longrightarrow \text{(ring)}\ CH_2-Cl,\ Cl,\ H,\ H \longrightarrow \text{(ring)}\ CH_2-Cl + HCl$$
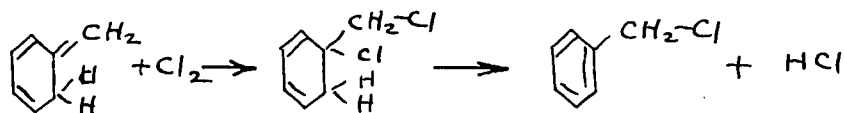
The rearranged toluene molecule recalls the formula postulated by Schmidlin and Banús (1$\overset{3}{2}$) for benzylmagnesium chloride.

$$\text{(ring)}-CH_2-MgCl \rightleftharpoons \text{(ring)} = CH_2,\ MgCl,\ H$$
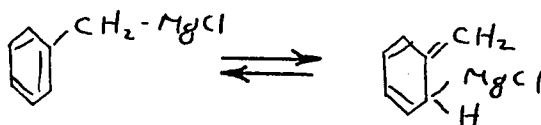
III. Discussion of Results.

The study of the reactions of benzylmagnesium chloride (5), begun with the purpose of testing the reliability of several reagents toward the Grignard reagent, was continued in an effort to strengthen the evidence in favor of the rearrangement mechanisms postulated by others and described above, or to suggest some alternative mechanism. In the course of these studies several large runs of benzylmagnesium chloride were made and hydrolyzed in an effort to trace any abnormal or rearranged products arising in the preparation of the Grignard solution itself. These runs were of great importance for the following reason. In practically all of the runs described below all tars were exhaustively oxidized in a search for ortho and para rearrangement products, which would yield phthalic and terephthalic acids when oxidized. It was highly desirable to preclude the possibility that these acids, when found, had arisen from by-products of the formation of the benzylmagnesium chloride itself.

The results of these several large runs proved to be of unusual interest and are described in detail in a paper by Gilman and Kirby (58) which will appear shortly. It will suffice to state here that di-p-tolyl, p-CH$_3$-C$_6$H$_4$-C$_6$H$_4$-CH$_3$-p, was obtained as an extremely minor product in these runs. The yields were about 0.2 to 0.3%. The possibility that this product re-

(58) Gilman and Kirby, J. Am. Chem. Soc., 51,(1929).

sulted from contamination of the benzyl chloride with p-chloro-toluene was carefully precluded. In one run qualitative evidence of ortho coupling was also found. Sufficient phthalic acid was isolated to give the characteristic fluorescein test. The importance of this discovery in connection with the preliminary formation of free radicals in the preparation of Grignard reagents is discussed in detail by Gilman and Kirby (58). It should be emphasized that in all of the rearrangement reactions previously known and in the new ones described here the yields of rearranged products, even in those cases in which the evidence is based on oxidation experiments, are all in significant amounts.

The reaction between benzylmagnesium chloride and carbon dioxide was submitted to a very careful investigation. This reaction has been cited by Schmidlin and Banús (13) as a typical "normal" reaction of benzylmagnesium chloride. The Grignard solution (0.5 mole) was sprayed into an atmosphere of dry carbon dioxide in the hope of obtaining rapid reaction in order to preclude the possibility of a shifting of the equilibrium, if such exist, in favor of the normal form, $C_6H_5-CH_2-MgCl$. The phenylacetic acid obtained was submitted to repeated fractional crystallization in the hope of separating traces of o-toluic acid. A technique for this separation had been previously developed. No indication whatsoever of the presence of this latter acid was found. Every fraction yielded only phenylacetic acid of high purity. Oxidation of the residual, non-acidic

oils gave only benzoic acid and no phthalic or terephthalic acids. It is highly probable that benzylmagnesium chloride behaves toward carbon dioxide in a wholly normal manner.

The quinoidal formula of Schmidlin and Banús (13) was then submitted to a rather critical test. It seemed probable that if benzylmagnesium chloride exists in solution as an equilibrium mixture of the following forms
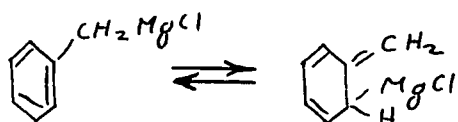
that bromine might add to the aliphatic double bond of the rearranged form
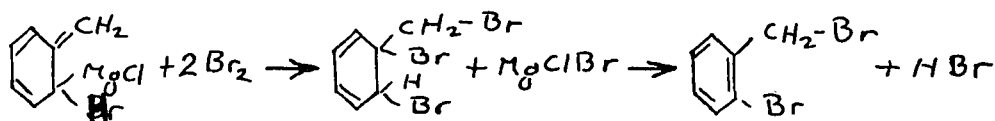
yielding o-bromobenzyl bromide, while the normal form would yield only benzyl bromide.
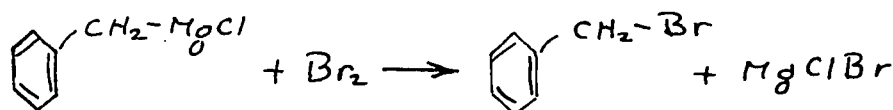
In order to prevent any direct bromination of the benzene ring and thus invalidate the results the reaction was carried out at the temperature of a carbon dioxide-ether mixture. The only product obtained was benzyl bromide of high purity.

It is not fair to conclude that this experiment wholly invalidates the quinoidal formula for benzylmagnesium chloride. Two possible explanations of the non-appearance of o-bromo-

benzyl bromide present themselves. First, low temperatures may
favor the normal form at the expense of the quinoidal form.
Second, there are many compounds, as will be recalled from the
historical introduction, that do not give rise to abnormal
products when treated with benzylmagnesium chloride. It is as
yet impossible to predict the course of any reaction of that
Grignard reagent. Recourse must be had to actual experimenta-
tion. The quinoidal formula may be definitely said to be in-
sufficient since it does not infallibly foretell the course of
reaction of benzylmagnesium chloride. The mechanism proposed
later in this paper meets with the same difficulty, but perhaps
better explains the known facts.

Several other substances have been added to the list of
compounds which react in a wholly normal manner toward benzyl-
magnesium chloride. Benzonitrile yielded only phenylbenzyl
ketone in good yield and in a high state of purity. Chloraceto-
phenone yielded an oil (59) from which no definite products
could be separated. Oxidation of this oil gave nothing but
benzoic acid and the reaction was not further investigated.

When benzylmagnesium chloride was added to an excess of
benzyl chloride a mixture of tar and a high melting solid was
obtained. This solid melted at 240° and was not identified.
The oil appeared to resist oxidation with alkaline permanganate,
although it gave a small amount of benzoic acid. It seemed pos-
sible that benzoyl chloride might give rise to rearranged

(59) See p.44, Master's Thesis, James E. Kirby, Iowa State Col-
lege, 1926.

products since two other acid chlorides react in part abnormally as will be described below.

Diphenylcarbamine chloride gave a tar which, when submitted to hydrolysis with alcoholic alkali, gave only phenylacetic acid. The reaction, therefore, proceeded in a normal manner.

$$C_6H_5\text{-}CH_2\text{-}MgCl + Cl\text{-}CO\text{-}N(C_6H_5)_2 \longrightarrow C_6H_5\text{-}CH_2\text{-}CO\text{-}N(C_6H_5)_2 + MgCl_2$$

$$C_6H_5\text{-}CH_2\text{-}CON(C_6H_5)_2 + HOH \longrightarrow C_6H_5\text{-}COOH + (C_6H_5)_2NH$$
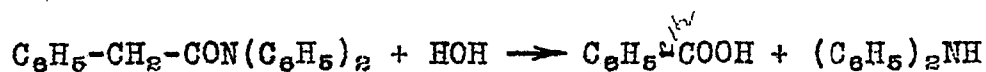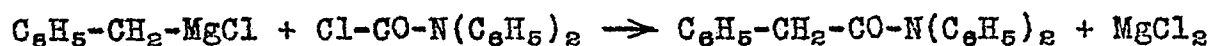
Two runs were made in which an excess of benzylmagnesium chloride was added to a cooled solution of acetyl chloride in ether. No attempt was made to isolate the normal product, dibenzyl methyl carbinol, but portions of the tarry product were submitted to oxidation with alkaline permanganate. The first run yielded only benzoic acid. From the second a trace of phthalic acid was isolated. Acetyl chloride may be concluded to react in an almost wholly normal manner with benzylmagnesium chloride. The amount of phthalic acid obtained was greater than that obtained by Gilman and Kirby (58) from the oxidation products of a one mole run of benzylmagnesium chloride. The runs here described employed only one-half mole of Grignard reagent, and acetyl chloride must, therefore, be included in the list of substances giving rise to rearranged products when treated with benzylmagnesium chloride.

Ethylene oxide was first employed by Grignard (60) in the

(60) Grignard, Compt. rend., 136, 1260 (1903).

synthesis of primary alcohols by means of the Grignard reagent. Apparently, however, the action of ethylene oxide, or of any of the higher oxides of that type, with benzylmagnesium chloride has not been previously investigated. From one experiment there was obtained a 48% yield of oil corresponding closely in boiling point with the expected γ-phenylpropanol. Oxidation of this oil led not alone to benzoic acid as would be expected of γ-phenylpropanol, but also to terephthalic acid in an equal amount. Four grams of the oil yielded about one gram of each of the two acids. No phthalic acid could be detected among the oxidation products. The separation of the phthalic acids and benzoic acid, as described in detail in the experimental part, is simple and it is not probable that if phthalic acid formed it would have excaped detection. It seemed probable that the oil was a mixture of γ-phenylpropanol and β-p-tolylethanol. An attempt was made to separate these isomeric and undoubtedly very similar alcohols by the slow fractional crystallization of their phenylurethanes. No success was had, probably due to a very similar solubility behavior of the isomeric urethanes.

The action of benzylmagnesium chloride with ethylene oxide constitutes, then, the first clearly defined case of a para rearrangement of that Grignard reagent. It must be remembered, however, that Chichibabin (11) reported p-benzoyl benzoic acid among the oxidation products of the reaction products obtained from benzylmagnesium chloride and benzaldehyde although Schmidlin and Banús (13) failed to obtain that substance. The

quinoidal formula of Schmidlin and Banús (13) gives no explanation of the formation of <u>para</u> rearrangement products. However, the assumption of a <u>para</u>-quinoidal form is equally as plausible as that of an <u>ortho</u>, and in conformation with Schmidlin and Banús the following equilibria may be postulated.
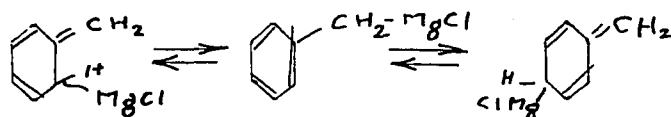
Carbon dioxide is considered a typical normal reagent in its mode of action toward benzylmagnesium chloride. Formaldehyde constitutes a case of exclusively <u>ortho</u>-rearrangement, no normal product having been found by anyone. Ethylene oxide, while behaving in part normally, gives rise to <u>para</u> rearrangement exclusively. Ethyl chloromethyl ether has been found to occupy an even more unique position. In the footnote of a paper by Banús and Vila mention (61) is made of an abnormal reaction between benzylmagnesium chloride and halogenated ethers. The reaction is obviously incorrectly formulated in the paper of Banús and Vila, probably due to typographical error.

$$Cl-CH_6-OR + C_6H_5-CH_2-MgCl \longrightarrow C_6H_4 \overset{\diagup CH_3}{\diagdown CH_6-OR}$$
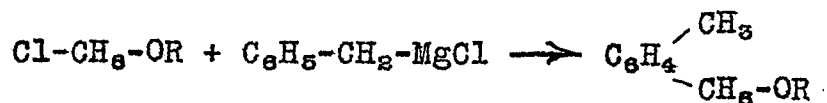
Obviously $Cl-CH_6-OR$ should read $Cl-CH_2-OR$. Since there seems to be no other literature reference to this reaction, the reaction between ethyl chloromethyl ether was carefully investigated. Four runs were made. From each there was obtained a constant-

(61) D. R. P. 154, 658, house of F. Baeyer.

boiling oil, distilling at approximately the temperature expected of ethyl β-phenylethyl ether, in yields of 40-75%. The oil from three of these runs yielded benzoic, phthalic, and terephthalic acids on oxidation. The oil from the fourth run failed to yield phthalic acid. The amounts of the phthalic acids were significantly high. For example, in one run 5.0 g. of oil yielded 1.5 g. of benzoic acid; 0.6 g. of phthalic acid; and 1.2 g. of terephthalic acid.

The oil obtained from ethyl chloromethyl ether and benzyl-magnesium chloride appeared to be a mixture of three isomeric ethers, ethyl β-phenylethyl ether, o-tolylmethyl ethyl ether, and p-tolylmethyl ethyl ether. An estimation of the percentage of ethoxyl groups in the mixture according to the Zeisel method was attempted in the hope of proving that the oil was really a mixture of three isomeric ethyl ethers. The results obtained were very unsatisfactory and in only one determination among the many tried was a value obtained approximating the calculated value. Further, the results were entirely inconsistent, consecutive runs often verying several percent. Several modifications of the ordinary procedure were resorted to. In some cases the decomposition was raised from 135° as ordinarily employed to 180° or even 190°. Decomposition was sometimes effected with mixtures of hydriodic acid and acetic anhydride according to suggestions of Dr. H. P. Clarke (62). In some cases the

(62) Private communication. See also, Honben-Weyl, Die Methoden der Organischen Chemie, published by Georg Thieme, Liepzig, 1923; Vol.III, p.147.

ethyl iodide was absorbed in warm pyridine and estimated by a
Volhard titration but without approaching the computed value.

In order to determine if the failure of the Zeisel method
in the case of the above described oil was exhibited by ethers
of the type at hand and of known purity, the preparation of a
pure sample of ethyl β-phenylethyl ether was undertaken. Several
methods were tried. Sodium ethylate and β-bromoethyl benzene
yielded only styrene and none of the desired ether. Sodium
phenylethylate and ethyl iodide yielded a product which a Zere-
witinoff estimation showed to contain phenylethyl alcohol. Only
indefinite products were obtained when ethyl β-bromoethyl ether
was treated with phenylmagnesium bromide. Finally a pure sam-
ple of ethyl β-phenylethyl ether was obtained by the action of
ethyl sulfate on sodium phenylethylate. Zeisel analyses of
this pure sample were equally unpromising. The average of nine
estimations was 3% low, only one of the nine values being satis-
factory. A Zeisel analysis of a sample of ethyl benzyl ether (63)
purified over metallic sodium was equally unsatisfactory. A
Zerewitinoff estimation showed this latter ether to contain free
alcohol and the Zeisel result is therefore invalidated. It has
not been proven, therefore, that the oil obtained from benzyl-
magnesium chloride and ethyl chloromethyl ether is, as assumed,
a mixture of ethyl β-phenylethyl ether, o-tolylmethyl ethyl
ether and p-tolylmethyl ethyl ether but there can be no question
that both ortho and para rearrangement took place.

(63) Obtained from the Eastman Kodak Co., Rochester, N.Y.

The action of an excess of benzylmagnesium chloride with ethyl chlorocarbonate was next investigated. This reagent had meanwhile been shown to give rise to a rearranged ester when treated with α-naphthylmethylmagnesium chloride as described in Part VI of this thesis. Reference to the action of ethyl-chlorocarbonate with other Grignard reagents will be found in Part V. Briefly, when one mole of Grignard reagent is employed the reaction proceeds as follows:

$$RMgX + Cl-CO_2-C_2H_5 \longrightarrow R-CO_2-C_2H_5 + MgXCl$$

The liquid ester obtained was submitted to hydrolysis with alcoholic potash and the acid obtained fractionally crystallized from hot water. A small amount (3%) of o-toluic acid was easily separated from the more soluble phenylacetic acid. However, the yield of phenylacetic acid was only 13.8% and so the rearranged acid formed 17% of the total yield of acid. In a second run the yield of o-toluic acid was 4% of the theoretical amount based on Grignard reagent used and amounted to 21.5% of the total acids obtained. Oxidation experiments in this second run showed no indication of para rearrangement.

Ethyl formate was also shown to behave abnormally with benzylmagnesium chloride. Evidence was based on oxidation experiments since no definite products could be isolated. Oxidation yielded benzoic acid and phthalic acid and an indication of terephthalic acid but insufficient to isolate. Ethyl formate, $C_2H_5-O-CHO$, contains an aldehyde group and as aldehydes are

known to give rise to rearranged products with benzylmagnesium chloride the appearance of phthalic acid on oxidation is not surprising. Ethyl formate has been employed (64) in the synthesis of aldehydes by treatment with Grignard reagents but the yields are low unless very low temperatures are employed. The reaction may be represented as follows:

$$RMgX + C_2H_5OCHO \longrightarrow \underset{OMgX}{R-\overset{H}{\underset{|}{C}}-OC_2H_5} \overset{HOH}{\longrightarrow} R-\overset{H}{C}=O + C_2H_5OH + MgXOH$$
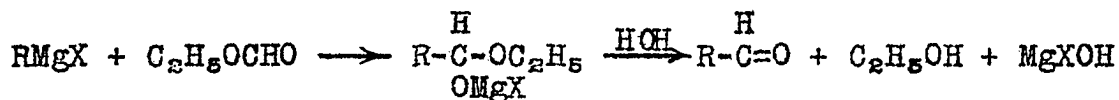
Two preliminary investigations on the reaction between p-anisaldehyde and benzylmagnesium chloride were carried out. This reaction has already been studied by Banús and Medrano (17) and is mentioned in the introduction of this paper. They obtained a white solid melting at 140-141° and which yielded phthalic acid on oxidation. In the first run made by us the aldehyde was slowly added to a well-cooled solution of benzylmagnesium chloride. When worked up in the customary manner a 43% yield of benzyl p-anisyl carbinol, (m.p. = 54°), was obtained and also a white crystalline solid melting at 123-125°. In the second run the Grignard reagent was added to the aldehyde, the condition employed by Schmidlin and Banús (13) to give optimum yields of diphenyl isochromane when benzaldehyde was employed. This second run yielded no benzyl p-anisyl carbinol whatever and two unidentified solids were obtained, one melting at 144-145°, the other at 134°. Mixed melting point determinations seemed

(64) Gattermann, Ann., 393,215(1912). The importance of low temperatures in the synthesis of aldehydes by the reaction of the Grignard reagent with ethyl formate is emphasized in this paper.

to indicate that this 134° solid was identical with the 123-125° solid from the first run. Oxidation experiments have not yet been carried out. The melting points of the solids obtained do not agree with that of the compound obtained by Banús and Medrano (17) although the 144-145° compound is perhaps identical with the 140-141° solid obtained by them. The appearance of two different solid compounds is not surprising inasmuch as Schmidlin and Banús (13) obtained two different compounds from benzaldehyde and benzylmagnesium chloride, and believed by them to be diphenyl isochromane and diphenyl isochromene.

One experiment was carried out on the reaction between benzylmagnesium chloride and p-dimethylamino benzaldehyde. This reaction has already been investigated by F. Sachs and L. Sachs (65) who obtained the expected reaction product, p-dimethylaminophenyl benzyl carbinol, p-$(CH_3)_2N$-C_6H_4-$CHOH$-CH_2-C_6H_5, in 86% yield. In repeating this work a compound corresponding in melting point with that described by Sachs and Sachs (65) was obtained in 74% yield. There was no indication of a less soluble, higher melting substance of the isochromane type.

The constitution of p-dimethylaminophenyl benzyl carbinol has not been proven either by independent synthesis or by conversion to a previously known derivative. However, its structure becomes quite certain from the fact that Sachs and Sachs (65) found that the carbinol readily dehydrates to a stilbene derivative, p-dimethylamino stilbene, p-$(CH_3)_2N$-C_6H_4-CH=CH-C_6H_5. A

(65) F. Sachs and L. Sachs, Ber., 38, 515 (1905).

dehydration of this nature would not be predicted for a rearranged isomer of p-dimethylaminophenyl benzyl carbinol of the following type.

$$\bigcirc\!\!-\!\!\underset{\underset{H}{}}{\overset{\overset{CH_3}{|}}{\underset{|}{C}}}\!\!\overset{OH}{-}\!\!\bigcirc\!\!-\!\!N(CH_3)_2$$
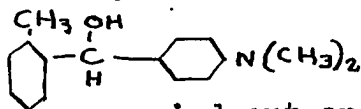
One experiment was carried out on the action of gaseous oxygen on benzylmagnesium chloride. This reaction has already been investigated by Beauveault (66) who obtained benzyl alcohol in 80% yield. In repeating this work with the object in mind of finding ortho or para rearrangement products benzyl alcohol was obtained although in a much poorer yield (30%) than was obtained by Beauveault. There was no evidence of abnormal reaction products. In view of the discrepancy in yields a repeat run might be advisable although it would probably furnish little evidence of the structure of benzylmagnesium chloride.

During the course of the studies on the formation of di-p-tolyl incidental to the formation of benzylmagnesium chloride, Gilman and Kirby (58) investigated the action of two compounds, cupric chloride and azobenzene, which are known to yield a smooth coupling reaction with Grignard reagents, forming the R-R compound. It was shown that these reagents do not increase the yield of di-p-tolyl but give instead good yields of dibenzyl. Another similar reaction is reported here. Benzylmagnesium chloride was found to react smoothly with benzyl chloride yielding 65% of dibenzyl. Oxidation of the residual oils showed no indication of ortho or para coupling products.

In considering the mechanism proposed below for the abnormal

(66) Beauveault, Bull. soc. chim., (3)29,1051(1903).

reactions of benzylmagnesium chloride it became important to investigate the behavior of formaldehyde with cyclohexylmethyl magnesium halides. Cyclohexylmethyl chloride may be considered as hexahydrobenzyl chloride. The new reaction mechanism will be shown to be based on the presence of the group, $-C=C-CH_2-X$, and the consequent relatively increased activity of the halogen atom. Cyclohexylmethyl halides do not contain such a grouping and consequently if the Grignard reagents prepared from them, $C_6H_{11}-CH_2-MgX$, give abnormal results with formaldehyde the new mechanism must be unequivocally rejected. Formaldehyde was chosen for this study since its reaction with benzylmagnesium chloride is the only example of completely abnormal behavior. It was felt that formaldehyde would be, therefore, a rigid test of the reliability of cyclohexylmethylmagnesium halides. When treated with formaldehyde cyclohexylmethylmagnesium bromide gave β-cyclohexylethanol in 46% yield, and identified by oxidation to cyclohexylacetic acid. A high-boiling oil was also obtained which has not as yet been identified. This oil did not appear to be the formal of β-cyclohexylethanol, $(C_6H_{11}-CH_2-CH_2O)_2CH_2$, since it could not be hydrolyzed to that alcohol with 10% sulfuric acid. Whether or not this oil is a rearrangement product of some kind cannot be definitely stated. Exhaustive oxidation obviously furnishes no proof in the case of aliphatic compounds.

The action of formaldehyde on three other Grignard reagents was also investigated. The reagents chosen, phenylethylmagnesium bromide, styrylmagnesium bromide, and phenylacetenylmagnesium bromide all have the -MgBr group two carbons removed from the

benzene ring. These Griguard reagents were of interest because, although containing an aromatic ring, they do not have the atomic grouping, $-CH=C'-CH_2-MgX$. The mechanism of rearrangement postulated below hinges on this grouping of atoms. If these Grignard reagents should likewise give rise to rearranged products the new theory would have necessarily to be abandoned. Formaldehyde was chose as the test case for the reasons stated in connection with cyclohexylmethylmagnesium bromide.

The results of these three experiments showed conclusively that with the Grignard reagents in question substitution in, or rearrangement to, the benzene ring does not occur. In no case was the slightest evidence of phthalic or terephthalic acid found among the oxidation products. Phenylethylmagnesium bromide yielded an oil, probably γ-phenylethanol, in 44% yield. Styryl-magnesium bromide gave no very definite products but no evidence of rearrangement to the ring. Phenylacetenylmagnesium bromide gave an oil, probably phenylpropargyl alcohol, in 20% yield.

IV. A New Mechanism for the Abnormal Reactions
of Benzylmagnesium Chloride

Holleman (67) has done a vast amount of work on the direct

entrance of substituents into the benzene ring and from this work

he concludes that all substitutions are preceded by addition re-

actions. If C_6H_5X is nitrated, assuming X to be an ortho-para

directing group, the reaction is supposed to proceed as follows:
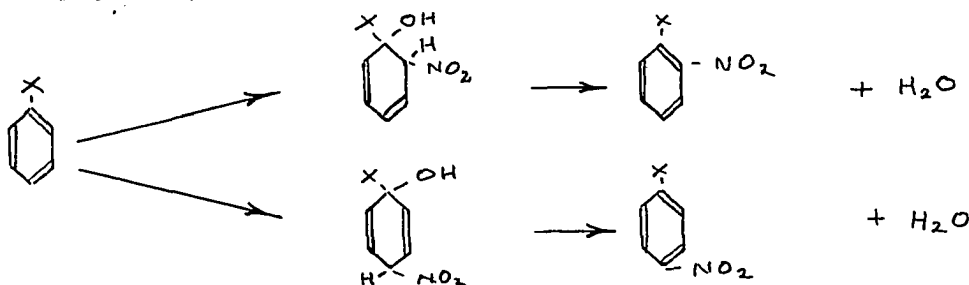
Flürscheim (68) uses diagrams of the following types to repre-

sent the distribution of affinity in aromatic compounds. The

first represents the case of an ortho-para directing group, the

second a meta directing group.
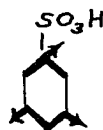
The heavy lines represent comparatively large amounts of valence

force. Thus in chlorobenzene the unreactive halogen atom is

tightly bound to the benzene ring and requires a large amount

(67) Holleman, Die direkte Einführung von Substituenten in den
Benzolkern, Leipzig; Viet and Co.(1900). See also Henrich,
Theories of Organic Chemistry, translated by Johnson and Hahn,
John Wiley and Sons, New York (1922), p.206.
(68) A review of the early work is found in a paper by Flürscheim
(Chem. and Ind., 44,247(1925). Recent papers by the same author
are (J. Chem. Soc., p.1562(1926); p.448(1928); p.453(1928);
p.1607(1928); p.2230(1928)). See, also, Holleman (Rec. trav.
chim., 42,356(1923)).

of the available affinity of the carbon atom to which it is attached. This leaves a comparatively weak bond between carbon atoms (1) and (2), and (1) and (6). These latter carbon atoms are thus in a state of partial unsaturation and have a comparatively large amount of available affinity as represented by the arrows. Following this scheme we see that carbon atom (4) also possesses a certain amount of available affinity. In a compound of this type ortho-para substitution takes place.

The theory of Holleman, that addition precedes substitution, has received a striking confirmation in the recent work of van Alphen (69). That such addition takes place was disputed by Prins (70) on the grounds that the intermediate addition product having aliphatic double-bonds is terpene-like in structure and therefore should char or resinify under the influence of nitric or sulfuric acids. van Alphen (69) has shown that dihydrophthalic acid is not charred by these reagents but is converted to phthalic acid. It is assumed that addition takes place and then elimination yielding a true benzene ring.
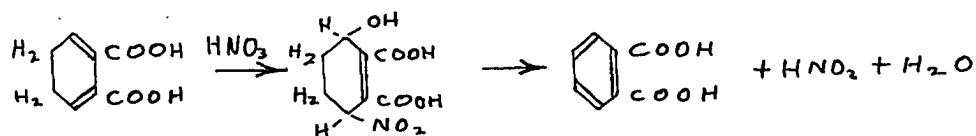
In the case of bromine the addition product was actually isolated.
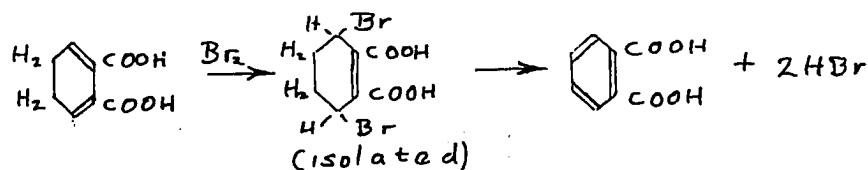
(69) van Alphen, Rec. trav. chim., 47,169(1928).
(70) Prins, ibid., 43,865(1924).

van Alphen concludes that the idea that hexadienes must resinify is incorrect at least with this compound.

In reviewing the various cases of abnormal behavior of benzylmagnesium chloride the equilibrium formula of Schmidlin and Banús (13) seems to become increasingly unsatisfactory. Its greatest fault is its flexibility; its ability to explain anything but predict nothing. It is easy to explain the failure of many reagents to yield rearranged products by simply saying that those reagents favor a shift in the equilibrium in favor of the normal form. The evidence at hand is not sufficient, however, to dismiss arbitrarily the equilibrium formula. The new mechanism proposed here is not without faults but is more in accord with modern ideas of benzene ring substitution. But it must also be remembered that the Flürscheim theory is not without opponents. (71). The disadvantages as well as the advantages of the new mechanism will be discussed below.

It has been shown that the halogen atom of benzyl chloride is of unusually great reactivity. Employing a Flürscheim diagram benzyl chloride may be represented as follows

$$CH_2 \underline{\qquad} Cl$$
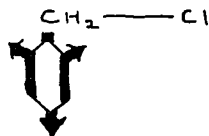
The -MgCl group of benzylmagnesium chloride may then be unusually loosely attached and the "available affinity" of the ortho and para position may become very great.

$$CH_2 \underline{\qquad} MgCl$$
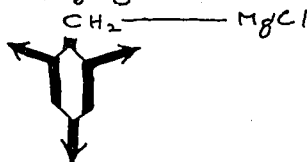
(71) See, Henrich, Theories of Organic Chemistry, translated by Johnson and Hahn, John Wiley and Sons, New York, 1922, p.197.

The very large and heavy arrows represent a relatively greater available affinity than exists in benzyl chloride itself. Indeed, the assumption may be made that this available affinity has become so great that ring substitution may take place simultaneously with the customary reaction of the -MgCl group. We would then have two reactions proceeding at once, one leading to normal products, one to rearranged products. Using the mechanism of ring substitution described above one case may be formulated as follows, where RCl represents ethyl chlorocarbonate or ethyl chloromethyl ether.

1. Normal Reaction.

$$C_6H_5CH_2{-}MgCl + RCl \longrightarrow C_6H_5CH_2{-}R + MgCl_2$$

2. Abnormal Reaction (ortho).

[structures: CH₂–MgCl aromatic + RCl → (I) → (II) + HCl → (III) CH₃ –R + MgCl₂]

An alternative mechanism may also be suggested here. The intermediate compound (I) might lose MgCl₂ from adjacent carbon atoms.

[structures: (I) → (IV) + MgCl₂ → CH₃ –R]

An analogy is found in the reaction between ethylene bromide and magnesium in which ethylene is formed. (72).

3. Abnormal reaction (para).

[structures: CH₂–MgCl + RCl → → + HCl → CH₃ + MgCl₂]

(72) Tissier and Grignard, Compt. rend., 132, 835(1901).

It would be difficult to submit the above mechanisms to direct experimental proof. The postulated intermediates would be unstable and unusually difficult to isolate. An indirect proof was therefore attempted. This mechanism being exactly parallel to that discussed above for the direct ring-alkylation of phenols some degree of support for this new mechanism would be had if it could be shown that the halides giving rise to ring-alkylation of phenols also give rearrangement products with benzylmagnesium chloride; and conversely if the halides giving rearrangement reactions with that Grignard reagent could be shown to give direct ring-alkylation of phenol. Several experiments of this nature were carried out but as yet no halide has been found which gives direct ring-alkylation in both cases.

The reaction between sodium phenolate and ethylchlorocarbonate was very rapid and gave good yields of ethyl phenyl carbonate. No ethyl salicylate could be detected although in one experiment the reaction was carried out at the temperature of a carbon dioxide-ether mixture to bring about slower reaction. When ethyl chloromethyl ether was allowed to react at -18° with sodium phenolate no ethyl o-hydroxybenzyl ether could be isolated. Sodium phenolate did not react with benzaldehyde at room temperature. A run is now being made employing a higher temperature.

Since benzhydryl bromide gives rise to direct ring-alkylation products of phenol (51) the action of that halide with benzylmagnesium chloride was next investigated. No ortho or

para rearrangement products could be isolated. sym-Tetraphenyl-ethane was found among the reaction products and a small amount of product agreeing in melting point with the normal reaction product, α-α-β-triphenyl ethane. Oxidation of residual tars gave only benzoic acid.

While the proposed mechanism for the abnormal reactions of benzylmagnesium chloride is based largely on analogy with the alkylation reactions of sodium phenolate the process does serve to explain the known facts. Its value in predicting the course of untried reactions is still open to question. Nevertheless it would be well to include here proposed mechanisms for the rearrangements that do not involve a halide such as ethyl chlorocarbonate or ethyl chloromethyl ether.

1. Ethylene oxide (para only).
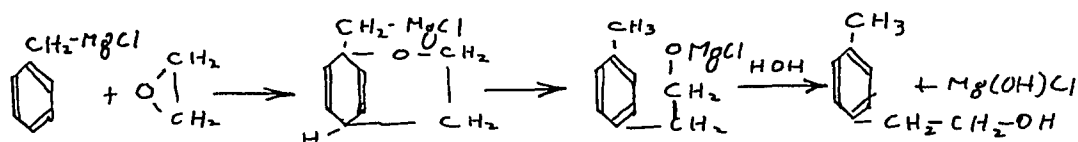
2. Formaldehyde (ortho only) (73).
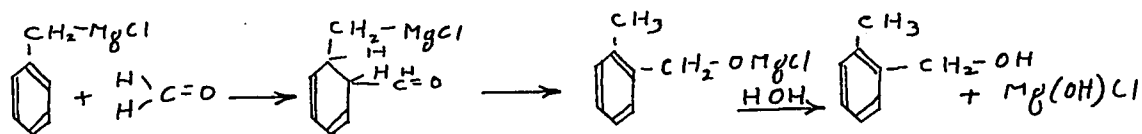
(73) This mechanism doesn't seem very plausible it must be admitted. Perhaps we are dealing with a case of divalent carbon, HCHO⇌H-C-OH. Then we can postulate a reaction of the following type
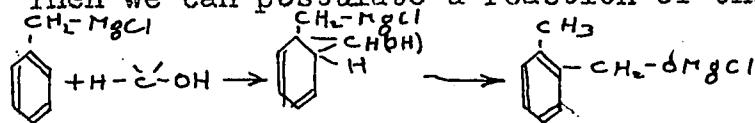
In any event, it is not surprising that the reaction of formaldehyde with benzylmagnesium chloride leads to an unusual amount of tarry by-products.

3. Benzaldehyde

$$\text{C}_6\text{H}_5\text{-CH}_2\text{-MgCl} + 2\,\text{C}_6\text{H}_5\text{CHO} \longrightarrow \begin{array}{c}\text{CH}_2\text{-CH-C}_6\text{H}_5 \\ |\quad\text{OMgCl} \\ \text{CH(OH)C}_6\text{H}_5\end{array} \longrightarrow \begin{array}{c}\text{CH}_2 \\ |\quad\text{CH-C}_6\text{H}_5 \\ |\quad\overset{O}{\text{C}}\text{H-C}_6\text{H}_5\end{array}$$
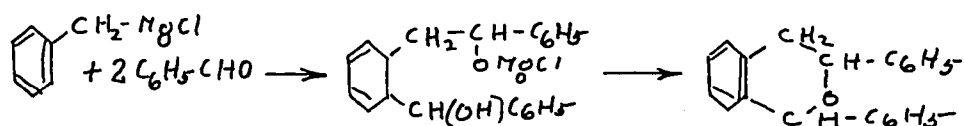
A rather striking confirmation of this mechanism is to be found in Part 2 of this paper. It will be shown there that the reaction of α-naphthylmethylmagnesium chloride with ethyl chlorocarbonate proceeds in an entirely abnormal manner, no normal product being detected. The new mechanism is based on the unusual looseness of attachment of the halogen atom of compounds containing the grouping -C=C-CH$_2$-X. It follows that an RX compound in which the halogen atom is relatively more loosely attached than is the case in benzyl chloride should give rise to more marked abnormalities. Olivier (74) has shown that α-napthyl-methyl halides are more reactive than the corresponding benzyl halides. The expected increased tendency to give rearranged products is experimentally demonstrated in the case just mentioned.

A few further suggestions should be included at this time. In connection with the quinoidal formula of Schmidlin and Banús (13) absorption spectra studies would be of exceptional value. One is led to question the quinoidal formula due to the absence of marked color in benzylmagnesium chloride solutions. Further, the highly active sodium benzyl (75) is deeply colored, although similar colorations are not the rule with sodium alkyls. Whether

(74) See reference (88) of this paper.
(75) See Part V of this paper.

the color of sodium benzyl is caused by quinoidal structure or the presence of free radicals, or both, is not known.

Another study of interest would be to investigate the possible reducing action of benzylmagnesium chloride on benzophenone. Gomberg and Bachmann (76) have demonstrated the nearly quantitative reduction of benzophenone to benzpinacone by means of magnesious halides, MgX. If benzylmagnesium chloride possesses a weakly attached -MgX group we might expect it also to have a reducing action on benzophenone.

$$2C_7H_7\text{-}MgCl + 2(C_6H_5)_2CO \rightarrow (C_6H_5)_2C(OMgCl)\text{-}C(OMgCl)(C_6H_5)_2 + C_7H_7\text{-}C_7H_7$$
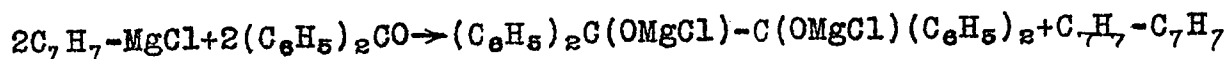
An experiment of this nature is now being tried.

In connection with the work on ethylene oxide it would be interesting to test the action of larger oxides, such as trimethylene oxide, with benzylmagnesium chloride. It is difficult to predict the course of such reactions but _para_ rearrangement would not be surprising.

(76) Gomberg and Bachmann, J. Am. Chem. Soc., 49,236(1927).

Table V.

Reagents showing abnormal behavior toward Benzylmagnesium chloride.

Reagent	Manner of rearrangement	Discoverer	Reference
Formaldehyde	ortho	Tiffeneau and Delange	(7)
Benzaldehyde	ortho; para(?)	Chichibabin	(11)
p-Anisaldehyde	ortho	Banús and Medrano	(17)
Acetyl chloride	ortho	Gilman and Kirby	This thesis
Ethylene oxide	para	Gilman and Kirby	This thesis
Ethyl chloromethyl ether	ortho and para	Gilman and Kirby[+]	This thesis
Ethyl chlorocarbonate	ortho	Gilman and Kirby	This thesis
Ethyl formate	ortho; para(?)	Gilman and Kirby	This thesis

[+]See reference (61).

2. Studies on the Capture of the Free Benzyl Radical.

The reaction between an organic halide and a free metal is supposed by some to take place through intermediate formation of free radicals. In a recent and comprehensive paper on the mechanism of the Wurtz-Fittig reaction Bachmann and Clarke (77) proposed the following reactions to account for the several products formed in the reaction between chlorobenzene and sodium.

$$C_6H_5Cl + Na \longrightarrow C_6H_5- + NaCl \qquad (1)$$

$$2C_6H_5- \longrightarrow C_6H_5-C_6H_5 \qquad (2)$$

$$2C_6H_5- \longrightarrow C_6H_6 + C_6H_4 \qquad (3)$$

$$C_6H_4 + 2C_6H_5- \longrightarrow C_6H_5-C_6H_4-C_6H_5 \qquad (4)$$

$$2C_6H_4 + 2C_6H_5- \longrightarrow C_6H_5-C_6H_4-C_6H_4-C_6H_5 \qquad (5)$$
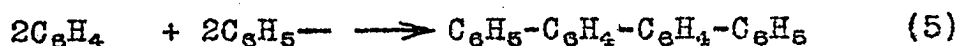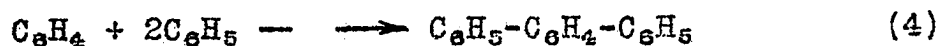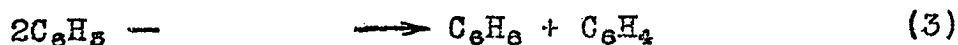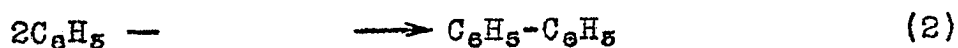
Gilman and Fothergill (78) agree with Gomberg and Bachmann (79) that free radicals are probably formed in the preparation of the Grignard reagent.

$$2RX + Mg \longrightarrow 2R- + MgX_2 \qquad (6)$$

$$2R- \longrightarrow R-R \qquad (7)$$

$$2R- \longrightarrow R(+H) + R(-H) \qquad (8)$$

$$RX + Mg \longrightarrow R- + -MgX \qquad (9)$$

$$R- + -MgX \longrightarrow R-MgX \qquad (10)$$
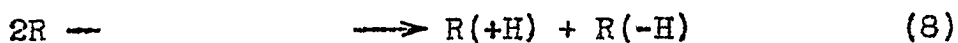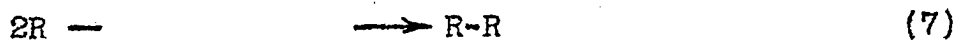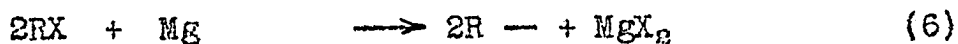
Proof of the intermediate formation of the free radical, R-,

(77) Bachmann and Clarke, J. Am. Chem. Soc., 49,2090,(1927).
(78) Gilman and Fothergill, ibid., 50,3334(1928).
(79) Gomberg and Bachmann, ibid., 49,236(1927).

according to Reaction 6 or Reaction 9 would be supplied by the capture of that radical by some other reagent before formation of the Grignard reagent according to Reaction 10, or coupling to the R-R compound according to Reaction 7, had occurred. Several such studies on the capture of free radicals are now being carried out by Gilman and co-workers (80).

Numerous studies (81) have clearly demonstrated that the Grignard reagent does not add to the ethylenic linkage. However, Ziegler and Bahr (82) have recently shown that potassium alkyls add smoothly to the ethylenic linkage and this suggested a possible method for the capture and identification of free radicals in the preparation of the Grignard reagent. It was proposed to prepare the Grignard reagent in the presence of metallic sodium or, better, in the presence of liquid sodium-potassium alloy and some compound containing an ethylenic linkage. Then if free radical formation occurs during the reaction between the RX compound and magnesium, the free radical might combine with sodium to form the corresponding sodium alkyl. The sodium alkyl, R-Na, might in turn, react with the ethylenic compound as shown in the following reactions.

(80) A preliminary report of these studies on the capture of free radicals was read by Gilman, Fothergill, Kirby and McGlumphy at the September, 1928, meeting of the American Chemical Society, held at Swampscott, Massachusetts. See footnote (16) of the paper by Gilman and Fothergill.
(81) Gilman and Crawford, J. Am. Chem. Soc., 45,554(1923).
    Gilman and Peterson, ibid., 48,423(1926).
    Gilman and McGlumphy, Rec. trav. chim., 47,418(1928).
(82) Ziegler and Bahr, Ber., 61,253(1928).

$$RX + Mg \longrightarrow R- + -MgX \qquad (11)$$

$$R- + Na \longrightarrow R - Na \qquad (12)$$

$$R-Na + R'-CH=CH-R' \longrightarrow R-R'-CH-CHNa-R' \qquad (13)$$

$$R-R'-CH-CHNa-R' + CO_2 \longrightarrow R-R'-CH-CH(COONa)-R' \qquad (14)$$
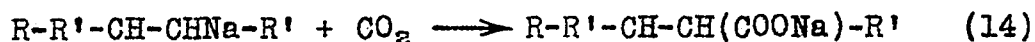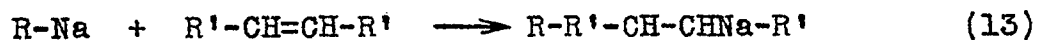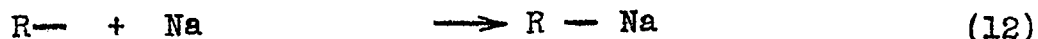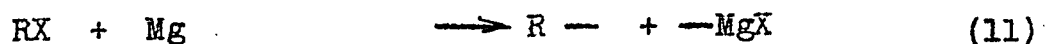
In order to test this hypothesis several orienting experiments were necessary. It was first necessary to demonstrate that metallic sodium, or sodium-potassium alloy, does not react with the Grignard reagent itself to form a sodium alkyl. The use of benzyl chloride as the RX compound was particularly desirable since Schlenk and Holtz (83) have described sodium benzyl as having a brilliant red color. Its presence in the solution would thus be immediately noticed. When benzylmagnesium chloride was treated with sodium at a temperature of -15° no red color developed. Subsequent hydrolysis yielded only 39% of the theoretical yield of toluene and while the loss was not accounted for it was evident that no sodium benzyl had formed as no red coloration whatever was noted. It must be remembered that Schlenk and Holtz (83) showed that sodium benzyl reacts with ether and the color is thereby destroyed, but that at low temperatures this reaction is comparatively quite slow.

When benzylmagnesium chloride was added to liquid sodium-potassium alloy the reaction mixture was likewise devoid of color. Subsequent treatment with carbon dioxide gave an excellent yield (82.4%) of phenylacetic acid. Oxidation of the small

(83) Schlenk and Holtz, Ber., 50,262(1917).

amount of residual oil gave only benzoic acid, and no phthalic or terephthalic acids. It was concluded that there was no reaction between benzylmagnesium chloride and sodium or sodium-potassium alloy.

It was then desired to see if known sodium benzyl would add to a typical ethylenic compound. Accordingly, sodium benzyl was prepared according to the method of Schlenk and Holtz (83) from mercury dibenzyl and sodium. When treated with α-α-diphenyl-ethylene the red color was soon removed. Carbon dioxide was then passed in. When worked up there was obtained a trace of solid acid melting unsharply from 90-105°. The expected acid α-α-γ-triphenyl n-butyric acid, ($(C_6H_5)_2CH-CH_2-CH(COOH)C_6H_5$), has been prepared by Staudinger and Suter (84) and melts at 178-179°.

In a second run stilbene was substituted for the α-α-diphenyl-ethylene. A trace of solid acid melting from 127-131° was obtained. The expected acid, α-β-γ-triphenyl n-butyric acid ($C_6H_5-CH_2-CH(C_6H_5)-CH(COOH)-C_6H_5$) has not been described in the literature. That either the yield of sodium benzyl was very meagre, or that practically no reaction with stilbene took place, was demonstrated by a practically quantitative recovery of the stilbene. In fact, it was shown by experiment that the yield of sodium benzyl was very poor. When a preparation of sodium benzyl was directly treated with carbon dioxide the yield of phenylacetic acid was too low to permit of isolation. Its

(84) Staudinger and Suter, Ber., 53,1093(1920).

presence was indicated by its characteristic odor. While the solutions of sodium benzyl were intensely red in color it is apparent that they contained very little of the compound.

In spite of the above unsatisfactory attempts to identify sodium benzyl when that substance was known to be present, nevertheless, the run proposed above for the capture of free benzyl radicals in the preparation of benzylmagnesium was attempted. A 0.2 mole run of benzylmagnesium chloride was carried out in the presence of stilbene and sodium-potassium alloy. Carbon dioxide was then led in until a negative RMgX color test was obtained. On working up in the customary manner a 47% yield of phenylacetic acid was obtained. No other acids could be separated. Oxidation of all tars yielded only benzoic acid.

In conclusion, it may be said that the results of these studies are at best inconclusive. It has not been proven that the free benzyl radical, if formed, would combine with sodium to yield sodium benzyl. Further, it has not been proven that sodium benzyl can be made to add to the ethylenic linkage of α-α-diphenylethylene, or stilbene.

3. Studies on α-Naphthylmethylmagnesium Chloride.

V. Introduction.

In 1912 an attempt was made by Wietzenböck and Lieb (85) to prepare the ethyl ester of α-naphthylacetic acid by allowing α-naphthylmethylmagnesium chloride to react with an excess of ethyl chlorocarbonate, in accordance with the following reactions (86).

The α-chloromethyl naphthalene employed by them was prepared by the direct chlorination of α-methylnaphthalene using the method described by Scherler (87) and others. Wietzenböck and Lieb (85) apparently experienced some difficulty in inducing their α-chloromethyl naphthalene to react with magnesium since they state that most of the magnesium was dissolved only after two hours warming of the reaction mixture. After treating with ethyl chlorocarbonate the only product obtained was the coupling product, di-α-naphthyl ethane. The residual oils yielded no α-naphthylacetic acid when saponified with alcoholic alkali.

The results of Wietzenböck and Lieb (85) were of unusual interest because of the close relationship between α-chloromethyl naphthalene and benzyl chloride. In fact, Olivier (88) has shown

(85) Wietzenböck and Lieb, Monatsh., 33,554(1912).
(86) The preparation of esters by means of this reaction was first described by Houben (Ber., 36,3087(1903)).
(87) See reference (126) of this paper.
(88) Olivier, Rec. trav. chim., 42,775(1923); see, also, Shoesmith and Rubli, J. Chem. Soc., 3098(1927).

that α-bromomethyl naphthalene is of greater reactivity than benzyl bromide since the former is more readily hydrolyzed by aqueous alcohol. In view of these facts it was proposed to attempt the preparation of α-naphthylmethylmagnesium chloride and, if successful, test its behavior toward several of the reagents already studied in connection with benzylmagnesium chloride.

VI. Discussion.

The α-chloromethyl naphthalene used in these experiments was obtained by converting α-naphthyl carbinol to the corresponding halide by means of thionyl chloride. The α-naphthyl carbinol was prepared by treating α-naphthylmagnesium bromide with monomolecular formaldehyde. While the process is rather costly the product obtained is very pure and readily reacts with magnesium turnings with the aid of a crystal of iodine as catalyst. The Grignard solution thus obtained readily gives a color test when treated with Michler's ketone in benzene. The Grignard reagent appeared to be formed in a very good yield and although customarily prepared in rather dilute solution presented no unusual difficulties in preparation. The reaction started easily and as quickly as phenylmagnesium bromide and at no time were encountered large quantities of the coupling product obtained by Wietzenböck and Lieb (85).

When carbon dioxide was passed into a solution of α-naphthyl-methylmagnesium chloride a 59.4% yield of the expected α-naphthyl-

acetic acid was obtained. Methyl sulfate also reacted in a wholly normal manner giving a 55.1% yield of α-ethyl naphthalene. In the case of phenylisocyanate several interesting observations were made. In the first run a product was obtained which appeared to be impure α-naphthylacetanilide although the yield was very small. In the second run an attempt was made to prepare the Grignard reagent in the presence of phenylisocyanate. It was found that the reaction stopped completely. This recalls the observation of Gilman and Kirby (5) that phenylisocyanate stopped the reaction of benzhydryl chloride with magnesium. In the third run a crystalline compound was obtained which melted at 136-137° and was not α-naphthyl acetanilide since the latter was prepared from a known sample of α-naphthylacetic acid and found to melt at 155°. The 136-137° compound was not identified. The fourth and largest run gave the expected product in a yield of 36%.

The reaction with ethyl chlorocarbonate proved to be of unusual interest since it presents the first case (89) in which this reagent reacts in an anomalous manner with a Grignard reagent. The Grignard solution was slowly added to an excess of well cooled ethyl chlorocarbonate. When worked up in the customary manner an oil was obtained which on hydrolysis yielded a solid acid melting at 174°. The normal reaction product, α-naphthylacetic acid, melts at 131°. A titration showed that the

(89) The abnormal reaction of benzylmagnesium chloride with ethylchlorocarbonate was found subsequent to the carrying out of this work.

acid is an isomer of α-naphthylacetic acid. The anilide was prepared and found to melt at 217-218°. A literature search revealed the following melting points for the known isomers of the formula $C_{12}H_{10}O_2$.

Table VI.

Acid	M.P.	M.P. of anilide	Reference
4-Methyl α-naphthoic	175°	179°	(90)
1-Methyl β-naphthoic	178°	--	(91),(92)
2-Methyl α-naphthoic	126-127°	167-168°	(90)
7-Methyl α-naphthoic	150-152°	--	(93)
4-Methyl β-naphthoic	198-199°	--	(94)

The only possible configuration on the basis of the above data appears to be that of 1-methyl β-naphthoic acid. Other facts support this view. The oil obtained from the reaction was very probably the ethyl ester of the unknown acid and boiled at 190-200° (15 mm.) and at 145-150° (3 mm.). Auwers and Möller (92) have reported the boiling point of the ethyl ester of 1-methyl β-naphthoic acid as 184° (13 mm.). Further, Mayer and Schenko (91) were unsuccessful in attempts to oxidize 1-methyl β-naphoic acid to the corresponding α-β-dicarboxy naphthalene. Our acid also gave no definite products on oxidation with permanganate or chromic acid. An authentic sample of 1-methyl β-naph-

(90) Mayer and Sieglitz, Ber., 55B,1835(1922).
(91) Mayer and Schenko, Ber., 56B,1408(1923).
(92) Auwers and Möller, J. prakt. chem., 109,124(1925).
(93) Weiszgerber and Kruber, Ber., 52,353(1919).
(94) Darzens, Compt. rend., 183,748(1926).

thoic acid for comparison has not yet been synthesized (95).
The conclusion is made still more probable by the fact that it
has been shown above that when the closely related benzylmag-
nesium chloride reacts with an excess of ethyl chlorocarbonate
ortho rearrangement occurs to some extent, leading to the ethyl
ester of o-toluic acid, along with the normal product, ethyl
phenylacetate.

The use of gaseous formaldehyde also led to an unusual re-
sult, the reaction product not being α-naphthyl ethyl alcohol
as expected. A solid carbinol was obtained melting at 121° and
whose phenyl urethane melted at 125°. By analogy with the re-
action of benzylmagnesium chloride with formaldehyde this com-
pound should be 1-methyl-2-hydroxymethyl naphthalene. This
latter compound has not been described in the literature.
2-Methyl-1-hydroxymethyl naphthalene (96) melts at 136-137° and
1-methyl-4-hydroxymethyl naphthalene (23) melts at 74-75°. An
attempt to oxidize the 121° carbinol to the corresponding carbo-
xylic acid by means of alkaline permanganate failed and the
carbinol was not recovered. This failure, and also that of the
failure to oxidize 1-methyl β-naphthoic acid as mentioned above
are apparently cases of steric hindrance.

β-Bromomethylnaphthalene reacted easily with magnesium in
ether and when carbon dioxide was led in a small yield of the
expected β-naphthylacetic acid was obtained.

(95) We have requested from Prof. von Anwers a sample of his
1-methyl β-naphthoic acid for a mixed melting point determina-
tion.
(96) Ziegler and Tiemann, Ber., 55B, 3406 (1922).

4. Experimental.

1. General procedure used for the oxidation of residual oils,
   etc.

Dilute alkaline permanganate is very generally used for the
(97) oxidation of side-chains of organic compounds. In this
manner the side-chain is removed, a carboxyl group being at-
tached to the ring in the position occupied by the oxidized
chain. In general an excess of permanganate was employed,
usually in concentrations of about 5% and containing about 10%
of sodium or potassium hydroxide. At the conclusion of the
oxidation, which required from 30 minutes to several hours,
depending on the nature of the material, the excess perman-
ganate was destroyed by adding a little alcohol, and the heavy
manganese dioxide precipitate filtered off with suction. After
washing the sludge of manganese dioxide with a little dilute
alkali, the filtrate and washings were combined and acidified
with hydrochloric acid. The acids looked for were benzoic,
o-phthalic and terephthalic acids. The solubilities of these
acids in water and chloroform are as follows.

Table VII.

Acid	Water	Chloroform
Benzoic acid	0.34g. in 100g. at 25°(98)	soluble
o-phthalic acid	0.54g. in 100g. at 14°(99)	insoluble(100)
Tere-phthalic acid	1 part in 67000(101)	insoluble(101)

(97) See Kamm, Qualitative Organic Analysis, published by John
     Wiley and Sons, New York, p. 166,1923.
(98) Hoffmann and Langbeck, Z. physik. Chem.,51, 394(1905).
(99) Graebe, Ann., 238, 321(1887).
(100) Zincke and Breuer, ibid., 226, 53(1884).
(101) Baeyer, ibid., 251, 284(1889).
(102) de La Rue and Müller, ibid., 121, 88(1862).

On acidification all of the terephthalic acid precipitates along with part of the benzoic acid which is usually present in the largest quantity. The phthalic acid remains in solution along with the remainder of the benzoic acid. The precipitated acids are separated by simply extracting the benzoic acid from the terephthalic acid with chloroform. The water solution is extracted two or three times with ether, the ether dried over sodium sulfate and evaporated to dryness. The residual benzoic acid and phthalic acid are separated by a chloroform extraction of the benzoic acid. Had iso-phthalic acid formed during any of the oxidations it would have escaped detection in the above procedure. The solubility of iso-phthalic acid in water is low (1 part in 7800) and it probably would have appeared along with the terephthalic acid.

2. Benzylmagnesium chloride and carbon dioxide.

A one liter 3-neck flask was fitted with a reflux condenser and highly efficient mechanical stirrer. A separatory funnel was fitted with a glass tube to lead the contents directly on to the vanes of the stirrer. An inlet tube for carbon dioxide was also provided. Two hundred cc. of dry ether was placed in the flask and a rapid stream of dry carbon dioxide led in. A solution of 0.5 mole of benzylmagnesium chloride was placed in the separatory funnel and slowly added to the contents of the flask. Vigorous stirring was maintained to insure good contact with the carbon dioxide. The flask was kept cool by means of an ice-salt mixture. Addition re-

quired forty five minutes and at the end of this time a negative R-MgX color test (103) was obtained. After hydrolyzing with ice and hydrochloric acid the ether layer was removed, the water layer twice extracted with ether, and the combined ether layers extracted twice with 10% potassium hydroxide. The alkaline extracts were extracted with a small portion of ether to remove suspended organic matter, warmed to drive out the last traces of ether, and acidified with hydrochloric acid. The crystalline precipitate weighed 46.5g. when fully air dried. This corresponds to a yield of 68.4% of the theoretical amount of phenylacetic acid or isomers of that acid. The fact that the material was essentially pure phenylacetic acid was shown by its melting point of 77° with the first noticeable softening occurring at 75°. A mixed melting point with phenylacetic acid showed no depression. In spite of the apparent purity of the product, fractional crystallization was resorted to in an effort to isolate any trace of toluic acids which might be present.

Fractional crystallizations. The solid acid was boiled with 500 cc. of distilled water and was largely dissolved. Since o- and p- toluric acids are less soluble in water than phenylacetic acid the former should be present in the undissolved residue to a greater degree than in the original material. The oil remaining from the first extraction was in turn boiled

(103) Wherever the RMgX color test is referred to in this paper the test of Gilman and Schulze (J.Am.Chem.Soc., 47.2002(1925); Bull. soc. chim., 41, 1479(1927) is indicated.

with 150 cc. of water and the clear extract decanted from a
still smaller amount of undissolved oil. On cooling, this
extract deposited crystals of phenylacetic acid melting at
76-76.5°(A). The oil remaining from (A) was recrystallized
from hot water and gave phenylacetic acid melting at 75°(B).
Sample (A) was again crystallized from 150 cc. of water. The
acid obtained melted at 75.5° with previous softening at
73-74°. No indication of toluic acids was found.

The ether layer remaining from the first alkali extractions
was distilled to remove the ether. The residue was a yellowish
oil weighing 7.5g., and was probably a mixture of dibenzyl,
ketone and tertiary alcohol bodies. No attempt was made to
separate this mixture but it was oxidized strongly with alkaline
permanganate to see if any of the residual oil contained products
of ortho or para rearrangement. The products looked for were
benzoic acid, o-phthalic acid, and terephthalic acid. The only
product found was 3.6g. of benzoic acid. The oxidation pro-
cedure is described above in detail.

3. Benzylmagnesium chloride and bromine.

Eighty grams (0.5 mole) of bromine was dissolved in well
cooled anhydrous ether, the solution placed in a 3-neck stir-
ring flask and cooled in a mixture of carbon dioxide snow and
ether. A solution of 0.25 mole of benzylmagnesium chloride was
also well cooled, placed in the separatory funnel and slowly
added to the bromine solution. Addition required about thirty
minutes and a precipitate formed in the reaction flask. At the

end of the addition a negative RMgX color test was obtained.
Hydrolysis was carried out immediately to prevent any direct
bromination of the reaction products when the solution warmed up
to room temperature. Hydrolysis was carried out by pouring
the reaction mixture onto cracked ice. Dilute hydrochloric
acid was then added and crystals of sodium thiosulfate to de-
stroy the excess bromine. The ether layer was then removed,
the water layer once extracted with ether, and the combined
ether extracts dried over sodium sulfate. The ether was then
distilled off on the water bath and the remaining oil vacuum
distilled. Practically everything came over at 73-74° under 10
mm. pressure, distillation being carried out using an oil-bath
at a temperature of 95-110°. The yield was 26.9g. of strongly
lachrimatory oil, corresponding to a yield of 62.9% of the
theoretical amount. A small portion redistilled under atmos-
pheric pressure (732 mm.) at 194-195° (uncorr.). The boiling
point of benzyl bromide is given by Kekule (104) as 198-199°.
Three grams of the oil was converted to benzyl phthalimide
by heating with 5g. of potassium phthalimide in an oil-bath
at 170-190° for one and three-quarters hours. After cooling,
the solid mass was extracted with 25 cc. of cold 10% sodium
hydroxide and the remaining solid filtered off and washed with
cold water. After two recrystallizations from alcohol the
compound was obtained in the form of long needles melting at
115-116°. This corresponds exactly with the figure given by

(104) Kekule, Ann., 137, 639(1866).

Kamm (105) for benzyl phthalimide.

4. Benzylmagnesium chloride and benzonitrile.

A solution of 31g. (0.3 mole) of benzonitrile was placed in a 500 cc. 3-neck flask and well cooled in an ice-salt mixture. A solution of 0.3 mole of benzylmagnesium chloride was then added through the separatory over a period of thirty minutes, vigorous stirring being maintained during the addition. A yellow color appeared in the reaction flask. The mixture was allowed to warm up to room temperature and was stirred for three hours. After standing over night, hydrolysis was carried out with ice and dilute hydrochloric acid. The mixture was very sticky and was only slowly decomposed by the acid. When most of the paste was dissolved the ether layer was removed and dried over sodium sulfate. The water layer on standing deposited a mass of sticky yellow cyrstals which were filtered off and easily recrystallized from 75% alcohol. Six and one tenth grams of white crystals melting at 53° was obtained. Concentration of the alcohol yielded a further 1.9g.

The ether layer was distilled on a water bath to remove the solvent and the residue, which showed a strong tendency to crystallize, was distilled under reduced pressure. Twenty three and four-tenths grams of a clear yellow oil was obtained having a boiling point of 154-155° under 7 mm. pressure. The oil readily solidified to white crystals melting at 54° and after

(105) Kamm, Organic Qualitative Analysis, John Wiley and Sons, New York, 1923, p. 165.

two recrystallizations from 80% alcohol melted at 55-56°.
These were shown by a mixed melting point to be identical with
the crystals obtained from the water layer. The total yield
was 31.4g. of crystalline solid identified, as shown below,
as phenyl benzyl ketone. The yield corresponds to 53.4% of
the theoretical amount. A mixed melting point with a sample
of phenyl benzyl ketone prepared as described below and melting
at 54-55° was found to be 56°. The oxime was found to melt at
94-95°. Anschütz and Berns (106) give the boiling point of
phenyl benzyl ketone as 177.4-177.6° under 12 minutes pressure.
V. Meyer and Oelkers (107) found the melting point of the
ketone to be 60° and its oxime to melt at 98°.

Several attempts to prepare a sample of phenyl benzyl
ketone for a mixed melting point by oxidizing phenyl benzyl
combined with nitric acid according to the method of Limpricht
and Schwanert (108) failed. The following method proved con-
venient. Ten grams of phenyl benzyl carbinol was oxidized by
stirring for one hour at 50-60° with a solution containing
4.5g. of sodium dichromate and 6 cc. of concentrated sulfuric
acid in 100 cc. of water. The solution was then cooled, ex-
tracted with ether, and the ether dried over calcium chloride.
The ether was then evaporated leaving heavy crystalline plates
melting at 53-55°. On recrystallization from 80% alcohol the
melting point was raised to 54-55°.

(106) Anschütz and Berns, Ber., 20, 1392(1887).
(107) V. Meyer and Oelkers, ibid., 21, 1298(1888)
(108) Limpricht and Schwanert, Ann., 155, 64(1870).

A small residue remained in the distilling flask from which the phenyl benzyl ketone was distilled. On exhaustive oxidation with permanganate following the general procedure described above only benzoic acid was obtained.

5. Benzylmagnesium chloride and chloracetophenone.

Seven-tenths mole of benzylmagnesium chloride was added over a period of one hour to 15.4g. (0.1 mole) of chloracetophenone at a temperature of -18°. The reaction mixture was worked up in the customary manner and the heavy yellow oil obtained oxidized in the customary manner. The only product obtained was benzoic acid.

6. Benzylmagnesium chloride and Benzoyl chloride.

(a) A solution of 0.6 mole of benzylmagnesium chloride was slowly added to an ether solution of 35g. (0.25 mole) of benzoyl chloride. The reaction mixture was kept cool by means of an ice-salt mixture. A heavy white precipitate formed. After addition was completed stirring was continued for two hours. Since the mass was almost solid, hydrolysis was carried out by adding all at once a large amount of cracked ice. The mixture was then acidified to dissolve the basic magnesium halide, the ether layer removed, and the water layer twice extracted with ether. The combined ether layers were steam distilled leaving a heavy yellow paste. After cooling, the residual water was decanted from the paste. Four hundred cubic centimeters of hot alcohol was then added. On cooling an oil

separated out. When this was redissolved in alcohol, 1.5g of a white solid melting at about 240° separated out. This solid was not identified.

Oxidation of the tars obtained by concentrating the alcohol mother liquors from the 240° compound yielded no definite products.

(b) A repeat run of the foregoing was carried out using one-half quantities. A portion of the tar remaining after the steam distillation was oxidized strongly with permanganate. The material did not appear to undergo oxidation readily and only a small amount of permanganate was decolorized. As usual, the excess permanganate was destroyed with alcohol and the sludge of manganese dioxide filtered off. There seemed to be crystal-line organic matter mixed with the manganese dioxide so the mass was washed with ether several times. On evaporation of the ether a yellow oil remained which was taken up in 80% alcohol and set aside to crystallize. No definite compound has yet been obtained.

The filtrate from the manganese dioxide was acidified but no solid acid precipitated. Extraction with ether yielded 3.3g. of benzoic acid.

7. Benzylmagnesium and diphenylcarbamine chloride.

A solution of 0.11 mole of benzylmagnesium chloride was slowly added to 23.1g. (0.1 mole) of diphenylcarbamine chloride in ether. A slight heat of reaction was noticed. After addition was completed the reaction mixture was stirred for two

hours. Hydrolysis was then carried out by means of iced hydrochloric acid. The ether layer was removed and steam distilled to remove diphenyl and steam volatile by-products. The residual oil was refluxed two hours with 10% alcoholic potassium hydroxide to hydrolyze the acid amides. On working up the mixture the only acid obtained was phenylacetic acid, melting at 73°. Recrystallization from hot water raised the melting point to 76°. No toluic acids could be isolated.

8. Benzylmagnesium chloride and acetyl chloride.

a. A solution of 0.5 mole of benzylmagnesium chloride was added with vigorous stirring to a solution of 15.7g. (0.2 mole) of acetyl chloride dissolved in ether. The reaction was carried out at the temperature of an ice-salt mixture. A heavy yellow precipitate formed. After hydrolyzing with dilute hydrochloric acid the mixture was steam distilled to remove volatile materials and a portion of the residual yellowish tar submitted to oxidation with permanganate. The only product obtained was benzoic acid.

b. A repeat run was made using 0.5 mole of benzylmagnesium chloride and 19.6 (0.25 mole) of acetyl chloride. A portion of the tar obtained gave an oxidation mostly benzoic acid, but a trace of phthalic acid, identified by the characteristic fluorescein test, was also found.

9. Benzylmagnesium chloride and ethylene oxide.

A solution of 0.5 mole of benzylmagnesium chloride was prepared from 63g. of genzylchloride and 12.2g. of magnesium turn-

ings. The ethylene oxide used was contained in a sealed bottle and was cooled in an ice-salt mixture. The tip of the bottle was then broken off and the bottle connected by means of a short piece of pressure tubing with a glass tube leading into the reaction flask. By warming to 14-15° in a pan of water ethylene oxide was distilled into the mixture until a color test showed the absence of unused Grignard reagent. A very heavy mass formed which made stirring difficult. A little toluene was added and the mass broken up with a stirring rod. Ether was distilled out of the flask and toluene added until the boiling point of the solvent was 65°. The mixture was then stirred and refluxed for one hour. After hydrolyzing in the usual manner with ice and hydrochloric acid, the reaction mixture was steam distilled without separating the ether and water layers. After the ether and toluene came over an oil slowly steam-distilled. The total distillate was saturated with salt, extracted with ether, and dried over sodium sulfate. The ether was then distilled off and the residue vacuum distilled. Thirty two and five-tenths grams (47.8%) of colorless oil having a fragrant odor was obtained, boiling at 113-115° under 10 mm. pressure. A very slight residue remained in the distilling flask. A residue also remained which was non-volatile in the steam distillation. This was a dark brown sticky tar. This residue was oxidized with permanganate and yielded a small amount of terephthalic acid.

An oxidation of 4g. of the oil obtained as the major reaction product gave 1.0g. of benzoic acid and nearly 1g. of terephthalic

acid. No indication of phthalic acid was found. The oil liberates a gas when treated with metallic sodium. It appeared to be a mixture of γ-phenylpropanol and one or more of its isomers.

An attempt was made to separate the oil into its constituents, assuming it to be a mixture of γ-phenylpropanol and β-p-tolyl ethanol. A small amount of the oil was treated with a few drops of phenylisocyanate in benzene solution and gently warmed. The mixture was then set aside to crystallize slowly. An oil separated which was taken up in alcohol and set aside in the hope of attaining slow fractional crystallization of one of the urethanes. After standing perhaps six months a semi-crystalline solid of very indefinite melting point had separated. Further attempts have proven equally fruitless.

10. Benzylmagnesium chloride and ethyl chloromethyl ether.

a. The ethyl chloromethyl ether employed was prepared from trioxymethylene and ethyl alcohol by passing in dry hydrogen chloride according to the method of Wedekind (108). Twenty two and five tenths grams (0.24 mole) of the chloro-ether was dissolved in 125 cc. of anhydrous ethyl ether in a 3-neck flask and cooled in an ice-salt mixture. A solution of 0.4 mole (excess) of benzylmagnesium chloride was then slowly added. When addition was completed a faint positive RMgX color test was obtained but after stirring a few minutes a negative test was obtained. Since an excess of Grignard solution was used it was surprising that it was all used. However, the ethyl chloro-

(108) Wedekind, Ber. 36, 1383(1903). This method has also been used by Ranedo, Anales soc. espan. fis. quim, XVI, 151,351(1918)

methyl ether seemed to contain some free hydrogen chloride and
this may have destroyed a part of the benzylmagnesium chloride.
After hydrolyzing with iced hydrochloric acid the ether layer
was removed, the water layer once extracted with ether, and the
combined ether layers dried over calcium chloride. The ether
was then distilled off and the remaining oil distilled under
reduced pressure. Twenty four grams (67%) of a colorless oil
boiling at 87-88° under 6 mm. pressure was obtained.

Five grams of the oil was oxidized with alkaline perman-
ganate in the customary manner. The acids obtained were benzoic
acid, 1.5g; -phthalic acid, 0.6g; and terephthalic acid, 1.2g.
Calculations based on these yields of acids account for only
3.46g. of the 5g. of oil used. Assuming the mixture to consist
of the following ethers, the amounts necessary to give the above
acids are (a) ethyl β-phenylethyl ether, 1.84g; (b) ethyl-o-
tolylmethyl ether, 0.54g; (c) ethyl p-tolylmethyl ether, 1.08g.
Making the assumption that equal amounts of each isomer are lost
during the oxidation the mixture of isomers is roughly of the
following percentage composition; normal, 53%, ortho, 16%;
para, 31%.

b. The ethyl chloromethyl ether used in this and subsequent
runs was prepared in the same manner as previously but was twice
distilled under slightly reducedpressure. It was found to boil
at 50-54° under a pressure of 230 mm. The run was carried out
as before except that one-sixth mole of benzylmagnesium chloride
and 15.8g. (1/6 mole) of chloromethyl ethyl ether were used.

There was obtained 9.9g. (39.6%) of colorless oil boiling at 77-79° under 6 mm. pressure.

Two and sixty four grams of the oil was oxidized with alkaline permanganate and yielded a total of 0.531 g. of benzoic acid, and 0.238 g. of terephthalic acid and no -phthalic acid.

c. A third run employed 0.3 mole quantities and yielded 21.9g. (50%) of oil boiling at 93-97° under 7 mm. pressure and an indefinite oil collected over a range of 170-220° under 7 mm. pressure. In this run the ethyl chloromethyl ether was added to the cooled Grignard solution in the usual manner. An RMgX color test in this run showed the presence of unused Grignard reagent and it was concluded that fractionation under reduced pressure gave more nearly pure ethyl chloromethyl ether than is obtained by distillation under atmospheric pressure. Refractive index of low boiling oil, $N_D^T = 1.4949$.

A 5.01 g. sample of the low boiling oil was oxidized with alkaline permanganate and gave 1.133g. of benzoic acid, 0.655g. of terephthalic, and 0.092g. of phthalic acid.

The high boiling oil was redistilled and a middle fraction of 1.9g. taken between 165-180° under 6 mm. pressure. Most of this came over around 175°. Oxidation of this oil with alkaline permanganate gave about 0.2g. of benzoic acid, 0.1g. of phthalic acid, and 0.2g. of terephthalic acid. The oil was not identified.

Zeisel Analyses of low boiling oil.

(1) 0.2201g. sample gave 0.1630g. Ag I.
    C_2H_5O = 14.21%.

(2) 0.2179g. sample gave 0.1670g. Ag I.
C_2H_5O = 14.70%.

(3) 0.2291g. sample gave 0.1764g. Ag I.
C_2H_5O = 14.77%.

(4) 0.1871g. sample gave 0.1668g. Ag I.
C_2H_5O = 17.10%.

(5) 0.2125g. sample gave 0.2013g. Ag I.
C_2H_5O = 18.17%.

(6) 0.1933g. sample decomposed with 15 cc. hydriodic acid
and 15 cc. acetic anhydride and ethyl iodide absorbed
in pyridine. Estimated by Volhard titration. Required
36.35 cc. 0.1003 N $AgNO_3$, and 21.6 cc. of 0.1170 N
KCNS. C_2H_5O = 23.70%.
Calc. for $C_{10}H_{14}O$, $-OC_2H_5$ = 30.0%.

Zerewitinoff analyses.

A sample weighing 0.1928g. gave with methylmagnesium iodide

in butyl ether no visual evidence of evolution of gas. After

heating 15 minutes at 60-70° about 0.5 cc. was obtained. A

second run gave about 3 cc. of gas but this was probably ex-

perimental error since a third run gave only about 0.5-1.0 cc.

of gas.

(d) In this run the same quantities were used as in the

one just preceding but addition was carried out in the "inverse"

manner as in (a) and (b). At the completion of the addition

of the Grignard solution an RMgX color test showed presence of

unused benzylmagnesium chloride. When worked up in the usual

manner 28g. (62.2%) of oil boiling at 93-97° under 7 mm. press-

ure and a yellowish oil weighing 5.4g. and collected at a

temperature of 130-220° under 7 mm. pressure. Refractive index

of low boiling oil, N_D^T = 1.4964.

When 10.68g. of the low boiling oil was oxidized in the

usual manner with alkaline permanganate, the acids obtained were benzoic acid, 3.934g.; o-phthalic acid, 0.465g.; and terephthalic acid, 1.750g.

Zeisel Analyses on low boiling oil.

(1) 0.2116g. sample gave 0.1591g. Ag. I.
C_2H_5O = 14.42%.

(2) 0.2198g. sample gave 0.1783g. Ag. I.
C_2H_5O = 15.84%.

(3) 0.4661g. sample gave 0.3295g. Ag. I.
C_2H_5O = 13.57%.

(4) 0.2900g. sample gave 0.2543g. Ag. I.
C_2H_5O = 16.82%.

(5) 0.3527g. sample gave 0.4680g. Ag. I.
C_2H_5O = 25.52%.

Calc. for $C_{10}H_{14}O$; $-OC_2H_5$ = 30.0%.

Zerewitinoff analyses.

(a) 0.1827g. sample gave 0.5 cc. of gas at 28° and 732 mm. After heating 15 minutes at 60-70°, 1.0 cc. at 28° and 732 mm.

(b) 0.2206g. sample gave 0.2-0.3cc. of gas at 28° and 732 mm. After 15 minutes heating at 60-70°, 0.5 cc. gas at 28° and 732 mm.

11. Attempts to prepare ethyl β-phenylethyl ether.

(a) About 8g. (0.35 mole) of metallic sodium in the form of thin slices was dissolved in 125 cc. of absolute alcohol under a reflux condenser and then 37g. (0.2 mole) of β-bromo-ethyl benzene added in small quantities through the condenser. A white precipitate, probably sodium bromide, immediately began to form. After addition was completed the mixture was gently

refluxed for thirty minutes and then cooled and diluted with water. The colloidal oil was extracted from the water by means of ether. Three extractions were made. The combined ether extractions were washed with a little cold water and then dried over night over calcium chloride. The ether was then decanted from the calcium chloride and distilled. When the ether was removed the remaining oil was fractionated under reduced pressure. The distilled oil had a distinct odor of styrene and readily decolorized a solution of bromine in carbon tetrachloride. Repeated distillation appeared to free the oil from much tarry material, probably polymerized styrene. The third distillation gave 6.5g. of oil boiling at 43° under 7 mm. pressure. This oil slowly decolorized bromine solution and gave no Beilstein test. The boiling point is higher than that of styrene which boils at 45° under 17 mm. pressure and at 33° under 10 mm. pressure. However, the compound is not the desired ether because when heated with hydriodic acid in the Zeisel apparatus no silver iodide was obtained even after one and one-half hours heating at 170°.

(b) Six and one-tenth grams (0.05 mole) of phenylethyl alcohol was refluxed in dry benzene for about three hours with 1.5g. (0.065 mole) of metallic sodium in the form of thin slices. The benzene and solid sodium phenylethlate were then transferred to a Carius tube, a little benzene being used to wash the solid material away from the unused sodium. Fifteen and six-tenths grams (0.1 mole) of ethyl iodide was then added, the tube sealed, and heated for five hours at 90°. The tube

was then opened and the contents washed out with water and ether.
The ether layer was removed, dried over calcium chloride, and
after distilling off the ether, benzene, and excess ethyl
iodide, the residual oil was distilled under reduced pressure.
The second distillation of the oil yielded 2.4g. of sweet
smelling oil boiling at 93° under 7 mm. pressure. The density
$D \frac{25°}{25°}$, was 0.9449, and the refractive index N_D^T, 1.4995. The
molecular refraction, mr, calculated by the Gladstone-Dale
formula is 79.29 and from the sum of the atomic refractions,
78.2. Using the Lorentz-Lorenz formula, mr, found 46.65; calc.,
46.43.

<div align="center">Zeisel Analyses.</div>

(1) 0.2256g. sample gave 0.1884g. Ag I.
C_2H_5O = 16.02%.

(2) 0.1997g. sample gave 0.1541g. Ag I.
C_2H_5O = 14.81%.

(3) 0.1978g. sample gave 0.1740g. Ag I.
C_2H_5O = 16.88%.

Calc. for $C_{10}H_{14}O$; OC_2H_5 = 30.0%.

(c) A solution of 25g. (0.163 mole) of β-bromoethyl ethyl ether
in ethyl ether was cooled in an ice-salt mixture. A solution of
0.17 mole of phenylmagnesium bromide was then slowly added. An
RMgX color test made after about one-fourth of the Grignard
solution had been added was negative but subsequent tests were
all positive. The first few drops of the phenylmagnesium brom-
ide caused a white solid to precipitate. This precipitate soon
dissolved and there was no other evidence of reaction. After
addition was completed the reaction mixture was stirred for

two hours at room temperature. The reaction mixture was worked up in the customary manner and yielded 17.5g. of oil boiling at 60° under 15 mm. pressure, and at 115-129° under atmospheric pressure. The oil gave a strong Beilstein test and was probably unchanged β-bromoethyl ethyl ether. This latter compound boils at 126-129°.

(d) This was a repeat run of the above but the reaction mixture was refluxed for nine hours. On working up no definite product whatsoever was obtained. Distillation yielded an oil boiling from 50-240° under atmospheric pressure.

(e) To 12.2g. (0.1 mole) of phenylethyl alcohol dissolved in 100 cc. of dry benzene was added 2.5g. (0.109 mole) of metallic sodium in the form of thin slices. After five hours of refluxing 30g. (0.2 mole) of ethyl iodide was added. Refluxing was then continued for about four hours. The reaction mixture was then cooled, poured into water, a little hydrochloric acid added, and the benzene layer then removed and dried over calcium chloride. The benzene was then distilled off and the remaining oil distilled under reduced pressure. Seven and one-tenth grams of fragrant oil boiling at 97-102° under 7 mm. was obtained. This corresponds to a yield of 47.3% of the theoretical amount. The oil was redistilled giving 4.1g. boiling at 98-100° under 8 mm. pressure. The density of this oil was 0.9545 $\frac{25°}{25°}$. The refractive index $N_D^{25°}$ was found to be 1.5080, and m_r calculated by the Gladstone-Dale formula 79.8 while the value computed from the atomic refractions is 78.2. Using the Lorentz-Lorenz

formula the value found from the data was 46.83 and the calculated value 46.43.

Analyses.

0.2182g. sample gave 0.1690g. H_2O and 0.6313g. CO_2; 0.2473g. sample gave 0.1960g. H_2O and 0.7155g. CO_2; 0.2403g. sample gave 0.1904g. H_2O and 0.6957g. CO_2. Found, %C, 78.93; 78.93; 78.98; %H, 8.67; 8.87; 8.87. Calc. for $C_{10}H_{14}O$, C, 79.95; H, 9.40.

Zerewitinoff Runs. Blank runs on benzoic acid.

(a) 0.2023g. sample gave 46.9 cc. methane at 28° and 733.4 mm. pressure after heating 15 minutes at 70°. Active hydrogens = 1.106.

(b) 0.1991g. sample gave 47.6 cc. methane at 29° and 736 mm. pressure after heating 15 minutes at 70°. Active hydrogens + 1.140.

(c) 0.2012g. sample gave 42.0 cc. of methane at 26° and 736 mm. pressure, no heating being used. Active hydrogens = 1.006. After heating 15 minutes at 70° the volume of methane was 45.8 cc. at 26° and 736 mm., corresponding to 1.096 active hydrogens.

(d) 0.2008g. sample gave 43.4cc. of gas at 26° and 736 mm. pressure before heating, corresponding to 1.04 active hydrogens. After heating at 70° for 15 minutes the volume of gas was 47.1 cc. at 26° and 736 mm., corresponding to 1.130 active hydrogens.

Titration to check purity of benzoic acid used.

(a) 0.2012g. sample required 16.45 cc., 0.1000 N KOH.
M = 122.32.

(b) 0.2012g. sample required 16.55 cc., 0.1000 N KOH.
M = 121.55.

(c) 0.2013g. sample required 18.65 cc., 0.0886 N KOH.
M = 121.8.

(d) 0.2021g. sample required 18.80 cc., 0.0886 N KOH.
M = 121.4.

Average M = 121.8.   Calc. for $C_7H_6O_2$ = 122.08.

Zerewitinoff analysis of oil from run (c).

A 0.1846g. sample gave 12.9 cc. of methane at 28°C. and
738 mm. pressure, corresponding to 0.0005072 mole of active
hydrogen.   After heating for 10 minutes at 70° the gas volume
increased to 13.5 cc. measured at 28° and 738 mm., and cor-
responding to 0.0005308 mole of active hydrogen.   If we assume
all of the methane to come from phenyl-ethyl alcohol contained
in the ethyl β-phenyl-ethyl ether as impurity, then the amount
of alcohol present is 0.0619-0.0647g., or about 35%.   The
theoretical analysis of a mixture of 35% β-phenylethyl alcohol,
and 65% ethyl β-phenylethyl ether is C, 79.37%, H, 9.00%.
The analyses given above, C, 79.93, and H, 8.87%, correspond
quite well to these theoretical figures.

(f) Eight grams (0.35 mole) of metallic sodium in thin
slices was added to a solution of 36.6g. (0.3 mole) of phenyl-
ethyl alcohol in dry benzene.   The mixture was stirred mechan-
ically and refluxed for about seventeen hours to insure as
nearly complete conversion of the alcohol to alcoholate as
possible.   Fifty-five grams (0.36 mole) of ethyl sulfate was
then added through the dropping funnel.   A pasty mass separated.
The mixture was stirred and refluxed for eight hours.   The mass
was then removed from the stirring flask and the small pieces

of unused sodium removed. Strong ammonium hydroxide was then added and the mixture warmed to hydrolize the excess of ethyl sulfate. The whole mixture was then steam distilled. The oil collected was washed three times with water, then with 50% calcium chloride solution, and then dried over anhydrous calcium chloride. The benzene was then distilled off and the residual oil vacuum distilled. The yield of oil boiling at 77-82° under 7 mm. pressure was 25.8g., corresponding to a yield of 57.3% of the theoretical amount. On redistillation using a carefully calibrated thermometer the boiling point was found to be 85-87° under 7 mm. pressure. The specific gravity, $D_{25°}^{25°}$, was found to be 0.9200; and the refractive index $N_D^{25°}$, 1.4708 (average of two determinations); mr calculated from data by Gladstone-Dale formula, 76.76; sum of atomic refractions, 78.2; mr calculated from data by Lorentz-Lorenz formula, 45.55; sum of atomic refractions, 46.43.

Zerewitinoff analysis.

In one determination using a sample of 0.1846g. no gas was obtained even after 15 minutes warming at 60-70°. A second run using a sample of 0.2259g. gave about 0.5 cc. of gas after warming to 60-70°, for 15 minutes.

Zeisel analyses.

(a) 0.2270g. sample gave 0.3001g. Ag I.
C_2H_5O = 25.44%.

(b) 0.1968g. sample decomposed with 15 cc. hydriodic acid and 10 cc. glacial acetic acid at 150° gave 0.2861g. Ag I. C_2H_5O = 27.89%.

(c) 0.1968g. sample decomposed as in (b) gave 0.2683g. Ag I. C_2H_5O = 27.16%.

(d) 0.1864 g. sample decomposed with hydriodic acid in the usual manner and ethyl iodide absorbed in pyridine and estimated by Volhard titration. 35.50 cc., 0.1013 N AgNO$_3$; 23.65 cc., 0.1170 N KCNS. C$_2$H$_5$O = 20.35%.

(e) 0.1974g. sample decomposed with 15 cc. hydriodic acid and 15 cc. acetic anhydride. 35.98 cc., 0.1013 N AgNO$_3$; 19.82 cc., 0.1170 N KCNS. C$_2$H$_5$O = 30.23%.

(f) 0.1961 g. sample decomposed as in (e). 35.80 cc., 0.1013 N AgNO$_3$; 20.53 cc. 0.1170 N KCNS. C$_2$H$_5$O = 28.10%.

(g) 0.2006g. sample decomposed as in (e). 35.52 cc., 0.1013 N AgNO$_3$; 19.85 cc., 0.1170 N KCNS. C$_2$H$_5$O = 28.61%.

(h) 0.1900g. sample decomposed with 15 cc. hydriodic acid and 15 cc. acetic anhydride at 160° for 1-1/2 hours. 35.35 cc., 0.1013 N AgNO$_3$; 20.26 cc., 0.1170 N KCNS. C$_2$H$_5$O = 27.82%.

(i) 0.1962g. sample decomposed with 15 cc. hydriodic acid and 15 cc. acetic anhydride at 160°. Absorbed ethyl iodide in pyridine at 70-80°. 36.50 cc., 0.1003 N AgNO$_3$; 21.46 cc. 0.1170 N KCNS. C$_2$H$_5$O = 26.35%.

Calc. for C$_{10}$H$_{14}$O; OC$_2$H$_5$ = 30.0%.

12. Zeisel analysis of ethyl benzyl ether.

A sample of ethyl benzyl ether obtained from the Eastman Kodak Company was purified by allowing it to stand for a week over metallic sodium at room temperature. The liquid was then suction filtered from the mass of sticky material that separated, and vacuum distilled discarding the first and last fractions. The fraction boiling at 67-69° under 7 mm. pressure was used for the control analysis. However, the ether was shown to be still impure by means of a Zerewitinoff analysis. The results of both the Zeisel and Zerewitinoff analyses follow.

Zeisel analyses.

(1) 0.1985g. sample gave 0.2510g. Ag I. C$_2$H$_5$O = 24.26%.

(2) 0.1939g. sample gave 0.1964g. Ag I. $C_2H_5O = 19.44\%$.
Calc. for $C_9H_{12}O$, $C_2H_5O = 33.09\%$.

Zerewitinoff analyses.

(1) 0.2249g. sample gave 7.0 cc. of gas at 30° and 738.5
mm; and after heating 15 minutes at 70° gave 8.6 cc.
of gas at 30° and 738.5 mm. Corresponds to 0.203 of
an active hydrogen

(2) 0.1927g. sample gave 4.9 cc. of gas at 31° and 728
mm.; and after heating 5.6 cc. of gas at 31° and 728
mm. Corresponds to 0.148 of an active hydrogen.

13. Benzylmagnesium chloride and excess ethyl chlorocarbonate.

(a) A solution of 0.25 mole of benzylmagnesium chloride was
prepared in the usual manner from 32g. of benzyl chloride and
6.1g. of magnesium turnings. The Grignard solution was quickly
filtered through glass wool into a separatory funnel. A so-
lution of 126g. (1.0 mole) of ethyl chlorocarbonate in twice
its volume of anhydrous ether was placed in a one liter 3-neck
flask and cooled in an ice-salt mixture. The Grignard solution
was then slowly added to the solution in the flask. The addition
required about forty-five minutes, vigorous stirring being
maintained during the addition. After hydrolyzing with iced
hydrochloric acid the whole mixture was steam-distilled. The
distillate was extracted with ether, the ether extracts dried
over sodium sulfate and the ether then distilled off. The re-
maining oil was refluxed three hours with 10% alcoholic potas-
sium hydroxide. The solution was then cooled, extracted with
ether to remove unhydrolyzed oils, and then acidified with
hydrochloric acid. The total volume was then about 800 cc.

The solution was milky but contained no crystals. After about two hours a few flaky crystals separated and were filtered off. These weighed 1.0g. (2.9%) and melted at 103-105°. A mixed melting point with o-toluic acid was found to be 103°. The remaining water solution was twice extracted with ether, the ether extracts washed with a little cold water and in turn extracted with 100 cc. of 10% potassium hydroxide. On acidification with hydrochloric acid and cooling, 4.7g. of slightly impre phenylacetic acid was obtained in the form of shining leaflets melting at 68°. A mixed melting point with phenyl-acetic acid was 71°.

This fractional separation of o-toluic and phenylacetic acids was of course not quantitive. Approximately 20% of orthc rearrangement appears to have occurred.

(b) This experiment was carried out in the hope of showing the presence of ethyl p-toluate in the reaction products along with ethyl phenyl-acetate and ethyl o-toluate. Two-tenths mole of benzylmagnesium chloride solution was slowly added to a well-stirred solution of 40g. (0.37 mole) of ethyl chloro-carbonate in 200 cc. of ether. The temperature was kept in the neighborhood of -13-15° by means of an ice-salt mixture. The addition required about one hour. A test showed the absence of unused Grignard reagent. After hydrolyzing with ice and dilute hydrochloric acid the mixture was steam-distilled until nothing more came over. The residual tar was exhaustively oxidized in the customary manner. A trace of o-phthalic acid

was found and a cloudiness indicative of terephthalic acid.

The oil and ether from the steam distillation were separated from the water and dried over sodium sulfate. The ether was distilled off and the temperature raised to 110° to remove unused ethyl chlorocarbonate. The residue yielded on vacuum distillation 9.5g. of liquid esters boiling at 98° under 6 mm. pressure. This amount corresponds to a yield of 29% of mixed, isomeric ester. The total amount of oil was hydrolyzed by refluxing for six hours with 10% alcoholic KOH. Acidification yielded an oily precipitate and attempts to crystallize from water were fruitless. The oil was recovered from the water by ether extraction, and then taken up in 95% alcohol and set aside to crystallize slowly. After about three months a crop of heavy, blunt needles, many over one-half inch long, had formed. These needles were removed from the oil and dried on filter paper. Yield, 1.1g.; m.p. = 100-101°. A mixed melting point showed them to be o-toluic acid. The residual oil weighed 4.0g. The yield of otoluic acid was 4% based on Grignard reagent used; 14% based on the total ester obtained; and 21.5% of the total acid derived by hydrolysis of the ester.

14. Benzylmagnesium chloride and ethyl formate.

A solution of 0.3 mole of benzylmagnesium chloride was added to 22.2g. (0.3 mole) of ethyl formate at a temperature of -18° over a period of 45 minutes. After hydrolyzing with iced hydrochloric acid the ether layer was removed and shaken with three portions of saturated sodium bisulfite solution. A heavy

precipitate formed but as no aldehyde could be isolated it was concluded that this solid was probably precipitated NaHSO$_3$. The ether layer was distilled to remove the ether and the residual oil oxidized with excess alkaline permanganate. There was an indication of terephthalic acid, a cloudiness in the acidified solution, but insufficient to isolate. Nine grams of benzoic acid and 0.75g. of phthalic acid were obtained.

15. Benzylmagnesium chloride and p-anisaldehyde.

(a) An ether solution of 30g. (0.25 mole) of p-anisaldehyde was very slowly added to a well stirred solution of 0.25 mole of benzylmagnesium chloride. The reaction mixture was kept cool by means of an ice-salt mixture. A heavy oily liquid separated from the mixture as an insoluble layer. After hydrolyzing with ice and dilute hydrochloric acid, the ether layer was separated and steam distilled until nothing more came over. A heavy yellow oil remained in the distilling flask. After cooling under the tap the water was decanted from this oil. When cool, alcohol was added to the oil and it was partially dissolved. The remaining white solid was filtered off and weighed 6.2g. when dried. It melted at 98-99°. The melting point was raised to 123-125° by recrystallizing twice from alcohol. A third recrystallization failed to raise the melting point.

The alcohol washings from the 123-125° solid were allowed to evaporate in air, leaving a semi-solid paste. This waste was washed four times with petroleum ether and by rubbing with a stirring rod was induced to solidify completely. The solid melted at

51-54° and when once recrystallized from warm petroleum ether
was obtained in beautiful clusters of long, slender needles.
A total of 24.7g. (43.3%) of fairly pure material was obtained.
This was identified as benzyl-p-anisyl carbinol by oxidizing to
the corresponding ketone, whose identity was proven by means
of a mixed melting point with an authentic sample prepared by
the method of E. Ney (109).

Oxidation. To a solution of 4.5g. of sodium dichromate and
6 cc. of concentrated sulfuric acid in 100 cc. of water was
added 10g. of the carbinol melting at 57°. The mixture was
stirred one and one-half hours in a water bath kept at room
temperature. The brownish solid was then filtered off, washed
with water, and then with 10 cc. of cold 95% alcohol. It
melted at 71-74°. It was then once recrystallized from 80%
alcohol and was obtained in the form of shining leaflets melt-
ing sharply at 76°. Benzyl p-anisyl ketone prepared by the
Friedel-Craft reaction from phenylacetyl chloride and anisole
as described by Vey (109) also melted at 76° and a mixed
melting point showed no depression.

(b) In this run the Grignard solution was added to the
p-anisaldehyde, the reverse of the procedure employed in the
preceding experiment. An ether solution of 54.4g. (0.4 mole)
of the aldehyde was placed in a 500 cc. 3-neck flask and then
cooled in an ice-salt mixture. A solution of 0.2 mole of

(109) Ney. Ber., 21:2450(1888).

benzylmagnesium chloride was then added through the separatory
funnel over a period of one and one-half hours. The reaction
mixture was very sticky. After hydrolyzing with ice and hydro-
chloric acid the ether layer was removed and steam distilled
as long as any oily drops came over. The pasty residue was
shaken with alcohol and was largely dissolved. The alcohol
was decanted and on standing 2.4g. of white solid separated.
This material melted at 122-130° and a mixed melting point with
the 123-125° solid from the preceding experiment was depressed
to the neighborhood of 100-110°.

The residue from the alcohol washings was recrystallized
from hot alcohol giving a small amount of white needles melting
at 144-145°.

The alcohol washings from which the 122-130° compound
separated were diluted with water and extracted twice with ether.
The ether extracts were dried over sodium sulfate, the ether
distilled off, and the residual oil vacuum distilled. A small
amount of anisaldehyde first came over and then between 160-270°
under a pressure of 10 mm. an oil came over which solidified in
the receiver. This distillate was washed several times with
petroleum ether and the undissolved solid weighed 8.7g. It
melted at 115-125° and after one recrystallization from alcohol
melted at 134°. Although there is a considerable discrepancy
in the melting points, this compound appeared to be the same as
the 123-125° compound from the preceding experiment for a mixed
melting point was 129°.

The petroleum ether washings from the 134° compound were

allowed to evaporate in an attempt to find benzyl p-anisyl carbinol. The only material obtained was a small additional amount of the 134° compound.

16. p -Dimethylamino benzaldehyde and benzylmagnesium chloride.

A solution of 0.3 mole of benzylmagnesium chloride was slowly added at room temperature to an ether solution of 15g. (0.1 mole) of p-dimethylamino benzaldehyde. At first a heavy ball of paste formed but this gradually broke up and stirring became easier. Stirring was continued for one hour after addition of the Grignard reagent was completed. Hydrolysis was carried out with ice and dilute hydrochlotic acid. The water layer was removed and washed once with a little ether. The water layer was then made alkaline and a mixture of crystalline material and magnesium hydroxide separated. This mass was filtered off with suction, partially dried and then extracted with ether to remove the organic material from the magnesium hydroxide. The ether was then evaporated leaving a crystalline mass which was washed with petroleum ether until almost white. On recrystallization from warm petroleum ether the compound was obtained in the form of small needles melting at 58-59°. A further small amount was obtained by concentrating the petroleum ether mother liquors. The total yield was 17.8g. (73.8%). The substance corresponds in properties with the compound described by Sachs and Sachs (65) as p-dimethylamino-phenyl benzyl carbinol and obtained by them in the same manner. No derivatives of that carbinol have been described. For a further discussion of the compound, see page 48.

17. Benzylmagnesium chloride and oxygen.

Dry oxygen was led into a solution of 0.5 mole of benzyl-magnesium chloride until a negative RMgX color test was obtained. On working up in the customary manner 16.6g. (30%) of benzyl alcohol boiling from 190-210° was obtained. The alcohol was identified by the preparation of the phenylurethane (110) melting at 74-76°. Oxidation of residual tars yielded only benzoic acid.

18. Benzylmagnesium chloride and benzyl chloride.

To a solution of 0.2 mole of benzylmagnesium chloride in ether was slowly added 25g. (0.2 mole) of benzyl chloride dissolved in ether. A white solid slowly separated. After three hours stirring at room temperature a positive RMgX color test was obtained, but after refluxing for two and one-half hours a color test showed absence of any unusual Grignard reagent. After hydrolyzing in the usual manner the ether layer was removed, combined with two ether extractions of the water layer, and dried over sodium sulfate. The ether was then removed by distillation and the remaining oil fractionated under atmospheric pressure. A small fraction was collected at 160-185° and was concluded to be unused benzyl chloride by its odor, and a Beilstein halogen test. The temperature then rose rapidly and a large fraction was obtained at 260-285°. This oil solidified on cooling the crystals melting at 48° and identified as

(110) Soden and Rojahn, Ber., 2809(1906).

dibenzyl by a mixed melting point. A small high boiling fraction was collected at 285-360°. This fraction was a brownish oil and partially solidified on cooling. The crystals were freed from the oil and were identifiedas dibenzyl by a mixed melting point. Total yield of dibenzyl, 23.6g., or 64.8% of the theoretical amount. It was thought that the oily material might be p-benzyl dibenzyl and so one gram was oxidized according to the method of Fuson (29) but no p-benzoylbenzoic acid could be isolated. Exhaustive oxidation of the oils yielded only benzoic acid.

19. Cyclohexylmethylmagnesium bromide and formaldehyde.

Cyclohexylmethyl bromide was prepared according to the method of Hiers and Adams (111). From 68g. (0.6 mole) of cyclohexyl carbinol and 65g. (20% excess over 0.2 mole) of phosphorus tribromide there was obtained 52g. (49%) of cyclohexylmethyl bromide boiling at 66-68° (3 mm.). A solution of 0.25 mole of cyclohexylmethylmagnesium bromide was prepared from 44g. of cyclohexylmethyl bromide and 6.08g. of magnesium. The Grignard reagent started easily with the aid of a crystal of iodine as catalyst. This Grignard solution was unique in that it was entirely free from any color or cloudiness whatsoever. Gaseous formaldehyde was then led in until a negative color test was obtained. The addition required about forty-five minutes. The reaction mixture was hydrolyzed with the aid of iced hydrochloric acid and steam distilled until no more came over. The total ether

(111) Hiers with Adams, J. Am. Chem. Soc., 48, 2385(1926).

and oil were dried over Na_2SO_4, the ether distilled off, and the residue vacuum distilled. Fourteen and seven-tenths grams of oil was collected at 75-82° (3 mm.), practically all distilling at 77-78°. Yield, 45.9% of the theoretical amount. B.p. = 198-202° (742 mm.); $N_D^{26°} = 1.4648$. The oil was identified as β-cyclohexyl ethanol (112) by its behavior on oxidation. Three grams of the oil was oxidized with 1.7g. of chromic anhydride (CrO_3) in 50 cc. of 50% acetic acid at 35-40°. The oil obtained yielded a semi-carbazone melting at 147-149° after recrystallization from alcohol.

Wallach (113) has recorded the melting point of cyclohexylacetaldehyde semi-carbazone as 132-134°. Zelinsky (114) has prepared β-cyclohexyl ethanol by the action of trioxymethylene on cyclohexylmethylmagnesium iodide. He recorded the boiling point as 206-207° (745 mm.) and the refractive index, $n_D^{20°} = 1.4647$. He further oxidized the alcohol to the corresponding aldehyde and prepared its semicabazone. He did not record its melting point but stated that it agreed with that found previously (115) for the semicarbazone of hexahydrobenzaldehyde (cyclohexyl ethanol). Obviously the name "hexahydrobenzaldehyde" is in error. An abstract of the latter paper

(112) Hiers with Adams, J. Am. Chem. Soc., 48:1091(1926). The boiling point of β-cyclohexyl ethanol is given as 86-89° (5 mm.); $n_D^{25} = 1.4698$.
(113) Wallach, Ann., 359:313(1908).
(114) Zelinsky, Ber., 41:2628(1908).
(115) Zelinsky, J. Russ. Phys. Chem. Soc., 38:930(1906).

(115) has not been located in any of the journals. A request has been sent to Professor Dr. O. Wallach of the University of Göttingen, Germany, for a sample of his semicarbazone for comparison with ours.

Obviously a further identification was necessary. Five grams of the oil was oxidized with 8.25g. of potassium permanganate in dilute potassium hydroxide solution. The acid obtained was converted to the acid chloride by means of thionyl chloride and then converted to the amide. After one recrystallization from alcohol the amide melted at 165-166° and a mixed melting point with cyclohexylacetamide was not depressed. The phenyl- and naphthylurethanes of β-cyclohexyl ethanol have not been described in the literature.

20. Phenylethylmagnesium bromide and formaldehyde.

Gaseous formaldehyde was passed into a solution of phenylethylmagnesium bromide prepared from 37g. (0.2 mole) of phenylethyl bromide and 4.86g. (0.2 mole) of magnesium until a negative RMgX color test was obtained. After hydrolyzing with dilute hydrochloric acid the reaction mixture was steam distilled. The distillate was dried over sodium sulfate and then distilled under atmospheric pressure. Eleven and nine-tenths grams (43.8%) of a slightly yellowish oil was obtained, boiling at 233-235°. Oxidation of portions of this oil showed that no rearrangements to ring-substituted products had occurred, as only benzoic acid was obtained. Attempts to positively identify

the oil as γ-phenylpropanol failed. The phenylurethane (116) could not be induced to crystallize, and attempts to oxidize the substance to hydrocinnamic acid (117) failed also. Oxidation of the residual tar from the steam-distillation gave only benzoic acid.

21. Styrylmagnesium bromide and formaldehyde.

A solution of styrylmagnesium bromide was prepared from 36.6g. (0.2 mole) of β-bromostyrene and 9.72 g. (0.4 mole) of powdered magnesium (30 mesh). The reaction was induced to start by the use of activated magnesium. Gaseous formaldehyde was then passed in until a negative color test was obtained. On working up in the customary manner 1.6g. (6%) of oil boiling at 125-130° (8 mm.). While this oil possessed the odor of cinnamyl alcohol it was not positively identified due to the small amount available for experimentation. As usual all tars were oxidized but only benzoic acid was obtained.

22. Phenylacetenylmagnesium bromide and formaldehyde.

An ether solution of 19.7g. (0.19 mole) of phenylacetylene was added to a solution of 0.22 mole of ethylmagnesium bromide. After evolution of ethane had ceased gaseous formaldehyde was led in until a negative color test was obtained. After hydrolysis with dilute hydrochloric acid the reaction mixture was steam-distilled. The distillate yielded on fractionation 5g.

(116) Walbaum, Ber. 33, 2300(1900). The melting point of phenyl-
  propyl alcohol phenylurethane is given as 47-48°.
(117) Fittig and Rugheimer, Ann., 172:123(1874).

(20%) of oil boiling from 125-130° (8 mm.). $D_{25°}^{25°}$ = 1.0806.
The constants of this alcohol agree quite well with those found
by Moureau and Desmots (118), for phenylpropargyl alcohol.
Oxidations of both this oil and all residual tars yielded only
benzoic acid.

23. Sodium phenolate and ethyl chlorocarbonate.

(a) Twenty eight grams (0.3 mole) of pure phenol was dis-
solved in anhydrous benzene and 7g. (0.3 mole) of sodium in
the form of thin slices added. A heavy paste of sodium phenol-
ate formed. The mixture was warmed one hour to insure as com-
plete reaction as possible. The mixture was then cooled to room
temperature and 32g. (0.3 mole) of ethyl chlorocarbonate added
in small portions. A rather vigorous reaction set in at once
and the paste disappeared. A colloidal suspension of sodium
chloride formed. The mixture was refluxed for five hours and
then poured into cold water. The benzene layer was extracted
four times with Claisen's solution (119). On acidification of
the extracts no oil whatever appeared. The solution contained
a large amount of phenol, identified as the tri-bromo derivative.
The reaction apparently went much too fast (120).

(b) The foregoing run was repeated using vigorous mechan-
ical stirring and at a temperature of -18° in toluene solution.

(118) Moureau and Desmots, Compt. rend., 132, 1224(   ).
    Phenylpropargyl alcohol, b.p. = 135-136°(13 mm.); D = 1.0811.
(119) Methyl alcoholic alkali. See Claisen (Ann. 442, 224(1925)
    footnote 2.
(120) For the effect of temperature on a similar reaction, see
    Claisen, loc. cit., p. 245.

The ethyl chlorocarbonate was added dropwise over a period of one hour. The heavy mass disappeared as before. The solution was allowed to warm slowly to room temperature. It was then poured into cold water and a trace of hydrochloric acid added. The benzene layer was twice extracted with Claisen's solution but these extractions on acidification yielded no oil or odor of ethyl salicylate. The toluene layer was dried over sodium sulfate and distilled under atmospheric pressure. A yield of 28.2g. (56.6%) of oil was collected at 222° under 737 mm. pressure. The material was very constant boiling. The (121) oil was identified as ethyl phenyl carbonate by hydrolysis to phenol (identified as the tribromo derivative). The following constants were determined, $D_{25°}^{25°} = 1.095$; $n_D^{25°} = 1.4870$.

(c) A repeat run was carried out at the temperature of a carbon dioxide ether mixture. Ethyl phenyl carbonate was obtained in 53% yield.

24. Sodium phenolate and chloromethyl ethyl ether.

To a suspension of 0.1 mole of sodium phenolate in toluene was slowly added 9.4g. (0.1 mole) of chloromethyl ethyl ether. The reaction mixture was kept at a temperature of -18° and vigorous stirring was employed. There was no evidence of reaction. The mixture was allowed to slowly warm up to room temperature. On account of sickness and vacation the mixture

(121) Palewski, Ber., 17, 1205(1884), b.p. = 200-210°, Sp. Gr. = 1.1134 at 0°; Fatianow, Jahresbericht, 477(1864); b.p. = 234°, Sp. Gr. = 1.117 at 0°; Peratoner, Gazz. chim. ital., 28, I, 236(1889). b.p = 227.5-229.5° at 762.5 mm.; Morel, Bull. soc. chim., (3), 21, 822(1899); $n_D^{16.1} = 1.49093$.

was not worked up for three weeks after the run was started. During this time a bright red color appeared in the reaction flask. After pouring into water and making slightly acid, the toluene layer was removed and combined with two ether extractions of the water layer. Alkali extracts of the toluene-ether layer yielded only phenol, identified as the phenylurethane (122). The recovered phenol weighed 4.5g. (48%).

25. Sodium phenolate and benzaldehyde.

Thirty-one and eight-tenths grams (0.3 mole) of benzaldehyde was added dropwise to a vigorously stirred suspension of 0.3 mole of sodium phenolate in toluene. The tempeature of addition was that of an ice-bath. The reaction mixture was allowed to slowly come to room temperature and then to stand for one and one-half days. The material was then poured into water and the layers separated. The water yielded only phenol and the toluene layer only benzaldehyde. It was evident that no reaction had taken place. A repeat run under a more elevated temperature is now being made.

26. Benzylmagnesium chloride and benzhydryl bromide.

A solution of 0.1 mole of benzylmagnesium chloride was slowly added to 12.35g. (0.05 mole) of benzhydryl bromide at the temperature of an ice-bath. The benzhydryl bromide was prepared according to the method of Claisen (123) from benzhy-

(122) Leuckart, Ber., 18, 875(1885).
(123) Claisen, Ann., 210, 245(1925).

drol and phosphorus tribromide in 80.6% yield. The boiling
point of the benzhydryl bromide was 161-165° (7 mm.). Addition
of the Grignard solution required about one hour, a heavy ball
of paste forming. After hydrolyzing with iced hydrochloric acid
3.0g. of undissolved solid was filtered off. This was identi-
fied as the highly insoluble sym-tetraphenylethane by a mixed
melting point. Yield, 36%. Steam distillation of the ether
layer yielded 0.77g. (4.2%) of dibenzyl. Slow fractional
crystallization of the residual tars from the ether layer
yielded a small amount of a solid melting at 51-54° and not di-
benzyl. α-α-β-Triphenyl ethane melts (124) at 54°. Identifica-
tion of this solid has not been confirmed. No trace of o-
benzhydryl toluene or p-benzhydryl toluene could be obtained
and oxidation of the residues gave only benzoic acid.

27. Preparation of α-naphthyl carbinol.

α-Naphthyl carbinol was prepared by the method of Ziegler
(125) by the action of gaseous formaldehyde on α-naphthylmagnes-
ium bromide. Gaseous formaldehyde was led into a solution of
0.3 mole of α-naphthylmagnesium bromide until a negative color
test was obtained. On working up in the customary manner,
α-naphthyl carbinol was obtained as a white, crystalline solid,
m.p. = 53-56°; b.p. = 160-163° (3 mm.). Yield, 50-53%.

28. Preparation of α-chloromethyl naphthalene.

α-Chloromethyl naphthalene has been prepared by Scherler

(124) Klages and Heilmann, Ber., 37, 1455(1904).
(125) Ziegler, Ber., 54, 737(1921).

(126) and by Wislicenus and Wren (127) by the direct chlorination of α-methyl naphthalene. A sample prepared in this manner (128) gave unsatisfactory results (129) and the method described here was therefor adopted. Twenty five grams (0.15 mole) of α-naphthyl carbinol was dissolved in 100 cc. of dry toluene in a 500 cc. balloon flask fitted with a reflux condenser and exit tube leading out of the window. Twenty five grams of thionyl chloride was then added in small quantities through the reflux condenser. Evolution of hydrogen chloride and sulphur dioxide commenced immediately. When spontaneous action had ceased the solution was gently refluxed until there was no longer an evolution of gas. This required about three hours. The toluene and excess thionyl chloride were removed under reduced pressure and the residue vacuum distilled. The α-chloromethyl naphthalene was obtained as a light yellow oil, boiling at 135-139° under 6 mm. pressure. The yield was 23.2g. or 79% of the theoretical amount.

29. Color test for α-naphthylmethylmagnesium chloride.

(a) To a few drops of α-chloromethyl naphthalene in a dry test tube were added about 5 cc. of dry ether, a few scraps of magnesium and a crystal of iodine. Reaction soon set in and when the red iodine color was discharged a few drops of a so-

(126) Scherler, ibid., 24, 3930(1891).
(127) Wislicenus and Wren, ibid., 38, 506(1905).
(128) Obtained from Frankel and Landau.
(129) The RMgX solution obtained was full of a white precipitate and gave only a weak color test. The solution thus prepared was not worked up.

lution of Michler's ketone in dry benzene added. The reaction continued for several minutes. The liquid was then decanted to another test tube and hydrolyzed with a few drops of water. When a few drops of an acetic acid solution of iodine were added, the characteristic blue color developed.

(b) A small amount of Grignard solution was prepared in the usual manner. No Michler's ketone was added while the halide and magnesium were reacting. When the reaction had ceased the liquid was decanted and a strong color test obtained in the normal manner.

30. α-Naphthylmethylmagnesium chloride and carbon dioxide.

To 1.38g. (0.057 mole) of magnesium turnings covered with 85 cc. of anhydrous ether was added a solution of 10g. (0.057 mole) of α-chloromethyl naphthalene in 50 cc. of ether. A crystal of iodine was sufficient catalyst to induce the reaction to start. The Grignard solution was of a yellowish-green color. When addition of the halide was completed a stream of dry carbon dioxide was led over the surface of the well-stirred solution until a negative RMgX color test was obtained. This required about 20 minutes. The reaction mixture was very heavy and sticky. After hydrolysis with ice and dilute hydrochloric acid the ether layer was removed and the water layer once extracted with ether. The combined ether extracts were washed with a little cold water and then twice extracted with 5% potassium hydroxide. The alkali extracts were acidified with hydrochloric acid giving a white precipitate. The yield of dry solid acid

was 6.3g. corresponding to 59.4% of the theoretical amount. It melted unsharply at 105°. One recrystallization from hot water raised the melting point to 129-131°. The melting point given by Boessneck (130) is 131°. In order to characterize the acid two grams of it was converted to α-naphthyl acetamide. The acid was refluxed for 30 minutes in dry benzene with six grams of thionyl chloride in order to convert it to the acid chloride. The benzene and excess thionyl chloride were removed by warming in a water bath under reduced pressure. Two and one-half grams of finely powdered ammonium carbonate was added to the oil thus obtained and the mass solidified. The crude material was washed with cold water and twice recrystallized from 80% alcohol. The pure α-naphthyl acetamide melted at 178°. Boessneck (130) has reported the melting point as 180-181°.

31. α-Naphthylmethylmagnesium chloride and dimethyl sulfate.

A solution of 0.057 mole of α-naphthylmethylmagnesium chloride was prepared as in the preceding experiment. Fourteen grams (0.11 mole) of dimethyl sulfate in ether solution was then slowly added with continuous stirring. The reaction was brought to completion by stirring and gently refluxing for 30 minutes. Hydrolysis was carried out by means of ice and dilute hydrochloric acid. The ether layer was shaken with dilute ammonium hydroxide to remove excess dimethyl sulfate, washed with water and dried over calcium chloride. The ether was distilled off and the residue vacuum distilled. Four and nine-tenths grams

(130) Boessneck, Ber., 16, 641(1883).

of colorless oil was collected at a temperature of 95-105° under 3 mm. pressure, corresponding to a yield of 55.1% of the theoretical amount. On redistillation under atmospheric pressure nearly all came over within a range of 2°. The boiling point was 247-249° under 742 mm. pressure, accompanied with a small amount of decomposition. Carnelutti (131) has recorded the following values for the boiling point of α-ethyl naphthalene; 257-259° under 757.7 mm. pressure (corrected); 100° under 2-3 mm. pressures. The picrate was prepared in the customary manner and found to melt at 98-99°. The value reported by Carnelutti (131) for α-ethyl naphthalene picrate is 98°.

32. α-Naphthylmethylmagnesium chloride and phenyl isocyanate.

Several runs were made and as the results of these differed somewhat they are all described here.

(a) An ether solution of 0.028 mole of α-naphthylmethylmagnesium chloride was prepared in the same manner as in the preceding runs. To this solution was slowly added an ether solution of 2.9g. (0.024 mole) of phenyl isocyanate. Hydrolysis was carried out with ice and dilute hydrochloric acid. The ether layer was removed and dried over calcium chloride. The ether was then allowed to evaporate off, depositing an oil and a few crystals. The oil was poured off from the crystals which were then taken up in alcohol and allowed to crystallize slowly. After about three days a small crop of crystals melt-

(131) Carnelutti, Ber., 13, 1671(1880).

ing unsharply at 144° was obtained. When these crystals were mixed with a sample of α-naphthyl acetanilide described below and melting at 155°, the melting point was raised to 149°, which seemed to indicate that the expected compound was obtained in low yield in an impure state.

(b) Into a 200 cc. 3-neck flask fitted in the usual manner with stirrer, reflux condenser and dropping funnel was placed 0.6g. of magnesium turnings, 30 cc. of dry ether, and a crystal of iodine. Five grams (0.03 mole) of α-chloromethyl naphthalene was dissolved in 20 cc. of ether and two or three ccs. added to the mixture in the flask. As soon as the reaction appeared to be well under way 2.3g. (0.02 mole) of phenyl isocyanate was added to the ether solution of chloromethyl naphthalene and thus added with the halide to the reaction proceeding in the flask. However, this procedure stopped the reaction with magnesium and it could not be induced to start again by warming or addition of iodine. The phenylisocyanate appears to be an efficient negative catalyst (132) for this particular reaction. The same observation was made by Gilman and Kirby (133) in the case of benzhydrylmagnesium chloride.

(c) A solution of 0.057 mole of α-naphthylmethylmagnesium chloride was prepared in the customary manner and then 7g. (0.59 mole) of phenyl isocyanate in ether slowly added. After additon

(132) A comprehensive study of the action of numerous reagents on the time of starting of Grignard reactions is being carried out in this laboratory by Gilman and Robert Vanderwal.
(133) Gilman and Kirby, J. Am. Chem. Soc., 48, 1734(1926).

was complete the mixture was stirred and refluxed for 30 minutes. It was then hydrolyzed with iced hydrochloric acid and the ether layer separated and dried over calcium chloride. The ether was allowed to evaporate leaving a yellow oil. The oil was taken up in alcohol and set aside to crystallize slowly. After three or four days a small crop of crystals melting at 136° was obtained. After one recrystallization from alcohol the melting point was 136-137°. This compound was not identified.

(d) To 2.4g. (0.1 mole) of magnesium turnings was added 75 cc. of ether and a crystal of iodine and then a solution of 17.6g. (0.1 mole) of α-chloromethyl naphthalene in 50 cc. of ether slowly added. After the Grignard solution had been made up, a solution of 10g. (0.08 mole) of phenyl isocyanate in ether was slowly added. A very vigorous reaction took place. When the addition was complete hydrolysis was carried out by dropping cold, dilute hydrochloric acid into the reaction flask. A white solid remained undissolved in either the ether or water layer and was filtered off with suction. This material weighed 5.5g. and melted unsharply at 140°. After two recrystallizations from alcohol the compound melted at 152°. A mixed melting point determination using the α-naphthyl acetanilide described below was 153°. By evaporation of the ether layer from the above filtration an additional crop of the same material weighing 3.8g. was obtained. The total yield of α-naphthyl acetanilide was 9.3g. corresponding to a yield of 36% of the theoretical amount.

33. Preparation of α-naphthyl acetanilide.

One gram of α-naphthyl acetic acid, obtained by the action of carbon dioxide on α-naphthylmethylmagnesium chloride as described above, was converted to the acid chloride by refluxing with two grams of thionyl chloride in dry benzene for 20 minutes. The excess benzene and thionyl chloride were removed by warming under reduced pressure. A few drops of aniline were added, causing a very vigorous reaction. An excess of aniline was then added and the mass stirred several minutes with a glass rod. The material was then washed twice with dilute hydrochloric acid and then with cold water. The remaining material was a dark reddish-brown paste. After two recrystallizations from alcohol the pure anilide melted sharply at 155°.

34. α-Naphthylmethylmagnesium chloride and ethyl chlorocarbonate.

Three runs were made, the results being similar. The largest run was the best in point of yield and is described here. A solution of 16.7g. (0.095 mole) of α-chloromethyl naphthalene in 100 cc. of ether was slowly added to 2.4g. (0.1 mole) of magnesium turnings contained in a 3-neck flask with 50 cc. of ether. As usual, as crystals of iodine was used to induce the reaction to start. After addition was completed the Grignard solution was stirred at room temperature for 15 minutes to allow the halide to react with the magnesium as completely as possible. The solution was then quickly decanted into a separatory funnel. Forty three grams (0.4 mole) of ethyl chlorocarbonate dissolved in 100 cc. of ether was then placed in the stirring flask and

cooled in an ice-bath. The Grignard solution was then slowly
added to the solution in the flask. This addition required
about 45 minutes, vigorous stirring being employed. The re-
action mixture was hydrolyzed with ice and dilute hydrochloric
acid. The ether layer was removed and dried over sodium sulfate.
The ether was removed on the water bath and the residual oil
fractionated under reduced pressure. A fraction weighing 8.3g.
was collected between 190-200° under 15 mm. pressure. This oil
was not further purified since it was considered to be an ester
and it was desired to obtain the acid by hydrolysis. However,
in another run the oil was redistilled and boiled at 145-150°
under 3 mm. pressure. The yield, based on the molecular weight
of ethyl α-naphthyl acetate or an isomer of that ester, was
0.039 moles corresponding to 41% of the theoretical amount.
The oil was hydrolyzed by refluxing one and one-half hours with
alcoholic potassium hydroxide. The solution was then cooled,
diluted with water, filtered and acidified with hydrochloric
acid. Five grams of white, solid acid was obtained. This acid
melted at 172-173°. It may be recrystallized either from hot
water or benzene. The recrystallized product melts sharply at
174°.

Neutralization Equivalent. 0.1097g. sample. 5.72 cc. of
0.1038 N KOH. Mol. wt. = 184.8. Calc. for $C_{12}H_{10}O_2 = 186$.

The acid appears to be an isomer of α-naphthylacetic acid,
the expected product.

A small amount of the acid was converted to the corres-

ponding chloride and the anilide prepared as described above in the preparation of α-naphthyl acetanilide. The anilide of the 174° acid melted at 217-218° after two recrystallizations from alcohol.

Attempts to oxidize the 174° acid with alkaline permanganate, and with chromic acid in glacial acetic acid led to no definite products.

35. α-Naphthylmethylmagnesium chloride and formaldehyde.

A solution of 0.1 mole of α-naphthylmethylmagnesium chloride was prepared from 18g. of α-chloromethyl naphthalene, 2.4g. of magnesium turnings and 125 cc. of dry ether. Gaseous formaldehyde was then led into the Grignard solution in the manner described above for the preparation of α-naphthyl carbinol. When an RMgX color test showed the absence of unused Grignard reagent the reaction mixture was hydrolyzed with ice and dilute hydrochloric acid. An insoluble white solid was filtered off with the aid of suction. This solid melted at 157-158° and was probably sym.-di-α-naphthyl ethane (134). The yield of this compound was 0.9g. (6.4%). The ether layer of the filtrate was separated, dried over sodium sulfate and the ether distilled off on the water bath. The remaining oil was fractionated under reduced pressure. A fraction was collected between 100-130° under 6 mm. pressure. This fraction was not investigated further. A second fraction, a yellow oil weighing 2.6g., (15%) was collected between 167-170° under 6 mm. pressure. When a

(134) Bamberger and Lodter, Ber., 21, 54(1888), have given the melting point of this compound as 160°.

drop of the oil was dissolved in warm benzene and cooled, crystals were deposited and the bulk of oil solidified when seeded with these crystals. The crystals obtained from benzene melted at 121°. A small amount of the compound was dissolved in carefully dried ether and when treated with slices of sodium, gas was liberated. The phenyl urethane of this unknown alcohol was prepared by allowing a small quantity to react with phenylisocyanate in benzene solution at room temperature. The benzene was allowed to evaporate leaving a white solid. The urethane was washed three times with petroleum ether and then twice crystallized from alcohol. It melted at 125°.

An attempt to oxidize one gram of this carbinol to the corresponding carboxylic acid using 1.4g. of potassium permanganate in 10% sodium hydroxide failed to give any definite product.

36. β-Naphthyl methylmagnesium bromide and carbon dioxide.

An ether solution of 11g. (0.05 mole) of β-bromomethyl naphthalene (135) was slowly added to 1.5g. of magnesium turnings. The reaction was easily started with the aid of a crystal of iodine. A slow stream of dry carbon dioxide was led in during the course of the addition of the halide. The mixture became very sticky and a little fresh magnesium was added to aid the reaction. After hydrolyzing with iced hydrochloric acid the ether layer was removed and extracted twice with 10% potassium hydroxide. The acid separated as a yellow paste. It was not found

(135) Obtained from Frankel and Landau.

possible to recrystallize the acid from methyl or ethyl alcohol, or ligroin. It was obtained after two recrystallizations from benzene in the form of shining leaflets melting sharply at 138°. The yield was low but could not be determined exactly due to the stickiness of the product. A mixed melting point with an authentic specimen of β-naphthyl acetic acid prepared according to the method of Blank (136) by the hydrolysis of β-naphthyl acetonitrile, showed no depression.

37. Preparation of mercury dibenzyl.

Mercury dibenzyl has been prepared (137) by the action of benzylmagnesium chloride on mercuric chloride. Recently an improved technique for the preparation of mercury dialkyls by the action of the Grignard reagent on mercuric chloride has been described by Gilman and Brown (138). The work described here was carried out before the method of Gilman and Brown was perfected and it is highly probable that, by employing their conditions, the yield may be materially improved. The following is a description of a typical run.

To a solution of 0.5 mole of benzylmagnesium chloride was slowly added 68g. (0.25 mole) of finely pulverized mercuric chloride. This addition required 1.5 hours. After stirring and refluxing for two hours a negative color test was obtained and an additional 0.1 mole of benzylmagnesium chloride was added.

(136) Blank, Ber., 29, 2372(1896).
(137) Pope and Gibson, J.Chem.Soc., 101, 735(1912).
       Jones and Werner, J.Am.Chem.Soc., 40,1266(1918).
       Wolff, Ber., 46, 64(1913).
(138) Gilman and Brown, J.Am.Chem.Soc., 51, Mar., (1929).

A positive test persisted after eight hours of heating. Stirring was very difficult, due to the unusually pasty nature of the reaction mixture. Hydrolysis was carried out with ice and dilute acetic acid. A small amount of insoluble material was filtered off, the ether layer separated, and dried over sodium sulfate. When the ether was removed by distillation, the remaining oil yielded 49.6g. (51.8%) of mercury dibenzyl, m.p. = 110-110°. Petroleum ether washings of the mercury dibenzyl yielded on steam distillation 6.8g. (12.4%) of dibenzyl.

38. Preparation of sodium benzyl.

The method of Schlenk and Holtz (83) was adopted. A typical run is described here. Nine grams (0.023 mole) of mercury dibenzyl and 120g. of benzene were placed in a 200 cc. dark, glass-stoppered bottle, and a sufficient quantity of sodium slices added to fill the bottle two-thirds full. The air was swept out with purified nitrogen (139) and the stopper then wired in. After shaking 48 hours the contents of the bottle were then decanted into another nitrogen-filled bottle, the sodium, coated with mercury, remaining behind. The second bottle was then centrifuged and the colorless benzene layer decanted by forcing with a stream of nitrogen into a nitrogen-filled separatory funnel. The remaining solid cake was well cooled in an ice-salt mixture and then extracted with 120 cc. of cold ether

(139) The nitrogen gas was purified by leading through chromous chloride to remove oxygen, and then through calcium chloride and sulfuric acid to remove moisture. All the experiments described here were carried out in this inert atmosphere.

through which nitrogen had been bubbled to remove air. The intensely red ether extract was decanted by forcing up into a separatory funnel by means of a stream of nitrogen. When a solution of sodium benzyl thus prepared was treated with carbon dioxide the red color was quickly discharged. On working up insufficient phenylacetic acid was obtained to permit of isolation. Its presence was indicated, however, by its characteristic odor.

39. Sodium benzyl, α-α-diphenylethylene, and carbon dioxide.

A solution of sodium benzyl prepared as above was run into an ether solution of α-α-diphenylethlene at room temperature. The red color disappeared after about 10 minutes and a yellow color took its place. Carbon dioxide was then led in for about one hour. On working up in the customary manner a trace of solid acid melting with decomposition at 90-105° was obtained. The amount was far too meagre to be purified.

40. Sodium benzyl, stilbene, and carbon dioxide.

A solution of sodium benzyl prepared as above was placed in a 200 cc. 3-neck flask and kept cool by means of an ice bath. A solution of two grams of stilbene in dry benzene was then added. The red color was not discharged as in the preceding experiment with α-α-diphenylethylene. After stirring 10 minutes the red color still persisted. Carbon dioxide was led in and the solution worked up as before. A trace of unidentified solid acid melting at 127-131° was obtained by precipitation from the alkali extractions when acidified. Ether extraction of the acidi-

fied solution gave a further trace of impure acid, melting from 115-130°. After washing with petroleum ether the melting point of this latter acid was raised to 140° with decomposition and previous softening. The recovered stilbene weighed 2.0g., that is, the amount of stilbene used up in the run was insufficient to be detected by a horn-pan balance.

41. Benzylmagnesium chloride and sodium.

A filtered solution of 0.2 mole of benzylmagnesium chloride in ethyl ether was added to 10g. (0.43 mole) of sodium in the form of thin slices at a temperature of -15°. The mixture was stirred and kept cool for six hours. No red color developed but a brown color and black precipitate appeared. The ether layer was then decanted on to ice and the remaining sodium washed three times with absolute alcohol. Fractional distillation of the ether layer of the hydrolyzed reaction mixture yielded 7.2g. (39%) of toluene and 1.5g. of indefinite, high-boiling oil. While the yield of toluene was poor it was quite apparent, due to the absence of red color, that sodium benzyl did not form. A repeat run was not made in view of the results of the succeeding experiment employing sodium-potassium alloy.

42. Benzylmagnesium chloride and sodium-potassium alloy.

Four grams of liquid sodium-potassium alloy was prepared by gently warming two grams of sodium and two grams of potassium under anhydrous xylene. The xylene was decanted and the alloy covered with dry ether. A filtered solution of 0.2 mole of benzyl-

magnesium chloride was then added. The reaction mixture was stirred for seven hours at the temperature of an ice-salt mixture but no red color developed. Carbon dioxide was then passed in and the reaction mixture worked up in the customary manner. The yield of pure phenylacetic acid, m.p. = 76°, was 27.2g. or 82.4%. Oxidation of 1.5g. of residual, non-acidic oil yielded only benzoic acid.

43. Attempt to capture the free benzyl radical. Benzyl chloride, magnesium, sodium-potassium alloy, stilbene, and carbon dioxide.

To four grams of liquid sodium-potassium alloy was added 125 cc. of anhydrous ether, 2g. of stilbene, and 4.86g. (0.2 mole) of magnesium turnings. A small amount of benzylmagnesium chloride was added as a catalyst and the reaction mixture cooled to 0°. Addition of 25.2g. (0.2 mole) of benzyl chloride was then begun. Since there was no evidence of reaction between the benzyl chloride and magnesium at the low temperature the mixture was allowed to come to room temperature during the addition of most of the benzyl chloride. Addition required 45 minutes and stirring was continued for another 15 minutes. Carbon dioxide was then led in for about one hour. Hydrolysis was carried out by very slowly adding water to the nitrogen-filled flask. On working up in the customary manner 12.5g. (47%) of phenylacetic acid was obtained. No other acids could be detected. Oxidation of residual tars yielded only benzoic acid.

VII. Summary

1. Benzylmagnesium chloride has been shown to give rise to rearranged products when treated with ethyl chlorocarbonate, ethyl chloromethyl ether, ethylene oxide, ethyl formate, and acetyl chloride.

2. The fact that benzylmagnesium chloride behaves normally toward carbon dioxide and some other reagents has been confirmed.

3. A new mechanism for the abnormal reactions of benzylmagnesium chloride has been suggested.

4. It has been shown that α-naphthylmethylmagnesium chloride gives rearranged products when treated with formaldehyde, and ethyl chlorocarbonate.

5. The reactions of formaldehyde with β-phenylethylmagnesium bromide, styrylmagnesium bromide, and phenylacetenylmagnesium bromide are normal at least in the sense that no rearrangement to the ring takes place.

6. The reaction of formaldehyde with cyclohexylmethylmagnesium bromide is normal at least as far as the major reaction product is concerned. Identification of all products has not yet been completed.

7. An attempt has been made to capture free benzyl radicals formed during the preparation of benzylmagnesium chloride.

B. NEW ORGANO-LEAD COMPOUNDS IN ANTI-KNOCK STUDIES.

I. Introduction

Tetra-ethyl lead is at present the most widely used anti-knock reagent. However, unsaturated and aryl groups apparently increase the anti-knock effectiveness of various gasolines. It is for this reason, in part, that an added emphasis is being placed by some on the superior qualities of gasolines obtained by cracking processes. (1). If this idea is sound then it is reasonable to expect that organo-lead compounds formed by re-placing some or all of the saturated ethyl groups in tetra-ethyl lead by unsaturated or aryl groups should be more effect-ive anti-knock agents than tetra-ethyl lead. Accordingly a study is being made of such compounds (2).

The compounds reported here are the n-butyl, iso-butyl, sec-butyl and tert.-butyl triphenyl leads. The preparation of tert.-butyl triphenyl lead is unusual. Hitherto, "No lead compound containing a tertiary hydrocarbon group has been pre-pared. All the attempts have resulted only in a reduction with deposition of metallic lead" (3). Related reduction re-

(1) One of the most recent and leading accounts of petroleum and its products is by Burrell, Ind. Eng. Chem., 20, 602(1928).
(2) This is part of a more general study of organo-lead com-pounds, particularly with a view of their applications in the treatment of cancer and some related plant diseases. See, Gilman and Robinson, J. Am. Chem. Soc., 49, 2315(1927) and 50, 1714(1928).
(3) Calingaert, "Organic Compounds of Lead," Chemical Reviews, 2, 43(1926). This is the most recent and authoritative treat-ise on organo-lead compounds. Prior to the preparation of tert. butyl triphenyl lead, Dr. Balassa prepared di-tert.-butyl-diphenyl lead in this laboratory.

actions were observed in the first attempts to prepare <u>tert.</u> butyl triphenyl lead. For example, when triphenyl-lead bromide was added to <u>tert.</u> butyl-magnesium chloride, a mixture resulted from which only the highly interesting triphenyl lead (or hexaphenyl di-lead) could be isolated. However, by reversing the order of addition by adding the Grignard (4) reagent to triphenyl lead bromide, the desired compound was obtained. With <u>tert.</u> butyl-magnesium chloride in excess, the Grignard reagent may act as a reducing agent according to the following reaction:

$$\underline{tert.}\ C_4H_9\text{-}MgCl+(C_6H_5)_3PbBr \longrightarrow C_4H_8+C_4H_{10}+(C_6H_5)_3Pb+MgCl\ Br$$
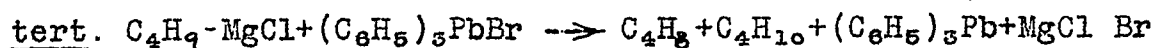
Gilman, Sweeney and Beaber (5) prepared tetra-phenyl lead in large quantities by means of the Grignard reaction and tested its anti-knock properties and its solubility in nitro-benzene, inasmuch as such nitro compounds have distinct anti-knock properties and were for a time sold as anti-knock agents. Their comparative tests indicated promisingly that tetraphenyl lead had distinct and superior qualities. The compounds described in the present report are, however, being tested with a series of related compounds by another method in a comprehensive study concerned with the correlation of chemical constitution and anti-knock effectiveness. This new method does not admit admixtures, to any great extent, with gasoline. By this method, organo-lead compounds that are solid at room

(4) One of the general methods for the large-scale production of tetra-ethyl lead involves the use of the Grignard reagent.
(5) Doctorate thesis of N. J. Beaber, Iowa State College, 1925.

temperatures and sparingly soluble in gasoline cannot be tested with any great reliability. However, related organo-lead compounds now being tested and having a lesser number of aryl groups indicate that the anti-knock effectiveness increases somewhat with the branching of radicals.

II. Experimental

1. Tetraphenyl lead; triphenyl lead bromide.

The tetraphenyl lead used in these studies was prepared according to the method of Pfeiffer and Truskier (6). Subsequently, Gilman and Robinson (7) devised improved directions for its preparation from the Grignard reagent and lead chloride.

Triphenyl lead bromide was prepared according to the method of Grüttner (8). It is essential that pure pyridine by used in this low temperature (-50°) bromination. With the use of pure pyridine and in runs one-half the size of that described by Grüttner, the yields were 80% or better.

2. n-Butyl-triphenyl lead. C_4H_9 $Pb(C_6H_5)_3$.

A solution of 0.08 mole of n-butylmagnesium bromide was prepared from 11 g. of n-butyl bromide and 1.95g. of magnesium. This solution was diluted to about 250 cc. with dry ether and then 20g. (0.04 mole) of triphenyl lead bromide was added in

(6) Pfeiffer and Truskier, Ber. 37, 1123(1904).
(7) Gilman and Robinson, J. Am. Chem. Soc., 49, 2315(1927).
(8) Grüttner, Ber. 51, 1298(1918).

small quantities. A slight heat of reaction was noticed. The reaction mixture was stirred and gently refluxed about one and one-half hours and then hydrolyzed by pouring on iced ammonium chloride solution. A little ammonium hydroxide was added and the entire mixture was filtered with suction to remove a small quantity of dark insoluble material. The ether layer was removed, dried over sodium sulfate, and then concentrated. The yellowish paste that resulted became solid when rubbed with alcohol. It was washed twice with 95% alcohol and air-dried to constant weight. The yield was 12.7g. or 66.5% of the theoretical amount. When once recrystallized from 95% alcohol the white crystals melted sharply at 47°.

Analysis. All of the organo-lead compounds reported here were analyzed for lead by the method described recently by Gilman and Robinson (9). Calc. for $C_{22}H_{24}Pb$: Pb, 41.82%. Found: Pb, 41.46 and 41.52%.

3. Iso-butyl triphenyl lead.

The procedure was the same as the one just described for the preparation of n-butyl triphenyl lead. The yield was 15.4g. or 80.6% of the theoretical amount. When twice recrystallized from alcohol the compound was obtained as fine needles melting sharply at 68-68.5°.

Analysis. Calc. for $C_{22}H_{24}Pb$: Pb, 41.82%. Found: Pb, 41.38 and 41.21%.

4. Sec.-butyl triphenyl lead.

(9) Gilman and Robinson, J. Am. Chem. Soc., 50, 1714(1928).

This compound was prepared according to the directions for the preparation of the two preceding compounds. The yield was 12.3g. or 64.4% of the theoretical amount. After one recrystallation from 95% alcohol the compound melted sharply at 84°.

Analysis. Calc. for $C_{22}H_{24}Pb$: Pb, 41.82%. Found: Pb, 41.59 and 41.43%.

5. Tert. butyl triphenyl lead.

A solution of 0.2 mole of tert.-butylmagnesium chloride was prepared according to the improved directions described recently by Gilman and Zoellner (10) from 18.4g. of tert.-butyl chloride and 5g. of magnesium turnings. To this solution was added 19.5g. of triphenyl lead bromide. The heat of reaction was very slight and the solution had a yellowish color. The insoluble material obtained subsequent to hydrolysis with iced ammonium chloride and ammonium hydroxide was filtered by suction and washed with ether. The yellow colored ether layer and washings were dried over sodium sulfate and then concentrated to give a yellowish solid that weighed 8.6g. and melted unsharply at 95°. Recrystallization from alcohol and then from benzene gave yellow crystals that melted unsharply and with decomposition at 150°.

The mother liquor and washings were diluted with alcohol and on standing two distinct types of crystals separated: flat, white plates and star-like clusters of yellow needles. These crystals were filtered, dried and then carefully separ-

(10) Gilman and Zoellner, ibid., 50, 425(1928).

ated by hand. The white crystals correspond closely with triphenyl lead obtained by Krause and Riezaus (11) who have described triphenyl lead as crystallizing from benzene in light yellow crystals which begin to melt at 155° and are completely melted at 225°, the melt being colored black with free metallic lead. These crystals contain 1.5 molecules of benzene. When the benzene is replaced by alcohol a compound is obtained which is nearly white and contains no solvent of crystallization. Their compound gave a green coloration when dissolved in benzene and treated with alcoholic silver nitrate. The white compound obtained in our experiment begins to decompose at 148° and at 220-222° breaks down to a gray mass. It also gives the green color test with alcoholic silver nitrate. This color test was found to be negative with n-butyl triphenyl lead and with triphenyl lead bromide.

Analysis. Calc. for $C_{18}H_{15}Pb$: Pb, 47.26%. Found: Pb, 47.33%.

The yellow crystals were not identified. They melt at 95-97° to an opaque yellow mass, with a red color which appears at 110°, turning to black at 112°. These crystals also give the silver nitrate color test.

In a second experiment the order of addition was reversed, the tert.-butylmagnesium chloride being added slowly to 10.4g. or 0.02 mole of triphenyl lead bromide suspended in ether. The

(11) Krause and Riezaus, Ber., 55, 888(1922).

Grignard solution was prepared from 4.6g. or 0.05 mole of <u>tert.</u>-butyl chloride, 1.22g. of magnesium turnings and 70 cc. of ether. In order to minimize the supposed reducing reaction of the Grignard reagent, only one-half of this RMgX solution was added; and, inasmuch as the yield of <u>tert.</u>-butylmagnesium chloride was only about 65% (10) the effective quantity of Grignard reagent added was less than the theoretical amount necessary for a complete reaction. This fact undoubtedly accounts in part for the low yield and for the difficulty encountered in the separation of the reaction product from unaltered triphenyl lead bromide.

During the addition of the Grignard solution a yellow color appeared. The mixture was hydrolyzed with iced ammonium chloride and filtered. On concentrating the yellow ether layer by evaporation a yellow solid resulted, and this underwent decomposition on heating with alcohol. This material was not further investigated. The residue from filtration was extracted with several small portions of hot alcohol, and on cooking white needles separated. Repeated crystallization from ether gave glistening needles that melted sharply at 150-150.5°. When mixed with a sample of diphenyl lead bromide (melting at 157°) the melting point was depressed to 130°.

<u>Analysis</u>. <u>Calc.</u> for $C_{22}H_{24}Pb$: Pb, 41.82%. Found: Pb, 41.60 and 41.69%.

III. Summary.

The four butyl triphenyl leads have been prepared from the

appropriate Grignard reagent with triphenyl lead bromide. Some triphenyl lead or hexaphenyl di lead was obtained in connection with the preparation of <u>tert.</u>-butyl triphenyl lead. This <u>tert.</u>-butyl derivative, apart from its value in anti-knock studies, is the first reported organolead compound having a tertiary radical attached directly to lead.