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The reaction of allylmagnesium Bromide with m-Tolualdehyde

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THE REACTION OF ALLYL MAGNESIUM
BROMIDE WITH m-TOLUALDEHYDE

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CHAPTER I

INTRODUCTION

In a systematic study which is being made in this laboratory of conjugated dienes it was decided to prepare m-methyl phenylbutadiene--1,3. This compound might be prepared by a number of methods, for example, the reaction of m-methyl cinnamic aldehyde with methylmagnesium bromide followed by the dehydration of the corresponding carbinol. This method has been used successfully in the synthesis of phenylbutadiene and similar compounds.\(^1\),\(^2\) However, since the methyl cinnamic aldehyde is not readily available, and most of the methods described for its preparation in the literature are rather cumbersome and give only poor yields, it was decided to investigate the reaction of allylmagnesium bromide and m-methyl benzaldehyde as a means of obtaining the desired hydrocarbon. A casual review of the literature dealing with the use of allyl chloride and allyl bromide as the halides in the Grignard reveals that many difficulties may be encountered in the preparation of a given compound by this method. In the first place, the reagent shows a great tendency to react in such a way as to yield diallyl as illustrated by the following equations:

\(^1\)Klages, Ber., 32, 2591 (1906).

Before 1928 allylmagnesium bromide was prepared by the batch method (Barbier-Grignard Procedure)\(^3\) to prevent the formation of diallyl. This method involved the alternate mixing of the allyl halide, anhydrous ether, and the compound to be reacted. In 1928, Gilman and McGlumphey\(^4\) synthesized allylmagnesium bromide and proposed a method for its preparation in which a large yield can be expected. The allylmagnesium bromide was prepared by using three equivalents of magnesium to one of the allyl halide and nine volumes of anhydrous ether. Vigorous stirring and the slow addition of the bromide were required. This procedure allowed the minimum contact of the allyl bromide with the allylmagnesium bromide which was being formed.

Later investigators, in determining the yield of the Grignard, confirmed Gilman's findings. Johnson and Adkins\(^5\) found that while allyl bromide reacts with copper-magnesium alloy to form only six percent yield of allylmagnesium bromide, allyl bromide reacts with magnesium in essentially Gilman's


proportion to give a seventy-two per cent yield of the theoretical.

An investigation of the effects of solvent upon the yields of crotyl and allylmagnesium bromide was made by Young, Prater, and Winstein⁶ who found that the usual diethyl ether proved to be a more satisfactory medium for the reaction than did ethers of higher molecular weights.

In a comparative study of the usefulness of RMgCl and RMgBr, Zoellner⁷ made the following observation: the chloride is to be preferred for most purposes, but in the case of the allylmagnesium halide the chloride is unsatisfactory because it becomes colloidal and useless in a great number of cases. The bromide was recommended for routine synthesis.

Henze, Allen, and Leslie⁸ investigated the reaction of allylmagnesium bromide with a few common aldehydes and ketones; and then with compounds containing both carbonyl and ether groupings. They compared the yields of the carbinols that they synthesized using the synthesis outlined by Gilman and McGlumphy⁹ in 1928 with the yields of the same carbinols prepared by other methods. They found that the yields were in some cases equal to and in other cases greater than yields previously reported.

---

⁶Young, Prater, and Winstein, J. Am. Chem. Soc. 55, 4908 (1933).
⁷Zoellner, Chem. Abs., 29, 5413.
In addition to the formation of diallyl, allylmagnesium bromide shows a tendency to rearrange, so that the product isolated may be entirely different from the one expected. Thermal rearrangements occurring in a three carbon system containing an allylic group have been the subject of recent investigations. Cope and Hardy\textsuperscript{10} reported the first instance of rearrangement of an allyl group by heating. They reported that ethyl (1-methylpropenyl)-allylcyanoacetate rearranged to ethyl (1,2-dimethyl-4-pentenylidene)-cyanoacetate.

\[\text{\begin{align*}
\text{CH}_3\text{CH} &= \text{C} \quad \text{CN} \\
\text{C}_3\text{H}_5 & \quad \text{COOEt} \\
\text{CH}_3\text{CH} &= \text{C} \quad \text{CN} \\
\text{C}_3\text{H}_5 & \quad \text{COOEt}
\end{align*}}\]

This rearrangement is an $\alpha\gamma$ shift of an allyl group in a three carbon system. Cope, Hoyle, and Heyl\textsuperscript{11} undertook to determine whether the rearrangement is general for an appropriately substituted three carbon system, just as the Claissen rearrangement is general for the $\gamma \text{C} = \text{C} - \text{OC}_3\text{H}_5$ system. They prepared cyanoacetic esters, malonic esters and malononitriles, each substituted by an alky1 or vinyl group and an allyl group. All of these compounds rearranged on heating and pure compounds were isolated except in two cases.

\textsuperscript{10}Cope and Hardy, \textit{J. Am. Chem. Soc.}, 62, 441 (1940).

\textsuperscript{11}Cope, Hoyle and Heyl, \textit{J. Am. Chem. Soc.}, 63, 1843 (1941).
To prove beyond doubt the question of structure, the rearranged products were cleaved with ammonia to ketones which could be identified by direct comparison, by synthesis of the rearrangement products, or by their reduction and conversion to solid derivatives which could be compared with known samples. In each case it was established that the allyl group shifted from the \( \alpha \) to the \( \gamma \) carbon atom and the double bond shifted to the \( \alpha, \beta \) position.

Some series in which allyl rearrangements have been reported follow:

**Cyanoacetic Ester Series:**

Ethyl-1-cyclohexenylallylcynoacetate did not rearrange during distillation at low pressures. However, it was isomerized by refluxing for eight to ten hours at pressures regulated so that the temperature of the liquid was 230, 200, and 170\( ^\circ \). The purest product was obtained at 170\( ^\circ \).
Three (1-methyl-2-alkyl-vinyl) allylcyanacetic esters were prepared and rearranged on heating.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CN} \\
\text{C}_2\text{H}_5\text{CH} & \quad \text{C} \quad \text{C} \quad \text{COOEt} \\
\text{C}_3\text{H}_5 &
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{CN} \\
\text{C}_2\text{H}_5\text{CH} & \quad \text{C} \quad \text{C} \quad \text{COOEt} \\
\text{C}_3\text{H}_5 &
\end{align*}
\]

The structures of the rearrangement products were established by their cleavage with ammonia to unsym-alkylallyl acetones.

Ethyl (1-phenyl-vinyl) allylcyanacetoate rearranged very rapidly on heating, and the product of the rearrangement was identified by cleavage with ammonia to allyl-acetophenone from which the oxime and the semicarbazone were prepared.
Ethyl (1-methylpropenyl) crotylcyanocacetate was prepared and rearranged by Cope, Hofmann and Hardy.\textsuperscript{12}

\[ \text{CH}_3\text{CH} = \text{C} - \text{C} = \text{C} - \text{COOEt} \quad \xrightarrow{180^\circ} \quad \text{CH}_3\text{CH} = \text{C} - \text{C} = \text{C} - \text{COOEt} \]

\[ \text{CH}_3\text{CH} = \text{CH} - \text{CH}_2 \]

**Malonitrile Series:**\textsuperscript{13}

1-Cyclohexanyl-allyl malononitrile and 1-ethylpropenyl-allyl malononitrile rearranged extremely easily and the products of the rearrangements were purified only in high vacuum. The structures were verified by cleavage with concentrated aqueous ammonia.

\[ \text{C}_6\text{H}_5\text{C} = \text{C} = \text{C} - \text{C} = \text{C} - \text{CN} \quad \xrightarrow{175^\circ} \quad \text{C}_6\text{H}_5\text{C} = \text{C} = \text{C} - \text{C} = \text{C} - \text{CN} \]

\[ \text{CH}_3\text{CH} = \text{C} - \text{C} = \text{C} - \text{C} = \text{CN} \quad \xrightarrow{150^\circ} \quad \text{CH}_3\text{CH} = \text{C} - \text{C} = \text{C} - \text{C} = \text{CN} \]

\textsuperscript{12} Cope, Hofmann and Hardy, \textit{J. Am. Chem. Soc.}, 63, 1852 (1941).

\textsuperscript{13} Cope, Halsey and Heyl, \textit{J. Am. Chem. Soc.}, 63, 1845 (1941).
**Malonic Ester Series:**

Three malonic ester compounds rearranged on heating. The rearrangement of the higher homologs in the malonic ester series involved side reactions of unknown character. Ethyl propenylallyl malonate rearranged in good yield.

\[
\begin{align*}
\text{CH}_2\text{CH} = \text{CH} \quad &\xrightarrow{\text{C(COOEt)}_2} \quad 200^\circ \quad \text{CH}_3\text{CH} = \text{CH} \quad \xrightarrow{\text{C(COOEt)}_2} \\
\text{C}_3\text{H}_5 
\end{align*}
\]

Ethyl (1-butenyl)allyl malonate rearranged on heating in the same way as ethyl-propenylallyl malonate. The rearranged product was identified by reduction and the consequent conversion into 5-(2-ethyl-pentyl) barbituric acid.

\[
\begin{align*}
\text{C}_2\text{H}_5\text{CH} = \text{CH} \quad &\xrightarrow{\text{C(COOEt)}_2} \quad 200^\circ \quad \text{C}_2\text{H}_5\text{CH} = \text{CH} \quad \xrightarrow{\text{C(COOEt)}_2} \\
\text{C}_3\text{H}_5 
\end{align*}
\]

**Nitriles and an Acid:**

(1-Cyclohexenyl) allylphenylacetonitrile when heated for three and one-half hours at 220° rearranged into (2-allyl-cyclo-hexadene)-phenylacetonitrile.

\[
\begin{align*}
\text{C}_6\text{H}_5 
\end{align*}
\]

---

The structure of (2-allylcyclohexylidene)-phenylacetonitrile was established by comparison with a known sample and cleavage with a solution of potassium hydroxide in diethylene glycol.

(1-Cyclohexenyl)-allylacetonitrile rearranged on heating at 185° for twelve hours to (2-allylcyclohexylidene) acetonitrile. The structure of the rearranged product was proved by cleavage with potassium hydroxide in diethylene glycol.

(1-Cyclohexenyl)-diallylacetonitrile was isomerized by heating for eleven hours at 175°. It rearranged to (2-allylcyclohexylidene)-allylacetonitrile. The product was identified by cleavage with potassium hydroxide in glycol.

Vinylidiallyl acetonitrile was isomerized on heating into an unsaturated nitrile. The structure of the rearrangement product was established by ozonolysis and the decomposition of the ozonide with hydrogen peroxide.
Vinylidiallylacetic acid rearranged on heating similar to the nitriles, yielding 2-allyl-6-heptadienoic acid. The structure of the rearranged product was established by ozonization studies.

\[
\begin{align*}
\text{CH}_2 = \text{CH} - \text{C} & \text{(C}_3 \text{H}_5\text{)} \text{COOH} & 185^\circ & \text{CH}_2 = \text{CH} - \text{C} & \text{(C}_3 \text{H}_5\text{)} \text{COOH} \\
\text{C}_3 \text{H}_5 & & \text{C}_3 \text{H}_5 & \\
\end{align*}
\]

Hydrocarbons:15

The following hydrocarbons rearrange on heating at 165-185° as shown in the equations:

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\text{C}_6 \text{H}_5 \text{CH} - \text{CH} = \text{CH}_2 & \quad \text{C}_6 \text{H}_5 \text{CH} = \text{CHCH}_2 \text{CH}_2 \text{CH} = \text{CH}_2 \\
\text{CH}_2 - \text{CH} = \text{CH}_2 & \\
\end{align*}
\]

\[
\begin{align*}
\text{III} & \quad \text{IV} \\
\text{C}_6 \text{H}_5 \text{CH} - \text{CH} = \text{CH}_2 & \quad \text{C}_6 \text{H}_5 \text{CH} = \text{CHCH}_2 \text{CH} \{(\text{CH}_3)\text{CH} = \text{CH}_2 \\
\text{CH}_2 - \text{CH} = \text{CHCH}_3 & \\
\end{align*}
\]

Compound (I) rearranged on heating at 176-178° to compound (II) without decomposition or polymerization. This rearrangement took place in a nitrogen atmosphere. Compound (III) was converted into (IV) by heating in a nitrogen atmosphere for sixty-five hours at 165-185°. All of these hydrocarbons were

---

rearranged similarly and the structures of the rearranged products were proved by ozonization.

The following diolefins, also rearranged when heated at 300°C. The reverse rearrangement proceeded at the same temperature.

\[
\begin{align*}
\text{CH}_3\text{CH} = \text{CH} = \text{CH}_2 & \quad \leftrightarrow \quad \text{CH}_3\text{CH} = \text{CHCH}_2\text{CH} = \text{CH}_2 \\
\text{CH}_2 = \text{CH} = \text{CH}_2 & \quad \leftrightarrow \quad \text{CH}_3\text{CH} = \text{CHCH}_2\text{CH} = \text{CH}_2
\end{align*}
\]

It may be concluded that the rearrangement of acyclic or allylic three carbon systems is quite general when the carbon atom is attached to two CN or COOEt groups or to one of each. Through kinetic studies it has been shown that the order of decreasing ease of rearrangement is malononitriles > cyanoacetic esters > malonic esters.

**Mechanism:**

Cope and Hardy\textsuperscript{16} proposed a cyclic mechanism as probable. If this mechanism is correct the isomerization is intramolecular and the allyl group is inverted during the shift.

Cope, Hofmann and Hardy\textsuperscript{17} tested the nature of the rearrangement by determining whether an interchange of groups took place during the rearrangement of mixtures. To test the nature of the rearrangement, mixtures that satisfied the following conditions were chosen: first, the migrating groups were different; second, the two compounds isomerized at similar

\textsuperscript{16} Cope and Hardy, J. Am. Chem. Soc. 62, 442 (1940).

\textsuperscript{17} Cope, Hofmann and Hardy, J. Am. Chem. Soc., 62, 1852 (1941).
rates; and third, the properties of the products of the rearrangements were such as to permit their complete separation. No interchange of migrating groups occurred when a mixture of two compounds of the nature just mentioned were isomerized. This indicated that the rearrangement proceeds by an intramolecular cyclic mechanism.

The fact that inversion occurred during the rearrangement was established by determining the structure of the rearranged product. The following equations show the course of the reaction, with and without inversion:

\[
\begin{align*}
&C=\overset{1}{\overset{1}{C}} \quad X \quad \overset{1}{\overset{1}{c}} \quad \overset{1}{\overset{1}{C}} \quad Y \\
\text{RCH} &= \text{CHCH}_2 \\
\rightarrow & \quad \text{RCH} - \text{CH} = \text{CH}_2 \\
\text{Product of rearrangement with inversion.}
\end{align*}
\]

\[
\begin{align*}
&C=\overset{1}{\overset{1}{C}} \quad X \quad \overset{1}{\overset{1}{c}} \quad \overset{1}{\overset{1}{C}} \quad Y \\
\text{RCH} &= \text{CHCH}_2 \\
\rightarrow & \quad \text{CH}_2\text{CH} = \text{CHR} \\
\text{Product of rearrangement without inversion.}
\end{align*}
\]

The influence of the groups, X and Y, is presumed to be derived from electron attraction, which enables the allyl group to release the electron pair binding it to the \(\alpha\) carbon atom. A conjugated double bond is formed in the position \(\alpha\) while at the same time, the allyl group becomes attached in the \(\gamma\) position. Less strongly activated systems in which negative groups, X and Y are phenyl and nitrile groups or in which a single nitrile or carboxyl group is attached to the carbon atom also undergo rearrangement.18

Levy and Cope19 undertook to find the least activation.

19 Ibid.
which would permit the occurrence of the rearrangement. 3-
Phenyl-1,5-diolefin rearranged on heating at 165-185° yielding
1-phenyl-1,5-diolefin. The inversion of two butenyl groups
occurred during the rearrangement of the following two compounds:

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

These reactions indicate possibly that a single phenyl group
provides sufficient activation for the rearrangements.

3-Methyl-1,5-hexadiene rearranged to the corresponding
heptadiene on heating to 300°. This isomerization is said to
establish the fact that no negative group need to be present to
weaken the bond between the allyl group and the carbon atom to
form a conjugated system. Supporting evidences to substantiate
the proposed idea concerning the function of negative groups
in labilizing such systems are the facts; that, the reaction is
reversible and that, a high temperature is required for the
reaction.

Some compounds that have not been reported to undergo
thermal rearrangements have been reported to polymerize.
Arnold and Coyner\textsuperscript{20} reported recently that in the Arylbutadiene

Maleic Anhydride reaction that the pure dienes of naphtylallylcarbinol and 2,3-dimethoxyphenylallylcarbinol polymerized so rapidly that they could not be isolated as such. The appropriate carbinol was reacted with maleic anhydride and the diene derivative was obtained. In order to see if the diene with a methyl group attached to the benzene ring could be isolated, the method used by Arnold and Coyner\(^2\) to prepare 3,4-dimethoxyphenylcarbinol was employed in this synthesis.

According to the literature, m-methylphenylbutadiene has not been prepared and isolated. However, the following are some of the phenylbutadienes that have been reported:

Phenylbutadiene,\(^2\) phenylmethylbutadiene,\(^2\) 1-phenyl-1,4-dimino-butadiene,\(^2\) 1-phenyl-4-aminobutadiene,\(^2\) 1-phenyl-4-chlorobutadiene,\(^2\) and 1-phenyl-4-bromobutadiene.\(^2\)

In this investigation allylmagnesium bromide was reacted with m-tolualdehyde by the method used by Arnold and Coyner\(^2\).

\(^{22}\) Klages, *Ber.*, 39, 2591 (1906).
\(^{25}\) Ibid.
and by the method of Gilman and McGlumphey as described by Henze, Allen and Leslie.29 In each case the addition product formed through the addition of the Grignard to m-tolualdehyde was hydrolysed with thirty per cent sulphuric acid. The resulting carbinol was dehydrated. The reactions may be represented by the following equations:

\[
\begin{align*}
\text{CH}_2=\text{CHCH}_2\text{MgBr} + \text{m-CH}_3\text{C}_6\text{H}_4\text{CHO} & \quad \rightarrow \\
\text{m-CH}_3\text{C}_6\text{H}_4\text{CHOMgBr} & \quad \text{CH}_2\text{CH}_2 \quad \rightarrow \\
\text{m-CH}_3\text{C}_6\text{H}_4\text{CHO} & \quad \text{CH}_2=\text{CH}_2 \quad \text{H}_2\text{SO}_4 \\
\text{m-CH}_3\text{C}_6\text{H}_4\text{CHO} & \quad \text{CH}_2=\text{CH}_2 \quad \text{H}_2\text{SO}_4 \\
\text{m-CH}_3\text{C}_6\text{H}_4\text{CHO} & \quad \text{CH}_2=\text{CH}_2 \quad \text{H}_2\text{SO}_4 \\
\text{m-CH}_3\text{C}_6\text{H}_4\text{CHO} & \quad \text{CH}_2=\text{CH}_2 \quad \text{H}_2\text{SO}_4 \\
\end{align*}
\]

The carbinol was dehydrated with difficulty. In each instance the yield was low. Most of the product polymerized. Of the three procedures used for the dehydration the yield was greater with fifteen per cent sulphuric acid. However, the highest yield was very poor in contrast to the large yield of carbinol.

An attempt to dehydrate the carbinol with acetic anhydride was made. The carbinol was refluxed with acetic anhydride for three hours. Direct distillation of the product under reduced pressure showed no signs of acetylation or dehydration. The original carbinol was recovered.

Hydrogen chloride was added to m-methylphenylallylcarbinol and the chloride formed was analysed by the Parr peroxide bomb method and found to be a mono-chloride. One portion of the chloride was refluxed with pyridine which removed the hydrogen chloride. Another portion was refluxed with alcoholic potash. The hydrogen chloride was removed with difficulty. The reaction with hydrogen chloride may be represented thus:

\[
\text{CH}_3\text{CHOH}-\text{CH}_2\text{CH}=\text{CH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{CHClCH}_2\text{CH}=\text{CH}_2
\]

m-Methylphenylallylcarbinol was dehydrated with sulphuric acid. Combustion analysis indicated that the product of the dehydration was a hydrocarbon, \( \text{CH}_3\text{C}_6\text{H}_4\text{CH} = \text{CH} - \text{CH} = \text{CH}_2 \)

Compounds containing conjugated systems react as a rule with unsaturated compounds such as maleic anhydride and maleic acid to form mono or poly-cyclic substances. This may be illustrated by the reaction of butadiene with maleic anhydride:

\[
\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 + \text{CHC}=\text{O} \xrightarrow{\text{Heat}} \text{C}_6\text{H}_6
\]

To find evidence of the diene structure the Diene Synthesis of Diels and Alder\textsuperscript{30} was carried out. The diene was refluxed

\[\text{Allen, J. Chem. Ed., 10, 494 (1933).}\]
with equimolar quantities of maleic anhydride in dry thiophene free benzene. The addition product was mainly tar. A few crystals were mixed in the tar but attempts to isolate and purify them failed.

Further evidence of the structure was obtained through ozonization studies. A hydrocarbon of the structure of compound (I) should yield on ozonization and subsequent hydrolysis formaldehyde, glyoxal, m-tolualdehyde and the corresponding acids.

\[
\begin{align*}
\text{CH}_3 & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{C} = \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{H}_2 \quad + \quad \text{O}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} \quad \text{C} \\
\text{C} & \quad \text{O}_3 & & \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{O}_3 & & & \\
\end{align*}
\]

The ozonide was decomposed by the method of Whitmore and Church.\(^{31}\) Formaldehyde was isolated as its methanederivative. m-Tolualdehyde was identified by its semicarbazone. Oxalic acid was identified by qualitative tests for this acid.

Further support for the structure of the diene was obtained by the oxidation of the side chains with potassium permanganate. The product isolated decomposed at 310°. The pure compound may decompose at 347°.

The practical application of this procedure as a synthetic method is limited because of the low yield of the hydrocarbon. Two things probably contribute to the low yields of m-methylphenylbutadiene; first, the compound polymerizes as shown by the large amount of polymer obtained. Arnold and Coyner made an observation that dienes of α-napthylallylcarbinol and 2,3-dimethoxyphenylethylcarbinol polymerized rapidly when attempts were made to isolate them. It seems rather strange that these hydrocarbons should polymerize so rapidly in as much as it is well known that the parent hydrocarbon, phenylbutadiene, can be kept for several weeks, without polymerization. Second, it might well be that the yield of m-methylphenylbutadiene may have been low because of the tendency of three carbon systems to rearrange. This point needs to be further investigated.

Although a rigorous proof of the structure has not been established due to the low yields of m-methylphenylbutadiene; the analysis, the reaction with maleic anhydride, and the oxidation experiments furnish supporting evidence that the hydrocarbon produced by the dehydration of the carbinol is m-methylphenylbutadiene-1,3.
Preparation of Allyl Bromide. Into a three liter round-bottom flask aqueous allyl alcohol (385 cc.) was added to a mixture of aqueous 4.8% hydrobromic acid (1000 g.) and concentrated sulphuric acid (300 g.). The three liter round-bottom flask was fitted with a mechanical stirrer, separatory funnel, and an efficient condenser set for downward distillation. Stirring was started and concentrated sulphuric acid (300 g.) was added through the separatory funnel to the warm solution. The allyl bromide distilled over completely in an hour. The crude product was washed with dilute sodium carbonate solution and dried over calcium chloride. The allyl bromide was redistilled. B.p. 69-72°. Yield 330 g.

All reagents used were purified before being used.

m-Tolualdehyde, technical grade, was distilled under reduced pressure. It distilled at 94° under 18 mm. Ether was washed with potassium permanganate solution until no further decolorization occurred, then with water, and successively dried with calcium chloride and sodium. It was stored in a dark stock bottle over sodium wire until used.

---

The Preparation of \( \text{m-}\text{MethylPhenylallyloarbinol} \).—Procedure 1.

Before attempting this synthesis all of the reagents and apparatus were dried. Into a two liter three necked round-bottom flask equipped with an efficient condenser, stirrer, and separatory funnel were placed dry ether (200 cc.) and magnesium (17 g.). Allyl bromide (5 cc.) was added to start the reaction and this was followed by a solution containing allyl bromide (87 g.), \( \text{m-tolualdehyde} \) (48 g.), and dry ether (300 cc.) which was added during the course of forty-five minutes. The reaction was exothermic and was stirred during the first six hours. After twenty-three hours the mixture was decomposed with ice and sulphuric acid (30%). The ether layer was separated from the acid layer, washed with a solution of sodium carbonate (5%), then with water and dried over calcium chloride. After which it was removed by distillation and the product distilled at \( 93-95^\circ \) under 1 mm. Yield 45.2 g.

Anal. Calcd. for \( \text{C}_{11}\text{H}_{14}\text{O} \): C, 81.41; H, 8.64. Found: C, 81.39; H, 8.67.

Procedure 2. — Into a two liter three necked round-bottom flask equipped with a stirrer, an efficient condenser, and a separatory funnel, finely powdered magnesium (73 g.) was covered with ether (200 cc.) and allyl bromide (121 g.) in anhydrous ether (500 cc.) was added slowly. After six hours of stirring at room temperature the mixture was warmed for thirty minutes and chilled. \( \text{m-Tolualdehyde} \), (.25 mole) was diluted with an equal volume of dry ether and added to the chilled reagent.
The product remained in solution. After cooling to room temperature it was decomposed by the action of sulphuric acid (30%). The addition compound which separated as an amber oil was dissolved in the ether layer. The two layers were separated and the acid extracted with ether. The combined ether layer and the extracts were washed with a solution of sodium carbonate, (5%) and then with water and dried over calcium chloride. The ether was removed by distillation, and the residue distilled at 110° under 8 mm. The compound was analysed for carbon and hydrogen by combustion.

**Anal. Calcd. for C_{11}H_{14}O : C, 81.41; H, 8.64.**

**Found: C, 81.38; H, 8.70.**

**Attempted Dehydration of m-Methyl Phenylallylcarbinol with Acetic Anhydride.** — m-Methyl phenylallylcarbinol (15 cc.) was refluxed with acetic anhydride (excess) for three hours and then poured into water (150 cc.). The oil was separated and the acid solution was extracted with ether. The combined ether extracts and oil were washed with sodium carbonate (5%), then with water and dried over calcium chloride. The ether was removed by distillation. Direct distillation under reduced pressure gave a compound which distilled at 93-95° under 1 mm. The compound was analysed for carbon and hydrogen by combustion. Analysis indicated that the compound had not been dehydrated to the diene.

**Anal. Calcd. for C_{11}H_{14}O : C, 81.41; H, 8.64. Found: C, 81.38; H, 8.66.**
Dehydration of m-Methyl Phenylallylcarbinol with Sulphuric Acid.— m-Methyl phenylallylcarbinol (21 g.) was refluxed with an equal quantity of sulphuric acid (15%) for one and one-half hours. The oil was separated from the water and the water extracted with ether. The oil and the ether extracts were combined and dried over potassium carbonate. After the removal of the ether the oil was distilled from under a column at 145° and 20 mm. A few cc. of the oil were collected but with continued heating the remainder charred.

In another experiment m-methyl phenylallylcarbinol (12.9 g.) was refluxed with an equal weight of sulphuric acid (15%) for one and one-half hours and then was steam distilled. The oil was separated from the water and the water extracted with ether. The oil and extracts were dried over calcium chloride, the ether removed by distillation, and the oil distilled at 65° under 2 mm. The compound was analysed by combustion. Analysis showed that the carbinol had been dehydrated.

Anal. Caled. for C_{11}H_{12}: C, 91.66; H, 8.33. Found: C, 91.64; H, 8.39.

1-m-Methyl Phenyl-1-chloro-butene-3. Into an ethereal solution of m-methyl phenylallylcarbinol, cooled in an ice salt bath, was passed hydrogen chloride for three hours. The product was washed with sodium hydroxide (5%) and then with water, and finally dried over calcium chloride. After the ether was removed, the compound distilled at 95° under 5 mm. It was analysed for Chlorine by the Parr peroxide bomb method.
The chloride (20 g.) was poured into alcoholic potassium hydroxide (14 g.) and allowed to stand for an hour. After which the mixture was refluxed for three hours and allowed to stand over night. The compound was separated from the salt formed, washed with water, extracted with ether, and dried over calcium chloride. After the ether was removed, the compound distilled at 65-67° under 1mm. The product gave a positive Beilstein test for halogen.

Anal. Calcd. for C$_{11}$H$_{12}$Cl : Cl, 19.65. Found: Cl, 19.63.

1-m-Methyl phenyl-1-chloro-butene-3 (16.8 g.) was refluxed with pyridine (84 g.) for five hours. The compound was washed with dilute hydrochloric acid, and extracted with ether. The ether was washed with sodium carbonate and water. Then it was dried over calcium chloride. The ether was removed by distillation and the product distilled at 93° under 5mm. Analysis indicated that the product obtained was the diene.

Anal. Calcd. for C$_{11}$H$_{12}$ : C, 91.66; H, 8.33. Found: C, 91.55; H, 8.35.

The Preparation of Diels and Alder Derivative. -- Maleic anhydride (2 g.) and m-methyl phenylbutadiene (2 g.) dissolved in dry thiophene free benzene were refluxed for eight hours. A mixture of tar and crystals separated. Attempts to isolate and identify the crystals failed.
Ozonization and Hydrolysis of m-Methyl Phenylbutadiene.

m-Methyl phenylbutadiene (2 g.) was dissolved in a slight excess of carbontetrachloride and a stream of ozone was passed through the cooled solution for two hours. The apparatus used was described by Henne. The ozonide was decomposed by the method of Whitmore and Church using a trace of silver nitrate as a catalyst zinc dust and a pinch of hydroquinone in an atmosphere of nitrogen. The products of the decomposition were identified as follows: formaldehyde was identified as its methone derivative. The melting point of the derivative was 186°. The melting point of a mixture of the methone derivative formed and authentic methone derivative of formaldehyde was taken. The mixture melted at 186°. Oxalic acid was identified by qualitative test. m-Tolualdehyde was identified as its semicarbazone. The semicarbazone prepared melted at 224°. This is the melting point given in the literature.

Oxidation with Potassium Permanganate. m-Methylphenylbutadiene (1 g.) was added to water (80 cc.) containing (4 g.) of

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34 Whitmore and Church, J. Am. Chem. Soc., 54, 3710 (1932).
potassium permanganate (4 g.) and sodium hydroxide (18 cc.) of ten per cent. The mixture was allowed to cool and was carefully acidified with sulphuric acid. The mixture was cooled and then heated one-half hour and then cooled. Excess manganese dioxide was removed by adding a little sodium bisulfite. The mixture was filtered and extracted with ether. The ether was removed and crystals formed. The compound was recrystallized from alcohol. The crystals decomposed at 310°. After recrystallization, the compound still decomposed at 310°.
SUMMARY

1. A brief discussion of the use of allylmagnesium bromide in synthesis was given.

2. Allylic rearrangements and the mechanism involved were discussed.

3. The Grignard reaction was used in the preparation of a new compound, m-methylphenylbutadiene.

4. m-Methylphenyl-1-chloro-butene was prepared, and analysed.

5. The structure of m-methylphenylbutadiene was proved through ozonization studies.

6. Oxidation studies on m-methylphenylbutadiene were carried out with potassium permanganate.
BIBLIOGRAPHY

Books


Articles


