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PART I: THE EFFECT OF METHYL SUBSTITUENTS AND THE STEREOCHEMISTRY IN THE COUPLING REACTION OF ALLYLIC CHLORIDES AND PHENYLLITHIUM

PART II: A KINETIC STUDY OF THE REACTION BETWEEN ARENEDIAZONIUM SALTS AND DIMETHYL PHOSPHONATE IN AQUEOUS BUFFER

PART III: THE TRITIUM ISOTOPE EFFECT IN HYDROGEN TRANSFER REACTION BETWEEN CARBON AND PHOSPHORUS

BY

Edward C. Nieh

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

Doctor of Philosophy

Thesis Director's signature

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February, 1972
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DEDICATION

To Beloved Aunt Renée
ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to Professor Edward S. Lewis and Professor Ronald M. Magid for their guidance, inspiration and patience during the course of the work presented in this dissertation.

The financial support provided by the Rice University in the form of a Rice Fellowship is gratefully acknowledged.

A special vote of thanks is due to Mrs. Janice D. Karam for her invaluable assistance in the preparation of this manuscript.

Finally, I wish to express my love and gratitude to my parents for their encouragement and help throughout these striving years.
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PART I

THE EFFECT OF METHYL SUBSTITUENTS AND
THE STEREOCHEMISTRY IN THE COUPLING REACTION
OF ALLYLIC CHLORIDES AND PHENYLLITHIUM
INTRODUCTION

The coupling reaction between allylic halides and organometallic reagents to form olefins has been a subject of numerous studies.\textsuperscript{1-7} The first reasonable scheme was put forth by Wilson, Roberts and Young.\textsuperscript{1} They reported that \( \alpha \)-methylallyl chloride and crotyl chloride react with phenylmagnesium bromide to give essentially identical product mixtures comprised of 28-23% of \( \alpha \)-methylallylbenzene and 72-77% of crotylbenzene. They suggested that coordination of magnesium with chlorine sufficiently weakens the chlorine-carbon bond that an ion-pair intermediate, with almost no memory of its origin is formed; this intermediate then collapses to the two products (Scheme 1).

\[
\text{SCHEME 1}
\]

\[
\begin{align*}
\text{CH}_3\text{-CH=CH-CH}_2\text{-Cl} & \quad \text{Cl} \quad \text{CH}_3\text{-CH=CH}_2 \\
\text{PhMgBr} \quad \text{Et}_2\text{O} & \quad \text{PhMgBr} \quad \text{Et}_2\text{O} \\
\text{CH}_3\text{-CH} \quad \text{+CH}_2 & \\
\text{Ph-Mg} \quad \text{Cl} \quad \text{Br} & \\
\text{CH}_3\text{-CH=CH}_2\text{-Ph} & \quad \text{CH}_3\text{-CH=CH}_2 \\
72-77\% & \quad 28-23\%
\end{align*}
\]

In 1951, Cristol, \textit{et al.},\textsuperscript{3} studied the reaction of \( \alpha \)-methylallyl chloride and crotyl chloride with phenyllithium in ether. The kinetic data showed that the reaction is first order in allylic chloride and first order in phenyllithium, and that the secondary allylic chloride is about three times more reactive than the primary allylic isomer. Product
distribution from the two chlorides was reported to be 5-10% of α-methylallylbenzene and 95-90% crotylbenzene. Since analysis was carried out by distillation, the product ratio was considered to be identical. These results are consistent with rate determining formation of a common ion-pair intermediate from which products were derived.

More recently, Prevost and coworkers\(^5\) published a detailed study of the reaction of cis- and trans-crotyl chloride and α-methylallyl chloride with butylsodium, butyllithium and n-, sec- and tert-butylmagnesium bromide. A portion of their results is listed in Table 1.

### Table 1.

Product Distributions in the Coupling of Monomethyl Substituted Allylic Chlorides with Organometallic Reagents

<table>
<thead>
<tr>
<th>RCl</th>
<th>R' M</th>
<th>Solvent</th>
<th>Product</th>
<th>Relative Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-methylallyl n-BuNa chloride</td>
<td></td>
<td>pentane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans-crotyl chloride</td>
<td>&quot;</td>
<td>&quot;</td>
<td>11.5</td>
<td>63</td>
</tr>
<tr>
<td>cis-crotyl chloride</td>
<td>&quot;</td>
<td>&quot;</td>
<td>24</td>
<td>75</td>
</tr>
<tr>
<td>α-methylallyl n-BuLi chloride</td>
<td></td>
<td>&quot;</td>
<td>29</td>
<td>2</td>
</tr>
<tr>
<td>trans-crotyl chloride</td>
<td>&quot;</td>
<td>&quot;</td>
<td>8</td>
<td>74.5</td>
</tr>
<tr>
<td>cis-crotyl chloride</td>
<td>&quot;</td>
<td>&quot;</td>
<td>15</td>
<td>84</td>
</tr>
<tr>
<td>α-methylallyl n-BuMgBr chloride</td>
<td></td>
<td>ether</td>
<td>29.5</td>
<td>2</td>
</tr>
<tr>
<td>trans-crotyl chloride</td>
<td>&quot;</td>
<td>&quot;</td>
<td>1</td>
<td>68.5</td>
</tr>
<tr>
<td>cis-crotyl chloride</td>
<td>&quot;</td>
<td>&quot;</td>
<td>11</td>
<td>80.5</td>
</tr>
<tr>
<td>cis-crotyl chloride</td>
<td>&quot;</td>
<td>&quot;</td>
<td>28.5</td>
<td>7.5</td>
</tr>
<tr>
<td>cis-crotyl chloride</td>
<td>sec-BuMgBr</td>
<td>&quot;</td>
<td>41.5</td>
<td>12</td>
</tr>
<tr>
<td>cis-crotyl chloride</td>
<td>tert-BuMgBr</td>
<td>&quot;</td>
<td>68</td>
<td>22</td>
</tr>
</tbody>
</table>

It is instructive to note the following features from this table.

1. A distinctly different product distribution is obtained from each allylic chloride with a given organometallic reagent.

2. The integrity of the double bond stereochemistry is preserved in the straight-chain hydrocarbon product from the coupling of \( n \)-butyl-sodium and \( n \)-butyllithium with cis- or trans-crotyl chloride.

3. Partial double bond isomerization occurs in the formation of the straight-chain hydrocarbons from the coupling of \( n \)-butylmagnesium bromide with cis- or trans-crotyl chloride.

4. Increasing loss of double bond stereochemistry and more branched product result from cis-crotyl chloride and the Grignard reagent as the butyl group changes from primary to secondary to tertiary.

Clearly, the original ion-pair mechanism is no longer adequate in explaining these results. A refined general mechanism (Scheme 2)

\[
\text{SCHEME 2}
\]
postulated that these coupling reactions have both an electrophilic and a nucleophilic component. The electrophilic component involves heterolysis of the carbon-chlorine bond as a result of prior coordination of the metal and chlorine; the nucleophilic component involves the breaking of the carbon to metal bond in the organometallic reagent concurrently with nucleophilic attack by the butyl group on the carbonium ion portion of the ion-pair. The relative importance of these two components was suggested to determine the longevity of the ion-pair, which in turn determines the composition of the product mixture. In particular, with the Grignard reagent, owing to the greater electrophilicity of magnesium and lesser nucleophilicity of the butyl group, the ion-pair is presumed to be long-lived and capable of bond rotation, thereby allowing partial loss of double bond geometry in products from cis- and trans-crotyl chloride; with the lithium or sodium reagents, the ion-pair is alleged to be short-lived and to give products before bond rotation can occur.

A variation of this ion-pair mechanism was offered by Wawzonek, et al., to account for the purported loss of double bond integrity in the products from cis- and trans-crotyl chloride with phenyllithium and phenylsodium. In their view, the ion-pair can return to covalent chloride and to the extent that α-methylallyl chloride is thus generated, both cis- and trans-crotylbenzene are expected (Scheme 3). The intermediacy of the α-methyl acetate in the acid catalyzed cis-trans interconversion of crotyl acetates and the rather high activation energy for rotation about the partial double bond of long-lived allylic cations would probably support this variation and argue against Scheme 2.
A distinctly different sort of mechanism was suggested by Gough and Dixon\textsuperscript{7} for the coupling of allyl bromide with Grignard reagents. Based on the relative rate data of phenyl-, n-butyl-, sec-butyl and tert-butylmagnesium bromide, the isolation of the minor product 2,2,3,3-tetramethylbutane, and the observation of ESR signals, a radical pair intermediate was put forth (Scheme 4). Certainly, organolithium reagents also exhibit radical character in many of their reactions,\textsuperscript{10-12} thereby
making the Gough and Dixon mechanism a likely possibility for their interaction with allylic halides. It should be noted that cis- and trans-crotyl radicals have been studied by esr techniques which show that they undergo absolutely no interconversion at or below 0°C in hydrocarbon solvents. 13

Thus, all of the suggested mechanisms have invoked an intermediate (ionic or radical) which by separation from the leaving group, bond rotation or internal return, has forgotten the identity of its precursor to some extent. In contrast to these proposals, the reaction of phenyllithium with allyl chloride gives no evidence requiring the intervention of an intermediate. Allyl chloride, labeled at the α-position with either 2H or 14C, produces labeled allylbenzene that shows that the majority of coupling has occurred at the γ-position. 14a,b

\[
\text{CH}_2=\text{CH-CH}_2-\text{Cl + Ph-Li} \rightarrow \text{Ph-CH}_2\text{CH=CH}_2 + \text{CH}_2=\text{CH-CH}_2-\text{Ph}
\]

76%  
24%

Clearly, a truly symmetrical intermediate (ionic or radical) is not involved here, nor can one account for the product distribution by secondary isotope effects. In order to gain some insight into the mechanism, a systematic study of the reaction between phenyllithium and substituted allylic chlorides was initiated in this laboratory. The results obtained by Magid, Welch and Gandour are summarized in Table 2.

Two significant features are immediately apparent from these data.

1. The product distribution from α-methylallyl chloride is distinctly different from that of either trans- or cis-crotyl chloride.
TABLE 2.

Product Distributions in the Coupling of Phenyllithium with Unsymmetrically Labeled and Monomethyl Substituted Allylic Chlorides

<table>
<thead>
<tr>
<th>Allylic Chloride</th>
<th>α-attack</th>
<th></th>
<th>γ-attack</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cis</td>
<td>trans</td>
<td>Total</td>
<td>cis</td>
</tr>
<tr>
<td>$\text{H}_2\text{C}=$CHCD$<em>2$Cl$</em>{14a}$</td>
<td>23-25</td>
<td></td>
<td></td>
<td>77-75</td>
</tr>
<tr>
<td>$\text{H}_2\text{C}=$CH$^{14}$CH$<em>2$Cl$</em>{14b}$</td>
<td>23.6</td>
<td>16</td>
<td>84</td>
<td>76.4</td>
</tr>
<tr>
<td>$\text{H}_2\text{C}=$CHCHCH$_3$ Cl</td>
<td>1.0</td>
<td></td>
<td></td>
<td>99.0</td>
</tr>
<tr>
<td>$\text{H}_3\text{C}=$CHC=CH$_2$Cl</td>
<td>100</td>
<td>0</td>
<td>75.0</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_3\text{C}=$CHH</td>
<td>0</td>
<td>100</td>
<td>74.9</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{C}=$CCD$_2$Cl</td>
<td></td>
<td></td>
<td></td>
<td>57.5±2</td>
</tr>
</tbody>
</table>

2. α-Attack on either cis- or trans-crotyl chloride gives the corresponding cis- or trans-crotylbenzene respectively. The geometry of the double bond is quantitatively preserved.

The first of the above features contradicts the results of Cristol, et al., that nearly identical product distributions are obtained from the reactions of α-methylallyl chloride and crotyl chloride. It should be recognized, however, that this work was performed before the advent of gas chromatography, the product separation was accomplished by distillation, consequently, they failed to identify 1-phenyl-2-methylcyclopropane as a product of the crotyl chloride reaction since
it most likely co-distilled with crotylbenzene.* Thus, the 90-95% relative yield quoted for crotylbenzene coming from crotyl chloride was too high be about 20%.

The second feature is in direct contrast to the claim of Wawzonek, et al., that the geometry of the double bond is not preserved starting with "pure" cis- or trans-crotyl chloride. In fact, Magid and Gandour demonstrated that the apparent loss of stereochemistry is due exclusively to the use of impure starting materials.\textsuperscript{14c}

The findings in this laboratory have cast strong doubts on existing mechanistic interpretations involving an intermediate. As a part of a continuing effort to clarify the mechanistic details of the coupling reaction, the work described in Part I of this thesis has the following principal objectives:

1. To test the generality of the findings in this laboratory regarding the influences of a methyl substituent on the relative amounts of α- and γ-attack and on the fate of double bond geometry, and to reach mechanistic conclusions based on any relevant trends that might be found. To this end, the coupling reactions of dimethyl substituted allylic chlorides with phenyllithium were investigated.

2. With the hope that the stereochemical course of the coupling reaction of a suitably designed substrate would shed further light on the mechanism, the reaction of optically active cis-3-chloro-1-butene-1-d with phenyllithium was also investigated.

The results are reported and discussed in the following section.

---

*The fact that 1-phenyl-2-methylcyclopropane and cis- and trans-crotyl benzene do not separate on a 10 ft. SE-30 column indicates that they have similar boiling points.
RESULTS AND DISCUSSION

The reaction of all of the possible dimethyl substituted allylic chlorides $\sim$ with phenyllithium was investigated first.

\[ \begin{array}{cccc}
H_3C & C=CH_2-Cl & H_3C & C=CH_2-Cl \\
H & C=CH_3 & H & C=CH_3 \\
\text{1} & \text{2} & \text{2} & \text{4} \\
H_3C & C=CH-CH_2-Cl & H_3C & C=CH-CH_2-Cl \\
H_3C & C=CH-CH_2-Cl & H_3C & C=CH-CH_2-Cl \\
\text{5} & \text{6} & \text{6} & \text{7} \\
\end{array} \]

Syntheses of 1-chloro-2-methyl-trans-2-butene (1), 1-chloro-2-methyl-cis-2-butene (2), 3-chloro-2-methyl-1-butene (3), and 3-chloro-3-methyl-1-butene (4) are reported in the literature; 1-chloro-3-methyl-2-butene (5) is commercially available. In practice however, none of these compounds (whether purchased or prepared) was sufficiently free of allylic isomers to be used directly for the coupling reaction. In addition, these compounds are relatively unstable, and often decompose and/or isomerize upon storage. Thus, it is necessary to carefully purify each material (see experimental section) and use it immediately.

Since allylic chlorides 6 and 7 are symmetrical in the sense that attack at either the $\alpha$ or $\gamma$ carbon would yield the same product, it was necessary to distinguish the termini of the allylic system by a suitable isotopic label.
A likely precursor for 6, 4-hydroxy-trans-2-pentene-5-$^{14}$C (8-$^{14}$C) was readily prepared by treatment of $^{14}$C-enriched methyl magnesium iodide with crotonaldehyde. Nearly every attempt to convert 8-$^{14}$C into 6-$^{14}$C, however, led to complete (or nearly complete) randomization of the label (see experimental section for a compilation of the unsuccessful methods).

The location of the radioactive carbon in alcohol 8-$^{14}$C and chloride 6-$^{14}$C was determined by degradation of the material by ozonolysis,** and analysis of the activity of the resulting acetaldehyde. Since the $^{14}$C trace labeled.

**This method of degradation was chosen because of its successful application in the analysis of $^{14}$C-labeled allyl chloride.$^{14b,15}$
alcohol $\sim^{14}_2$C was position specific in its label, we considered the possibility that some or all of the chloride-producing reaction had, in fact, afforded unscrambled $\sim^{14}_2$C and randomization was occurring during the degradation itself. To clarify this point, $^2$H-labeled alcohol $\sim^8$-d was prepared, the idea being that one can locate the label in alcohol $\sim^8$-d and the corresponding chloride $\sim^6$-d by nmr analysis both before and after ozonolysis. The numerous failures of position specific labeling were once again encountered when alcohol $\sim^8$-d was treated with a variety of reagents. Complete or nearly complete scrambling was the general result, the largest label spreads at $\alpha$: $\gamma$ carbons being 57:43 and 65:35 with phosphorus trichloride and phosphorus oxychloride, respectively, in all cases 7-13% of the cis-chloride $\sim^7$ was also produced. It would, therefore, appear that the difficulty resides in the synthesis of the chloride, and in confirmation of this, ozonolysis of a sample of $\sim^6$-d having 56% of deuterium at the $\alpha$-carbon and 44% at the $\gamma$-carbon yielded acetaldehyde, trapped as the dimedone derivative, which was deuterated to the extent of 44%.

Thus, the method of degradation is reliable, and it must be concluded that none of the alcohol conversions that we tried were very satisfactory. Consequently, the synthesis of the even more labile cis-chloride $\sim^7$-d or $\sim^{14}_7$C was not pursued.
The reaction of dimethyl substituted allylic chlorides 1, 2, 3, 4, 5, 6-d and 6-^{14}C with phenyllithium gave the corresponding coupling products as the only isolable and identifiable materials. The yields and product distribution are summarized in Table 3.

In general, 70-80% material balances were obtained. The remainder of starting materials appears to be in the form of a high boiling material tentatively identified as a mixture of coupling products from starting material with biphenyllithium (formed in small quantity during the preparation of phenyllithium) and a nondistillable polymeric oil (perhaps by elimination of HCl and anionic polymerization of the resulting diene). In no case do we find any C_{10}-diene, a product which would result from initial halogen metal exchange followed by coupling of the resulting allyllithium with the starting allylic chloride, nor are any dimethyl cyclopropenes produced from dimethyl substituted allylic chloride.

The possibility that some of the high boiling materials result from abstraction of the benzylic proton of the hydrocarbon product producing an anion \(^{16}\) which then couples with starting material was considered. Such a complication would not only lower the overall yield, but more seriously, might selectively remove one of the hydrocarbon products from the reaction.
TABLE 3.
YIELDS AND PRODUCT DISTRIBUTIONS IN THE COUPLING OF PHENYLLITHIUM WITH DIMETHYL-SUBSTITUTED ALLYLIC CHLORIDES

<table>
<thead>
<tr>
<th>Allylic Chloride</th>
<th>cis:trans</th>
<th>Total Yield (%)</th>
<th>cis:trans</th>
<th>Total Yield (%)</th>
<th>Ratio α-γ-attack</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ζ</td>
<td>0:100c</td>
<td>74.8</td>
<td>3.5</td>
<td>95.5/4.5</td>
<td></td>
</tr>
<tr>
<td>Ζ</td>
<td>100:0c</td>
<td>80.2</td>
<td>6.4</td>
<td>92.6/7.4</td>
<td></td>
</tr>
<tr>
<td>Ζ</td>
<td>7.8</td>
<td>30±2:70±2c,d</td>
<td>69.8</td>
<td>10.0/90.0</td>
<td></td>
</tr>
<tr>
<td>Ζ</td>
<td>trace</td>
<td>68.2</td>
<td>0/100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ζ</td>
<td>80.0</td>
<td>trace</td>
<td>100/0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-d</td>
<td>g</td>
<td>39.2</td>
<td>g</td>
<td>39.2</td>
<td>50/50</td>
</tr>
<tr>
<td>6-d</td>
<td>g</td>
<td>40.0</td>
<td>g</td>
<td>40.0</td>
<td>50/50</td>
</tr>
<tr>
<td>6-14-c</td>
<td>i</td>
<td>36.6</td>
<td>i</td>
<td>36.6</td>
<td>50/50</td>
</tr>
</tbody>
</table>

---

a The allylic chloride was added to a two-fold excess of ethereal phenyllithium at 25°C; product yields were determined by quantitative glpc.
b The isomeric purity of each of the starting materials is given in the Experimental Section.
c According to the naming of these compounds as 1-phenyl-2-methyl-2-butenes, the trans compound has the geometry of 1 and the cis that of 2.
d This material was obtained as an inseparable mixture of cis and trans alkenes; the isomer ratio was determined both by nmr peak areas and by glpc (300 ft capillary column, polyphenyl ether).
e The starting material had 57% of deuterium at the α-carbon and 43% at the γ-carbon and contained 12.5% of the cis isomer.
f The starting material had an α:γ label spread of 65:35, and contained 7% of the cis isomer.
g In both cases, the cis:trans alkene ratio was 12:88, but since neither starting material was free of cis isomer, the mechanistic significance is not clear.
h The starting material had 58.1% of 14C at C5 and 41.9% at C1.
i The cis:trans product ratio was not determined.
mixture, thereby making the $\alpha/\gamma$ attack ratios unreliable. However, based on a number of observations, such a process is not occurring to any appreciable extent. For example, each of the products from the dimethyl compounds $\sim$-$\sim$ can be recovered unchanged when subjected to the reaction conditions; in none of the reaction mixtures are any substituted styrenes found, and products having a benzyllic deuterium showed no loss of label during the reaction. Thus, it is not unreasonable to assume that the lack of material balance is due exclusively to processes independent of the coupling reaction. Consequently, the isomer distributions listed in Table 3 may be used for meaningful discussion.

First, one notes the absence of one of the more important processes observed in the reaction of phenyllithium with allyl chloride and mono-methyl substituted allyl chlorides: $\alpha$-elimination to a vinyl carbene which closes to a cyclopropene. This cyclopropene may either be converted into a "stable" organolithium compound by addition of phenyllithium across the strained double bond or lose a proton to phenyllithium to form 1-cycloprophenyllithium.

In this work neither a substituted cyclopropene nor its phenyllithium adduct were ever detected as a product. This is understandable since an additional methyl group undoubtedly increases the reactivity of allylic chlorides for reactions involving rate determining cleavage.

\[
\begin{align*}
\text{CH}_2=\text{CH}-\text{CH}_2-\text{Cl} + \text{PhLi} & \quad \longrightarrow \quad \text{CH}_2=\text{CH}-\text{CH}_2 + \text{C}_6\text{H}_6 + \text{LiCl} \\
\downarrow \quad & \\
\text{H}_2\text{C} & \quad \text{CH-Ph} \quad \text{H}^+ \\
\text{CH} & \quad \text{H}_2\text{C} \quad \text{CH-Ph} \quad \text{PhLi} \\
& \quad \text{H}_2\text{C} \quad \text{CH-Li} \quad \text{H}_2\text{C} \quad \text{CH} \quad \text{PhLi} \\
& \quad \text{H}_2\text{C} \quad \text{C-Li} \quad \text{H}^+ \\
& \quad \text{H}_2\text{C} \quad \text{CH} \quad \text{CH}
\end{align*}
\]
carbon chlorine bond, and at the same time lowers the acidity of the allylic proton by induction. Furthermore, Magid, et al.,\textsuperscript{17} have presented evidence that the presence of lithium bromide or lithium alkoxide in the phenyllithium solution inhibits $\alpha$-elimination with 3-chloro-2-methylpropene while allowing formation of coupling products in high yield.* The definite presence of lithium salts in phenyllithium used in this work may also play a role in inhibition of the $\alpha$-elimination process.

An alternative path (Scheme 5) to the coupling product which is not operative involves initial halogen metal exchange of phenyllithium

\textbf{SCHEME 5}

\[
\begin{align*}
\text{CH}_3\text{CH}=\text{CHCHCH}_3 \quad \text{PhLi} & \quad \text{CH}_3\text{CH}=\text{CHCHCH}_3 \quad \text{PhCl} \\
& \text{Li} \\
& \text{CH}_3 \\
\text{CH}_3\text{CH}=\text{CHCHCH}=\text{CHCH}_3 & \quad \text{CH}_3\text{CH}=\text{CHCHCH}_3 \\
& \text{Ph}
\end{align*}
\]

with the allylic chloride followed by coupling of the resulting chlorobenzene and allyllithium.**

* Use of halide-free phenyllithium for reaction with 3-chloro-2-methylpropene provides a highly efficient and convenient synthesis of 1-methylcyclopropene.

** Allylbenzene is quantitatively converted by $n$-butyllithium in THF into phenylallyl anion which couples with allyl chlorides in high yields.\textsuperscript{17}
Such a two-step mechanism in our system would certainly produce chlorobenzene and $C_{10}$ diene. This pathway can be dismissed, since neither chlorobenzene nor any $C_{10}$ dienes are among the products.

The influences of methyl substitution on $\alpha/\gamma$ product ratio with all the dimethyl substituted allylic chloride studied, strongly resembled that observed by Magid and Gandour. The prominent effect of $\alpha$- or $\gamma$-methyl substitution retarding attack at its point of attachment is demonstrated by all the entries in Table 3. The influence of the $\beta$-methyl group is also similar to that encountered earlier. It will be recalled that the $\alpha/\gamma$ product ratio increases from 24/76 to 57/43 when a $\beta$-methyl group is introduced into the allyl chloride (Table 2). In the same manner, this ratio increases from 75/25 with either trans- or cis-crotyl chloride to 95/5 for chloride; this ratio increases from 1:99 with $\alpha$-methylallyl chloride to 10:90 for chloride $\gamma$.

The origin of the influence of $\alpha$, $\beta$, or $\gamma$ substitution on the product distribution is not immediately apparent. While the retardation by the $\alpha$- and $\gamma$-methyl group is most likely attributable to steric hinderance to reaction at the point of attachment, no explanation can be offered for the influence of the $\beta$-methyl group.

The product distributions from chlorides $\alpha$, $\beta$ and $\gamma$ are similar, but definitely not the same, as a mechanism involving a common intermediate would demand.

The product distributions from chlorides $\delta$, $\epsilon$ and $\zeta$, each of which has two methyl groups attached to the allylic termini, are less informative. The fact that $\delta$ and $\zeta$ give only one product, 1-phenyl-3-methyl-2-butene is consistent with the trend that $\alpha$- and $\gamma$-methyl
groups retard reaction at the point of attachment, but it is also consistent with a common intermediate mechanism. By the same token, the fact that chloride 6 gave equal amounts of \( \alpha \)- and \( \gamma \)-attack could be due to an offsetting effect of the \( \alpha \)- and \( \gamma \)-methyl groups or the intervention of a symmetrical intermediate. In view of the enormously greater SN\(_1\) reactivity\(^2\) of these chlorides in solvolysis reactions, a change in mechanism in the direction of ion-pair intermediates is not unreasonable.

One of the principal reasons for investigating the reactions of chlorides 1, 2, 6, and 7 was to ascertain whether substrates bearing substituents that are capable of stabilizing ionic or radical intermediates would still lead to products of retained stereochemistry. This attempt was at least partially successful since chlorides 1 and 2 undergo \( \alpha \)-attack with complete retention of their stereochemical integrity. Unfortunately, the difficulties in synthesis described earlier, prevented the use of double bond geometry of chlorides 6 and 7 as a mechanistic probe.

A more sensitive probe for differentiating between a concerted and a stepwise mechanism is the stereochemistry of the reaction involving a chiral center.

In order to fully elucidate the stereochemistry of the coupling reaction, a substrate which meets all of the following conditions is required:

1. It must have an asymmetric \( \alpha \)-carbon.

2. Two different substituents must be present on the \( \gamma \)-carbon, and the geometry of the double bond must be well defined.
3. Coupling reactions should occur at both allylic positions, and the \(\alpha\) and \(\gamma\)-coupling products must be cleanly separable.

4. \(\gamma\)-Attack must produce a separable mixture of \textit{cis}- and \textit{trans}-olefins.

5. The absolute configuration and the maximum rotation of the allylic chloride and of its coupling product should be determinable with a reasonable degree of accuracy.

The reaction of phenyllithium with a substrate (of generalized structure A) meeting all of these conditions is illustrated in Scheme 6.

\*The terms \textit{syn} or \textit{anti} used for \(\gamma\)-attack refer to processes in which coupling occurs on the same or opposite side of the allylic system, respectively, as the departing chloride.
Initially, optically active 4-chloro-trans-2-pentene \((R_1=R_5=\text{CH}_3; R_2=R_3=R_4=\text{H})\) unsymmetrically labeled with either \(^2\text{H}\) or \(^{14}\text{C}\) appears to meet all the above conditions. However, this approach was abandoned in view of the difficulties encountered in the conversion of alcohol \(~\text{d}~\) and \(~^{14}\text{C}~\) into the corresponding chloride \(~\text{d}~\) and \(~^{14}\text{C}~\). We were further discouraged by the lack of reliable methods for the determination of maximum rotation in a substrate in which the chiral center is associated with a very labile carbon-chlorine bond. We were therefore forced to consider using a less reactive allylic chloride, one that is only mono substituted. A substrate such as \(1\)-chloro-trans-2-buten-1-d\ or the corresponding cis isomer, satisfies all but condition 4. The two products of \(\gamma\)-attack cannot be separated and, since the newly generated asymmetric centers of the two 3-phenyl-1-buten-1-d's would be of opposite chirality, the total sample would give no rotation.

Thus, we turned our attention to optically active 3-chloro-cis-1-buten-1-d \((17)\) as substrate for this study. Unfortunately, 3-chloro-1-butene is known to couple almost exclusively by \(\gamma\)-attack, \(^{14}d\) and thus condition 3 is not met. In order to determine the stereochemistry of \(\alpha\)-attack, a compound such as \(1\)-chloro-trans-2-buten-1-d is required. Since there are several reports on the coupling reaction of organometallic reagents with benzylic chiral substrates, \(^{19}\) we concentrated our entire effort on the preparation and reaction of optically active chloride 17 for which the stereochemistry of allylic attack can be determined.
The synthesis of optically active (R)-(−)-17 is summarized in Scheme 7. In general, these reactions were performed so as to obtain pure material at each step; the yields reported in the experimental section are based on the isolated >99% pure products in each reaction. Some of the steps of the synthesis merit a few words of explanation.

Conversion of alcohol 9 into benzoate 10 was necessary for two reasons: first, deuterium exchange on 9 is difficult owing to its complete miscibility with water which makes isolation of 9 after each exchange laborious; use of 10 and the two phase D$_2$O/CCl$_4$ exchange system not only avoids this recovery problem but also allows the exchange to be conveniently monitored by nmr. Second, hydroboration of alcohol 9 produces none of the desired reduction product, whereas benzoate 10 gives quite acceptable yields.
The hydroboration–protonolysis sequence for stereospecific cis reduction has been studied in some detail, but the reproducibility of yields appears to be rather poor. For example, Brown and Zweifel, claimed an 80% conversion of 1-hexyne into 1-hexene, but the same reaction in the hands of Murray and Williams gave only 40%. In the case of deuterated benzoate, the literature procedure gives in only 10-15% yield. We discovered, however, that if both hydroboration and protonolysis are carried out at -5 to 0° and if protonolysis is performed immediately after completion of the first stage typically 40% yield of could be realized. One can speculate that the low yields with the literature procedure result from a competing reaction in which the initial adduct undergoes intramolecular catalyzed elimination to an allene before acetic acid is added; proceeds regiospecifically to because of the directing influence of the adjacent ester. A similar rationalization was offered by Brown and Gallivan in the hydroboration of allylic acetate. Zweifel, et al., have indeed found that disiamylborane reduction of internal propargylic chlorides yields allenes upon treatment of base; with the borane adduct , the needed base is present within the molecule itself. To the extent that such a mechanism is indeed responsible for low yield of , suitable modifications of the conditions would offer a new and facile synthesis of a wide range of optically active allenes.
That the reduction does, in fact, proceed stereospecifically cis is clearly demonstrated by first order analysis of the nmr spectra of \( \underline{12}, \underline{13}, \underline{14} \) and \( \underline{17} \) as compared to their undeuterated analogs (see experimental section for complete spectral data). Briefly, (1) each of the labeled compounds lacks the lower field of the absorption due to the terminal vinyl hydrogen;\(^{21}\) (2) the remaining pair of vinyl hydrogens give \( J_{\text{vic}} = 10.0 \) Hz (typical of cis coupling); the other \( J_{\text{vic}} = 16.6-17.3 \) Hz found in the unlabeled compound is absent;\(^{23}\) (3) each of the deuterated compounds shows coupling of the internal vinyl hydrogen to deuterium \( J = 2.0-2.5 \) Hz, as expected for their trans relationship.\(^{23}\)

Treatment of benzoate \( \underline{12} \) with LiAlH\(_4\) gave alcohol \( \underline{13} \), which was resolved according to the standard procedure\(^{24}\) via the brucine salt of the corresponding phthalate.

Optically active (+)-phthalate \( \underline{15} \) (75.6% optically pure\(^{24}\)) yields (+)-alcohol \( \underline{16} \), known to have the S-configuration\(^{24a}\) (75.6% optically pure\(^{11b}\)) which is converted into chloride \( \underline{17} \) (50.4% optically pure\(^{25}\)) according to the procedure of Young, et al.\(^{25}\) It is interesting to note that the 25.2% recemization compares favorably with Young's data, whereas the double bond geometry in the resulting chloride showed no sign of isomerization.

Reaction of this chloride with phenyllithium produces three coupling products, \( \underline{20}, \underline{21} \) and \( \underline{22} \), in a ratio of 86.0:13.5:0.5. Pure samples of \( \underline{20} \) and \( \underline{21} \) could be obtained by preparative glpc. Identification was based upon glpc and nmr comparisons with undeuterated materials; both products displayed a full deuterium atom at the benzylic position. The product of \( \alpha \)-coupling, \( \underline{22} \), could not be isolated but its identity was established by glpc retention times on three different columns. Based


\[ \text{HO-CH}_3 \]

\[ \text{Cl} \]

\[ \text{PhLi} \]

\[ \text{CHD} \]

\[ \text{Ph} \]

\[ \text{CH}_3 \]

\[ \text{D} \]

\[ \text{Ph} \]

\[ \text{CHCH}_3 \]

\[ (S)-(+)\sim \text{16} \quad (R)-(\sim)\sim \text{17} \]

\[ 20 \quad 21 \quad 22 \]

upon the preservation of double-bond geometry when \( \delta \)-substituted allylic chlorides are converted into unrearranged coupling products\(^{14c}\) the stereochemistry shown in \( \sim \) is assumed.

Careful distillation of the crude reaction mixture afforded an 86.0:13.5:0.5 mixture of \( \sim \) 20, \( \sim \) 21, and \( \sim \) 22, 2.500 g of which was diluted to 9.500 g with a sample of authentic unlabeled racemic materials of exactly the same composition. Spinning band distillation then gave an 86.5:13.5 mixture of \( \sim \) 20 and \( \sim \) 21, free of \( \sim \) 22 whose removal is important because of its expected large rotation. This sample was diluted with an exactly equal weight of unlabeled racemic \( \sim \) 20 and \( \sim \) 21 in the same ratio. The mixture now contains 13.2\% of deuterated materials.

Since neither the absolute configuration nor maximum rotation of alkenes \( \sim \) 20 and \( \sim \) 21 is known, this sample was divided into two portions, A and B which were treated as follows: A was reduced with diimide to optically active 1-phenylbutane-1-\( \Delta^1 \) D\( \sim \), \( \sim \) 23a, \( \sim \) 26 \( \alpha \)\( \sim \)1\( \Delta^1 \) D -0.0253\( \pm \)0.0002\( ^0\) (neat, \( \sim \) = 0.298); B, by preparative gcpc, yielded pure \( \sim \) 20 which was similarly reduced to \( \sim \) 23b, \( \sim \) \( \alpha \)\( \sim \)1\( \Delta^1 \) D -0.0329\( \pm \)0.0002\( ^0\) (neat, \( \sim \) = 0.298).

Adjustment of these observed rotations for the fact that the samples\( \sim \) 22b are only 13.2\% deuterated leads to specific rotations: \( \sim \) 23a, \( \sim \) \( [\alpha] \)1\( \Delta^1 \) D -0.780\( ^0\) (neat) and \( \sim \) 23b, \( \sim \) \( [\alpha] \)1\( \Delta^1 \) D -1.02\( ^0\) (neat), corresponding to optical purities\( \sim \) 26 of 35.0\% and 45.6\%, respectively.
One of the plausible mechanisms for γ-coupling involves concerted C–Cl cleavage and C–C formation in a six-membered transition state. Were such a mechanism in fact operative, the phenyl group would enter syn to the departing halide. Other mechanisms proceeding via ionic or radical intermediates could also result in syn attack if it is assumed that coordination of metal with halide is the initial step, and that the intermediate collapses to product without rotation about the partial double bond. By either view, the mechanism resembles that for the reaction of secondary amines with allylic chlorides27 for which syn attack has been established with a cyclic allylic ester.28*

*It is unfortunate that the stereochemistry of reaction with an acyclic substrate has not been determined, since the observed syn attack on the cyclohexenyl system28 may be due to conformational factors (anti-parallel attack) peculiar to such a cyclic system rather than to any inherent stereoelectronic preference of the $S_N^2'$ reaction.
A possible variation of the above would involve coordination of phenyllithium to halide concerted with, or followed by, attack of a second molecule of phenyllithium either from above (anti) or below (syn) the plane.

The optical rotations observed for reaction of (R)-(−)-17 with phenyllithium can easily be interpreted in terms of a mechanism proceeding by syn attack. Scheme 8 illustrates the expectations for such a process: cis product 21 should have the (S) configuration and on reduction should produce (S)-(+-)-23, whereas trans olefin 20 should be (R) and should give (R)-(−)-23.

**SCHEME 8**

![Chemical structure images showing the reaction mechanism and optical rotations](image-url)
Sample B, above, from which pure trans olefin \( \sim \) could be isolated, led to \( \sim \) (R)-(−)-23, which was 45.6% optically pure. Since starting chloride \( \sim \) (R)-(−)-(17) was 50.4% optically pure, this corresponds to an asymmetric transfer to the extent of 91% (i.e., >95% syn attack). Because of the uncertainty in the maximum rotation of \( \sim \) 26 it is not unlikely the syn attack is the exclusive process.

Sample A \( \sim \) containing 20 and 21 in a ratio of 86.5:13.5 produced \( \sim \) (R)-(−)-23 which was 35.0% optically pure. If one assumes 100% syn attack leading to the two components, then the result may be analyzed as follows. Product 20 should be composed of 86.5% of the (R)-(−)-enantiomer and 13.5% of the (S)-(−). Since chloride 17 was only 50.4% optically pure, one expects a contribution of \(-0.97^\circ\) from \( \sim \) (R)-(−)-23 \( \sim \) (-2.23) X \( \sim \) (0.504)(0.865) and of \(+0.16^\circ\) from \( \sim \) (S)-(−)-23 \( \sim \) (+2.23)(0.504)(0.135) making the net rotation \(-0.81^\circ\), in excellent agreement with the observed \([\alpha]_{27}^D\) \(-0.78^\circ\). To exactly reproduce this number, one need only assume that both reactions are stereospecific to the extent of 95%.

In summary, this investigation of the reaction between allylic chlorides and phenyllithium was directed towards distinguishing between a concerted and a stepwise mechanism. In a stepwise mechanism, the intermediate by definition would reside in a potential energy well having barriers separating it from the reactants and products. In this particular case, the intermediate allylic cation or radical can have "sub-barriers" within the well. These "sub-barriers" could be associated with rotation about the partial double bond, symmetrization between the two allylic carbons, and symmetrization about a chiral center involved in the reaction. In the event that the barrier leading to product is higher than those "sub-barriers" mentioned earlier, the intermediate will
be revealed by the part of the product formed from intermediates that have crossed these "sub-barriers" and which will show isomerization of the double bond, symmetrization of allylic center and most certainly loss of chirality. If, on the other hand, the barrier leading to product is sufficiently lower than the "sub-barriers", the reaction will take on the characteristics of a concerted process.
Product analysis and stereochemical data established in this work as well as in that of Welch and Gandour, support the conclusion that coupling at both the α- and γ-carbon is either a direct one-step process or involves intermediates (ionic or radical) which are separated from products by a very low energy barrier (i.e., their life-times are not long enough to allow loss of memory of the geometric structure of their precursors).
EXPERIMENTAL SECTION

Instruments

Analytical glpc was performed on a Perkin-Elmer Model 800 Gas Chromatograph (flame ionization detector) and utilized the following columns: A, 10 ft x 1/8 in., $\beta,\beta'$-oxydipropionitrile, (15%) on chromosorb P; B, 20 ft x 1/8 in., (10%) Carbowax 20 M on Chromosorb W; C, 12 ft x 1/8 in., TCEP (15%) on Chromosorb W; and D, 20 ft x 1/8 in., diethylene glycol succinate (20%) on Chromosorb P (HMD5). In those cases in which quantitative glpc was used for yield determination, the internal standard method was employed. Peak areas were measured with a Disc integrator, an integral part of a Speedomax H recorder.

Preparative glpc was performed on either a Varian Aerograph Model 202-B Gas Chromatograph (thermal conductivity detector) or a Hewlett-Packard F & M Prep Master Jr., Model 776 (flame ionization detector) and utilized the following columns: E, 10 ft x 1 in., $\beta,\beta'$-oxydipropionitrile (15%) on Chromosorb P; F, 10 ft x 3/8 in., Carbowax 20 M (20%) on Chromosorb W; and G, 12 ft x 3/8 in., TCEP (15%) on Chromosorb P.

Nmr spectra were obtained on a Varian Association A56/60A Spectrometer. Radioactivity measurements were made with a Packard Tri-carb Model 3365 Liquid Scintillation Spectrometer. The scintillation solution consisted of Packard 25 x concentrated scintillator and was diluted 25-fold with toluene.

Optical rotations were measured with a Bendix Automatic Polarimeter; the cell length was 0.298 dm. Rotations were taken either of solutions (reported as $[\alpha]_D^T$) or of neat liquids (reported as $\alpha_0^T$)
adjusted to a path length of 1 dm or as \( [\alpha]_D^T \) adjusted for path length
and density).

All reactions involving lithium or organolithium reagents were run in an argon atmosphere.

**Materials**

Reagent grade commercial materials were used without further purification, except for the following: thionyl chloride (Matheson, Coleman and Bell) was purified according to the procedure of Fieser and Fieser,\(^{28}\) phosphorus trichloride (J. T. Baker Chemical Co.) was fractionated through a column packed with glass helices immediately before use; methyl-\(^{14}\)C iodide (50 μCi) (Amersham/Searle) was diluted with 500 g of methyl iodide (Matheson, Coleman and Bell). Phenyllithium was prepared by the slow addition of bromobenzene in ether to lithium shot\(^{30}\) in ether at 0-10\(^\circ\)C, after which the mixture was stored at 0\(^\circ\)C for 12 hr and filtered through glass wool. By performing this reaction slowly and at relatively low temperature, the 0.7 to 0.8 M solution instead of being dark brown was pink in color, and gave relatively less biphenyl as by-product; analysis of the solution was done by "double titration."\(^{31}\) Ether used in reactions involving phenyllithium was freshly distilled from lithium aluminium hydride. Bis-(2-methoxyethyl)-ether (Matheson, Coleman and Bell) was purified according to the procedure of Zweifel and Brown;\(^{32}\) disiamylborane was prepared according to the literature procedure.\(^{32}\)
Reactions

Preparation and Purification of Allylic Chlorides. Each of the starting materials, whether purchased or synthesized, was purified as indicated below and used immediately. All of the materials gave spectra consistent with their structures.

A. 3-Methyl-3-Chloro-1-butene (5). Commercial material (Aldrich Chemical Co.) was purified by preparative glpc (column E) and was shown to be >99% isomerically pure (column A).

B. 1-Chloro-2-methyl-trans-2-butene (1). Following the procedure of Young, et al., 33 3-hydroxy-2-methyl-1-butene was treated in dilute ether solution with thionyl chloride at -50°. Glpc analysis (column A) showed that the crude product was composed of 68% of the desired chloride 1, 30% of cis-chloride 2, and 2% of allylic isomer 3. Preparative glpc (column E) yielded material which, by nmr and glpc, was judged to be >97.5% isomerically pure; no improvement in purity was achieved after a second preparative glpc.

C. 1-Chloro-2-methyl-cis-2-butene (2). Angelic acid (2-methyl-cis-2-butenoic acid) was prepared from butanone in five steps, according to the procedure of Buckles and Mock. 34 Reduction with LiAlH₄ yielded 1-hydroxy-2-methyl-cis-2-butene which, after fractionation through a glass helices packed column, was judged (nmr and glpc analysis, column A) to be >99% pure. Conversion into chloride 6 was achieved by thionyl chloride and tri-n-butylamine in ether at -50°. 33 Flash distillation yielded a material which was >90% chloride 2 (column A); preparative glpc (column E) yielded material which was >99% pure.

D. 3-Chloro-2-methyl-1-butene (3). Chlorine was bubbled into a solution of 2-methyl-2-butene and one equivalent of NaHCO₃ in ether at
Fractional flash distillation yielded a sample which contained 85% (column A) of the desired chloride; two more flash distillations increased the purity to >98%.

E. 3-Chloro-3-methyl-1-butene (A). Reaction of gaseous HCl with isoprene in ether at -50⁰, followed by neutralization with NaHCO₃ and distillation through a glass helices packed column bp 30-32⁰ (120 mm) yielded material which (nmr and glpc analysis, column A) was >97% pure.

F. 4-Chloro-trans-2-pentene-4-d (6-d). Reduction of trans-2-pentene-4-one with LiAlD₄ produced the corresponding alcohol (6-d) which, by nmr analysis, was at least 98% monodeuterated at C-4. Reaction of the alcohol with PCl₃ and pyridine at -40⁰⁰ yielded material which, after two flash distillations, was shown (column B and C) to be composed of 97% of trans-chloride and % of cis; nmr analysis showed that substantial allylic rearrangement had occurred, 57% of deuterium being at C-4 and 43% at C-2. When POCl₃ was substituted for PCl₃ in the above reaction, a somewhat greater label spread was achieved: 65% of deuterium at C-4 and 35% at C-2; 3% of cis-chloride was present.

G. 4-Chloro-trans-2-pentene-5-¹⁴C (6-¹⁴C). Reaction of methyl-¹⁴C-magnesium iodide with crotonaldehyde yielded 4-hydroxy-trans-2-pentene-5-¹⁴C (8-¹⁴C); the position of the label was confirmed by ozonolysis (>99.5% at C₅). Numerous attempts to convert this alcohol into the corresponding chloride while avoiding allylic rearrangement were made, but most of them failed. To summarize, the following reagents led to complete (or nearly complete) scrambling of the label (as determined by ozonolysis): PCl₃ and pyridine in ether at either 0⁰ or -30⁰; PCl₃ and LiCl in hexamethylphosphoramide at -5⁰; hexachloroacetone and
triphenylphosphine at $15^\circ$ (modeled after the established procedure with $\text{CCl}_4$ and triphenylphosphine$^{37}$ which is unsuitable because of the similar boiling points of $\text{CCl}_4$ and product); thionyl chloride in ether, with or without pyridine (an attempt to prepare the chloride with complete allylic rearrangement$^{33}$). The procedure of Stork, et al.,$^{39}$ but with methyllithium replaced by pyridine led to extensive elimination.

The best sample of $^{14}\text{C}$-labeled chloride was obtained by application of the procedure used to prepare $^2\text{H}$-labeled chloride 6-d having a 65/35 label spread. From 4.30 g (0.050 mole) of 4-hydroxy-trans-2-pentene-5-$^{14}\text{C}(\sim^{14}\text{C})$ (2.53 x $10^6$ dpm/mole), 7.60 g (0.050 mole) of $\text{POCl}_3$, and 1 ml of pyridine was obtained 3.60 g (69%) of labeled chloride, ozonolysis of which produced acetaldehyde whose dimesdine derivative had an activity of $1.06 \times 10^6$ dpm/mole; thus the distribution of $^{14}\text{C}$ in the chloride is 58.1% at $\text{C}_5$, 41.9% at $\text{C}_1$.

**General Procedure for Ozonolysis of Labeled Allylic Alcohols,**

**Allylic Chlorides, and Coupling Products.** The procedure of Young, and coworkers,$^{15}$ for cleavage of allyl chloride was modified to allow milder conditions and to trap acetaldehyde as it was formed. Excess ozone was bubbled through a solution containing ca. 0.02 mole of the substrate in 30 ml of methylene chloride maintained at $-15^\circ$. Solvent was removed with a rotary evaporator (without external heating) and the residue was added to 5 g of zinc dust and 50 ml of 10% aqueous acetic acid at room temperature. Acetaldehyde, thus generated, was swept by a stream of argon (30 ml/min) through an ice-water condenser and into a dimesdine trap (ca. 300 ml of 0.1 N dimesdine in sodium
acetate/acetic acid buffer, adjusted to pH 5.8). After ca. 30 min, the decomposition was complete; the contents of the trap were acidified to pH 4 with acetic acid. Typically, 80% (based upon dimedone) of the 1:2 derivative, mp 140-143°, was formed. Three recrystallizations from methanol/water followed by drying in a vacuum desiccator provided the pure derivative, mp 142-143°.

**General Procedure for Reaction of Allylic Chlorides with Phenyl-lithium.** All reactions were performed by adding a 20% ethereal solution of 0.02-0.10 mole of freshly purified allylic chloride over 15 min to a two-fold excess of 0.7-0.8 N phenyllithium in ether at room temperature. The reaction mixture was stirred for 2 hr and was hydrolyzed with water. The organic phase was washed with water, dried over Drierite, and concentrated. Quantitative glpc analysis for product yields (ethylbenzene, internal standard) and product distribution were performed on columns B and C. All materials amounting to more than 1% of the total were purified by reduced pressure distillation followed by preparative glpc using columns F or G. All products thus isolated were pure (>99%) and their structures were confirmed by nmr analysis and by comparison with authentic samples when available. For reactions in which low-boiling products (methyl-substituted butadienes and cyclopropenes) were anticipated, a stream of argon was swept through the reaction vessel into a Dry Ice-acetone trap whose contents were analyzed by glpc (column B and C); in every case, the only materials found were ether and unreacted allylic chloride. High-boiling materials (formed in low yield) which other than biphenyl would not distill easily at reduced pressure were analyzed by nmr without further purification; they appeared to be mixtures of polymeric material and the
coupling products from biphenyllithium and starting material.

Preparation of Optically Active 3-Chloro-cis-1-butene-1-d 
(R)-(−)-17

A. 1-Butyn-3-yl Benzoate (10). To a mixture of 210 g (3.0 moles) of 1-butyn-3-ol (9), 234 g (3.0 moles) of pyridine, and 300 ml of ether was added 415 g (3.0 moles) of benzoyl chloride over 20 min. The resulting solution was gently refluxed for 2 hr. Pyridine hydrochloride which precipitated upon cooling was removed, and the filtrate was washed with 300 ml of 1 N acetic acid, 300 ml of 5% Na₂CO₃, and 300 ml of water, and was dried (CaSO₄). Solvent was removed (rotary evaporator) and 1.5 l of pentane was added. The white prisms which separated were combined with a second crop obtained by concentration of the mother liquor. The combined solids were crystallized once from pentane yielding 432 g (83%) of ester 6: mp 46–47°; nmr (CCl₄) δ 1.60 (d, 3, J = 7 Hz, methyl), 2.38 (d, 1, J = 2 Hz, acetylenic), 5.54 (d of q, 1, J = 2 and 7 Hz, methine), and ca. 7.4 and 8.0 (m, 5, aromatic).

B. 1-Butyn-1-d-3-yl Benzoate. (11). Benzoate 10, 430 g, was dissolved in 500 ml of CCl₄ and was stirred for 6 hr with 20 ml of a 1% solution of sodium methoxide in D₂O (99.8%, Stohler Isotope Chemicals). This procedure was repeated 12 times with fresh portions of D₂O solution until the area of the nmr acetylenic absorption peak had decreased to less than the area of one of the ¹³C satellites of the methyl protons (ca. 98.5% exchanged). The organic layer was dried (CaSO₄), concentrated (rotary evaporator), and treated with pentane as above to induce deposition of the product. One crystallization from pentane afforded 414 g (96%) of deuterated ester 11: mp 46–47°; nmr (CCl₄) δ 1.59
(d, 3, J = 7 Hz, methyl), 5.55 (q, 1, J = 7 Hz, methine), and ca.
7.4 and 8.0 (m, 5, aromatic).

C. cis-1-Buten-1-d-3-yl Benzoate (12). By adaptation of the method
of Brown and Zweifel, ~6a a solution of 51.0 g (0.29 mole) of acetylenic
benzoate 11 in 100 ml of dried ether was added over 30 min to 400 ml
of 0.9 N disiamylborane in THF ~20 which was stirred under argon and
maintained at -5 to 0°. The mixture was stirred at this temperature
for an additional 15 min at which time glpc analysis (column B) showed
that no starting material was left. With the temperature of the
mixture held at -5 to 0°, 200 ml of glacial acetic acid was added over
25 min, and the resulting solution was stirred for an additional 4 hr
at 0°. The solution was extracted thoroughly with several portions
each of ice-water, saturated Na2CO3, and water, and was dried (CaSO4).
Removal of solvent (rotary evaporator) produced a residue which was
distilled through a 14-in. glass helices packed column, and the fraction
boiling from 65 to 85° (0.6 mm) was treated with 100 ml of 30% H2O2.
The organic layer after washing and drying was distilled through a
spinning band column giving allylic ester 12 in yields ranging from
30 to 46% (glpc yields, column B, before oxidation were typically 50
to 85%): bp 67-68° (0.5 mm); nmr (CCl4) δ 1.41 (d, 3, J = 6.8 Hz methyl),
5.03 (d of d, 1, J = 10.0 and 1.0 Hz, terminal vinyl), 5.52 (m, 1,
consisting of a quartet, J = 6.8 Hz, each line of which is split into
a doublet of doublets, J = 5.3 and 1.0 Hz, methine), 5.85 (m, 1, con-
sisting of a doublet of doublets, J = 10.0 and 5.3 Hz, each line of
which is further split into a 1:1:1 triplet, J = 2.5 Hz, internal
vinyl), and ca. 7.3 and 7.9 (m, 5, aromatic).
D. 3-Hydroxy-cis-1-butene-1-d (13). According to the method of
Doering and Zeiss,41 a solution of 140 g (0.79 mole) of ester 12 in
150 ml of dried ether was added dropwise over 1 hr to a stirred sus-
pension of 25.0 g (0.66 mole) of LiAlH₄ in 500 ml of ether at 0-5°.
The mixture was allowed to warm to room temperature and was stirred
for an additional 1 hr. Saturated NH₄Cl was carefully added and the ether
layer was decanted leaving a powdery residue which was thoroughly
triturated with several 100-ml portions of ether. The combined ether
solutions were washed with saturated NaCl, dried (BaO), and concentrated
at atmospheric pressure through a 14-in. glass helices packed column.
Distillation of the residue through a spinning band column gave 41.4 g
(72%) of allylic alcohol 13: bp 97-98° lit. 24 bp 96-97° for 3-hydroxy-
1-butene; glpc analysis (column B) >99% pure; nmr (CCl₄) δ 1.19
(d, 3, J = 6.5 Hz, methyl), ca. 3.8 (broad s, 1, hydroxyl, concentra-
tion-dependent chemical shift), 4.13 (m, 1, consisting of a quartet,
J = 6.5 Hz, each line of which is further split into a doublet of
doublets, J = 5.5 and 1.0 Hz, methine), 4.88 (d of d, 1, J = 10.0 and
1.0 Hz, terminal vinyl), and 5.75 (m, 1, consisting of a doublet of
doublets, J = 10.0 and 5.5 Hz, each line of which is further split into
a 1:1:1 triplet, J = 2.5 Hz, internal vinyl).

E. cis-1-Buten-1-d-3-yl Hydrogen Phthalate (14). Following the procedure
of Kenyon and Snellgrove,24 a mixture of 41.0 g (0.56 mole) of labeled
alcohol 13, 44.5 g (0.56 mole) of pyridine, and 84.0 g (0.57 mole) of
phthalic anhydride in 150 ml of dried ether was stirred at 50° for 5 hr.
The cooled clear solution was poured into 500 ml of 2 N HCl at 0°. The
resulting mixture was stirred vigorously for 5 min, the organic layer
was separated, and the aqueous phase was extracted with several 100-ml
portions of ether. The combined organic phases were dried (CaSO$_4$) and concentrated (rotary evaporator). Benzene (100 ml) was added and the small amount of phthalic anhydride which precipitated was removed. The solution was again concentrated (rotary evaporator) and the last trace of benzene was removed by heating at 40° (1 mm). The residue, 110 g (89%) of a colorless oil, was the desired phthalate 15: nmr (CCl$_4$) δ 1.41 (d, 3, J = 6.3 Hz, methyl), 5.03 (d, 1, J = 10.0 Hz, terminal vinyl), 5.46 (m, 1, consisting of a quartet, J = 6.3 Hz, each line of which is further split into a doublet, J = 6.0 Hz, methine), 5.82 (m, 1, consisting of a doublet of doublets, J = 10.0 and 6.0 Hz, each line of which is further split into a 1:1:1 triplet, J = 2.0 Hz, internal vinyl), ca. 7.4 (m, 4, aromatic), and 12.3 (s, 1, carboxyl).

F. Optically Active cis-1-Buten-1-d-3-yl Hydrogen Phthalate (15).

According to the method of Kenyon and Snellgrove, a solution of 110 g (0.50 mole) of phthalate 14 in 100 ml of acetone was added to 240 g (0.61 mole) of anhydrous brucine in 700 ml of warm acetone. The pale yellow solution was stirred and the white salt which precipitated was crystallized seven times to constant mp 160-162° [lit. mp 120-122°], 43 g. Systematic work-up of the mother liquor yielded two more crops of the less soluble diastereomer, 55 g. Hydrolysis of the combined salts was accomplished by shaking with 400 ml of 4 N HCl at 0°. The solution was extracted with ten 50-ml portions of ether, and the combined extracts were dried (CaSO$_4$), concentrated (rotary evaporator), and the last trace of ether removed at 40° (1 mm). The residue, 32.5 g (30%), was the desired optically active ester 15: nmr identical to racemic ester 14, $[\alpha]_{D}^{30} = +30.6°$ ($c$ 2.12, EtOH) (75.6% optically pure).
The mother liquors from the fractional crystallization were concentrated and decomposed with 4 N HCl, as above, yielding 43.7 g (40%) of optically active ester 15: [α]_{D}^{30} = -19.9° (c 5.03, EtOH) (49.2% optically pure). 

G. Optically Active 3-Hydroxy-cis-1-butene-1-d (S)-(+)-(16). Optically active (−)-phthalate 15, 44.0 g (0.20 mole), was treated with 22 g (0.58 mole) of LiAlH₄ according to the procedure described above for benzoate 8. Work-up and spinning band distillation gave 9.8 g (67%) of optically active allylic alcohol (S)-(−)-(16): bp 96-98°; [α]_{D}^{30} = -14.1° (neat) (51.1% optically pure). Similarly, 33.2 g (0.15 mole) of (+)-phthalate gave 7.9 g (72%) of (+)-alcohol: [α]_{D}^{30} = +20.9° (neat) (75.7% optically pure).

H. Optically Active 3-Chloro-cis-1-butene-1-d (R)-(−)-(17). Following the procedure of Young, et al., 33 13.0 g (0.11 mole) of thionyl chloride in 30 ml of dried ether was added dropwise over 30 min to a solution of 7.7 g (0.11 mole) of (S)-(+)−alcohol 16 and 21.5 g (0.12 mole) of tri-n-butylamine in 180 ml of ether at -50°. The mixture was stirred for 3 hr during which time it slowly warmed to -20°, and was flash-distilled into a Dry Ice-acetone trap. The distillate after drying (CaSO₄) was shown by glpc (column B) to contain a 69:31 ratio of 3-chloro-1-butene and 1-chloro-2-butene in an overall yield of 92%. Concentration of the solution followed by preparative glpc (column P) gave 4.6 g (48%) of (R)-(−)-chloride 17: [α]_{D}^{30} = -30.8° (neat) (50.4% optically pure); nmr (CCl₄) δ 1.58 (d, 3, J = 6.5 Hz, methyl), 4.42 (m, 1, consisting of a quartet, J = 6.5 Hz, each line of which is further split into a doublet of doublets, J = 7.0 and 0.8 Hz, methine), 5.00 (d of d, 1, J = 10.0 and 0.8 Hz, terminyl vinyl), and 5.86 (m, 1, consisting of
a doublet of doublets, \( J = 10.0 \) and 7.0 Hz, each line of which is further split into a 1:1:1 triplet, \( J = 2.5 \) Hz, internal vinyl).

**Reaction of Optically Active 3-Chloro-cis-1-butene-1-d (R)-(−)-(17) with Phenyllithium.** Optically active (-)-chloride 17, 4.0 g (0.044 mole), in ether was added to 0.8 N phenyllithium in ether according to the general procedure. Analysis of the crude reaction mixture by glpc (column B) revealed a 73% yield of three hydrocarbons in a ratio of 86.0:13.5:0.5. Preparative glpc (column Q) of a small portion of the crude product led to isolation of the major component, 1-phenyl-trans-2-butene-1-d (20), identified by comparison with unlabeled material and by its nmr spectrum (CCl\(_4\)) \( \delta \) 1.65 (m, 3, methyl), 3.2 (m, 1, methine), 5.4 (m, 2, vinyl), and 7.0 (m, 5, aromatic). A small sample of the next most abundant product was similarly isolated and identified as 1-phenyl-cis-2-butene-1-d (21). The third component was not present in sufficient quantity to permit isolation, but its structure was confirmed as 3-phenyl-1-butene (presumably deuterated at C\(_1\) with cis geometry, 17) by glpc comparison (columns B, C, and D) with authentic unlabeled material.

Distillation of the crude product yielded 2.80 g of a mixture of 20, 21, and 22 in a ratio of 86.0:13.5:0.5, bp 62-64° (10 mm). A 2.500 g portion of this distillate was diluted to 9.500 g with a mixture of optically inactive compounds in exactly the same ratio. Careful distillation through a spinning band column gave 5.15 g of a mixture containing only hydrocarbons 20 and 21 in a ratio of 86.5:13.5 which was then diluted to twice its weight with 5.15 g of the identical mixture of
unlabeled materials. This mixture (containing 13.2% of deuterated optically active hydrocarbons) was separated into two portions.

A 5.0 g-portion (0.038 mole) was reduced by diimide (formed by treatment of 30.0 g of anhydrous hydrazine in 50 ml of ethanol (containing a few crystals of CuSO₄) with oxygen, 30 ml/min for 2 hr).⁴² After the usual work-up, the organic layer was distilled through a 6-in Vigreux column yielding 2.94 g (59%) of 1-phenylbutane-1-d (23a): bp 62⁰ (10 mm); [α]²⁷D⁻⁰.78⁰ (neat).

From a 5.3 g-portion, preparative glpc (column G) gave 4.30 g of pure trans olefin 20 which was reduced with diimide to 2.30 g (53%) of 1-phenylbutane-1-d (23b): bp 62⁰ (10 mm); [α]²⁷D⁻¹.02⁰ (neat).
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PART II

A KINETIC STUDY OF THE REACTION BETWEEN ARENEDIAZONIUM SALTS AND DIMETHYL PHOSPHONATE IN AQUEOUS BUFFER
INTRODUCTION

The reactions between aromatic diazonium salts and dimethylphosphonate in neutral, weakly acidic, or weakly basic medium lead to the formation of dimethyl arylazophophonates according to equation (1).

\[
\text{ArN}_2^+ + \text{HP(O)(OCH}_3\text{)}_2 \rightarrow \text{ArN=N-P(O)(OCH}_3\text{)}_2 + \text{H}^+ \tag{1}
\]

\[\begin{align*}
\lambda^a & \quad \text{Ar} = \text{p-NO}_2\text{C}_6\text{H}_4 \\
\lambda^b & \quad \text{p-CNC}_6\text{H}_4 \\
\lambda^c & \quad \text{p-ClC}_6\text{H}_4 \\
\lambda^d & \quad \text{p-OCH}_3\text{C}_6\text{H}_4 \\
\lambda^e & \quad \text{p-SO}_3\text{C}_6\text{H}_4 \\
\lambda^f & \quad \text{p-CH}_3\text{C}_6\text{H}_4 \\
\lambda^g & \quad \text{C}_6\text{H}_5
\end{align*}\]

Although the synthetic aspect of this reaction has been extensively explored,\(^1\) the detailed mechanism is not well understood. As a part of the continuing interest in the reactions between diazonium salts and nucleophiles,\(^2\) we have undertaken a kinetic study of the above mentioned reaction. The results are reported and discussed.
METHOD AND RESULTS

The reaction kinetics were studied spectrophotometrically by following the change in absorbance of reaction mixture at the appropriate absorption maxima of the product 2.

Before kinetic studies were carried out several of the dimethyl arylazophosphonates (2) were prepared. Table 1 lists the absorbance maxima $\lambda_{\text{max}}$ and the corresponding extinction coefficients $\varepsilon$ for these compounds.

**Table 1**

UV Absorptions of Dimethyl Arylazophosphonates

<table>
<thead>
<tr>
<th>$X$-C$_6$H$_4$N=N-P(OCH$_3$)$_2$</th>
<th>$\lambda_1$ nm</th>
<th>$\varepsilon_1$</th>
<th>$\lambda_2$ nm</th>
<th>$\varepsilon_2$</th>
<th>$\lambda_3$ nm</th>
<th>$\varepsilon_3$</th>
</tr>
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<tr>
<td>2a p-NO$_2^a$</td>
<td>510</td>
<td>108</td>
<td>287</td>
<td>21800</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>2b p-CN$^a$</td>
<td>505</td>
<td>84</td>
<td>286</td>
<td>16000</td>
<td>235</td>
<td>11000</td>
</tr>
<tr>
<td>2c p-Cl$^a$</td>
<td>496</td>
<td>96</td>
<td>310</td>
<td>17000</td>
<td>230</td>
<td>10900</td>
</tr>
<tr>
<td>2d p-OCH$_3^{a,b}$</td>
<td>475</td>
<td>235</td>
<td>345</td>
<td>20000</td>
<td>242</td>
<td>12600</td>
</tr>
<tr>
<td>2e p-SO$_3^{c}$</td>
<td>485</td>
<td>ca</td>
<td>100$^c$</td>
<td>d</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>2f p-CH$_3$</td>
<td>490</td>
<td>107</td>
<td>304</td>
<td>14700</td>
<td>220</td>
<td>9370</td>
</tr>
<tr>
<td>2g H</td>
<td>485</td>
<td>73</td>
<td>293</td>
<td>12000</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>2g H$^e$</td>
<td>487$^e$</td>
<td>73</td>
<td>293$^e$</td>
<td>12000</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

$^a$In spectral grade methanol.

$^b$A time dependent spectrum, probably corresponding to a syn-anti conversion, was noticed when the spectrum was taken from a freshly prepared sample. The values reported here correspond to the spectrum of the more stable isomer.

$^c$Pure sample cannot be isolated. The spectrum was taken from the aqueous solution resulting from kinetic run. The $\varepsilon$ was estimated based on limiting reagent dimethyl phosphonate.

$^d$These values were not determined.

$^e$In dioxane solution. See reference 3.
Since aranediazonium ions absorb more strongly than the dimethyl arylazophosphonates between the region 340 nm to 220 nm, the peaks suitable for analysis are those in the visible region. Unfortunately, the extinction coefficients of these peaks are in general quite low. In order to obtain sufficient absorbance for measurement, and at the same time maintain pseudo-first order kinetics with respect to dimethyl phosphonate, a $10^{-2}$ molar solution was required for reactions to be carried out in a 10 cm cell.

Preliminary experiments indicate that the reaction would proceed at measurable rate when the pH of the buffer solution is higher than 6.0. Under these conditions, most aranediazonium ions undergo decomposition and yield yellow precipitates. No attempt was made to characterize the yellow precipitates since they turned into organic tar very readily. Among the aranediazonium salts (\(\text{Ia, Ib, Ic, Id, Ie and If}\)) tested, only \(\text{Ib}\) showed no appreciable decomposition, and \(\text{Ie}\) decomposes sufficiently slow to allow kinetic study.

Another complication came from the hydrolysis of the dimethyl arylazophosphonates presumably to the corresponding aryldiimide, i.e.,

\[
\text{ArN=NP(O)(OCH}_3)_2 + \text{OH}^- \rightarrow [\text{ArN=N}^-] + \text{HOP(OCH}_3)_2 \\
\rightarrow \text{H}_2\text{O} \\
\text{ArN=NH} + \text{OH}^-
\]

This hydrolysis is not a serious problem in the synthesis of dimethyl arylazophosphonates. Since the dimethyl arylazophosphonates in general are very insoluble in water, they are extracted into the organic
phase soon after their formation and thus any appreciable decomposition is averted. However, under the condition of kinetic study, some of the arylazophosphonate esters do hydrolyze to a small extent. The resulting product absorbs strongly at 350 nm and the envelope extends into the visible region where the reactions were followed, and therefore, introduces a significant uncertainty in the later part of the kinetic measurement.

Various conditions were tried; it was found that reasonably good kinetic measurement can be performed on the reaction of diazonium salt \( \mathcal{J}_e \), and acceptable analysis could be obtained on the reaction of diazonium salt \( \mathcal{J}_b \) under the conditions described in the experimental section.

The kinetic curve (Figure 1) for the reaction of \( \mathcal{J}_e \) can be best described as the sum of a linear term and an exponential term. The linear term existed even before the introduction of dimethyl phosphonate, and is attributed to a pseudo-zero order decomposition of diazonium salt \( \mathcal{J}_e \). The exponential term which appears immediately after the introduction of dimethyl phosphonate, is most certainly due to the formation of the dimethyl p-sodosulfonylphenylazophosphonate. After four half-lives of the reaction, the rate of increase in absorbance becomes virtually identical with what was observed before the introduction of the dimethyl phosphonate. If we graphically subtract the zero-order contribution from the decomposition of diazonium salt \( \mathcal{J}_e \), and plot log (\( \Delta A \)) against time, a straight line which covers four half-lives of the reaction can be obtained. In actual practice, 2n values of \( \Delta A \) were taken at regular intervals over three to four half-lives of the
reaction. Then, \( \log (A_{2n} - A_n), \log (A_{2n-1} - A_{n-1}) \ldots \) etc., was plotted against time according to the method of Guggenheim. A typical plot is shown in Figure 3. The slope of Guggenheim plot was used to calculate the observed rate constant, \( k_{\text{obsd}} \), according to equation (2).

\[
k_{\text{obsd}} = \frac{-2.303}{60} \times \text{Slope} \text{ sec}^{-1}
\]  

(2)

In the reaction of the diazonium salt \( 1b \) (Figure 2) no change in absorbance was observed before the introduction of dimethyl phosphonate into the reaction mixture. Upon addition of dimethyl phosphonate, an exponential increase in absorbance appeared immediately. However, in the later part of the reaction a linear increase in absorbance which superimposed on the exponential term appeared. After about four half-lives, the absorbance eventually surpassed the expected absorbance maxima for the stoicheometric amount of product. This linear contribution probably resulted from the hydrolysis of product mentioned earlier. Application of the Guggenheim treatment to the first two half-lives of the reaction yielded a straight line containing negligible error from the side reaction. The slope of the Guggenheim plot was used to calculate \( k_{\text{obsd}} \). The results are summarized in Table 2 and Table 3.
Figure 2.

Absorbance vs Time for the Reaction Between p-CN-C₆H₄N⁺ and HP(0)(OCH₃)₂ in Aqueous Buffer Solution
Figure 3
The Guggenheim Plot of a Typical Kinetic Run
<table>
<thead>
<tr>
<th>Concentration of Diazonium Salt x 10^-2 M</th>
<th>Concentration of HP(O)(OCH_3)_2 x 10^-4 M</th>
<th>pH</th>
<th>k_{obsd} x 10^{-3} sec^{-1}</th>
<th>k^{b} x 10^{6} M^{-2} sec^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1le]^{c} 0.8</td>
<td>6.8</td>
<td>7.0</td>
<td>3.57</td>
<td>4.46</td>
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<td>&quot; 1.0</td>
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<td>&quot;</td>
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<td>&quot;</td>
<td>4.33</td>
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<td>&quot;</td>
<td>&quot;</td>
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(TABLE 2 contd.)

Duplicate reactions were carried out in buffer solutions containing 0.1 M total phosphate at 6±0.1°C; preliminary results indicate no observable change in rate when reactions were carried out in buffer solution containing 0.2 M total phosphate.

The entry labeled $k^d$ is a third order constant defined by equation (4). The dependency of this constant on diazonium salt concentration will be discussed (see Discussion).

The rate constant $k_{obsd}$ was obtained by the Guggenheim treatment on the first three to four half-lives of the reaction.

The rate constant $k_{obsd}$ was obtained by the Guggenheim treatment on the first two half-lives of the reaction.

---

TABLE 3
Effect of pH on Reaction Rate.a

<table>
<thead>
<tr>
<th>Run</th>
<th>pH</th>
<th>$k_{obsd} \times 10^{-3}$ sec$^{-1}$</th>
<th>log $k_{obsd}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.2</td>
<td>0.93</td>
<td>-3.03</td>
</tr>
<tr>
<td>2</td>
<td>6.4</td>
<td>1.53</td>
<td>-2.81</td>
</tr>
<tr>
<td>3</td>
<td>6.6</td>
<td>2.34</td>
<td>-2.63</td>
</tr>
<tr>
<td>4</td>
<td>6.8</td>
<td>3.78</td>
<td>-2.42</td>
</tr>
<tr>
<td>5</td>
<td>7.0</td>
<td>5.32</td>
<td>-2.26</td>
</tr>
<tr>
<td>6</td>
<td>7.2</td>
<td>7.82</td>
<td>-2.10</td>
</tr>
<tr>
<td>7</td>
<td>7.4</td>
<td>14.70</td>
<td>-1.83</td>
</tr>
</tbody>
</table>

a Duplicate runs were carried out with $1.6 \times 10^{-2}$ M p-diaziobi/benzene-sulfonate, and $6.8 \times 10^{-4}$ M dimethyl phosphonate in appropriate buffer solution containing 0.1 M of phosphate.
When pH of the buffer remains constant, a plot of diazonium salt concentration against the corresponding value of $k_{\text{obsd}}$ resulted in a straight line (Figure 4, 5, 6 and 7) indicating that the reaction has a first order dependence on the concentration of diazonium salt. At constant diazonium salt concentration, of log $k_{\text{obsd}}$ plotted against pH gave a straight line of unit slope (Figure 8) indicating that the reaction has a first order dependence on hydroxide ion concentration. Since the reactions were carried out under pseudo-first order condition with respect to dimethyl phosphonate, the rate law for the reaction is therefore in the form of equation (3),

$$\frac{d \text{Product}}{dt} = k'[\text{HP}][\text{ArN}_2^+][\text{OH}^-] \quad (3)$$

where

$$k' = \frac{k_{\text{obsd}}}{[\text{ArN}_2^+][\text{OH}^-]} \quad (4)$$
Figure 4

$k_{\text{obsd}}$ vs Concentration of $p-$SO$_3$C$_6$H$_4$N$_2^+$ at pH 7.
Figure 5

$k_{\text{obsd}}$ vs Concentration of $p$-$SO_3C_6H_4N^+$ at pH 6.8
Figure 6

$k_{obsd}$ vs Concentration of $p$-$SO_3C_6H_4N_2^+$ at pH 6.6
Figure 7

$k_{\text{obsd}} \times 10^{-3}$ sec$^{-1}$

$1.0 \quad 1.2 \quad 1.4 \quad 1.6 \quad 1.8 \times 10^{-2}$ M

$k_{\text{obsd}} \text{ vs Concentration of } p\text{-CNC}_6H_4N^+_2 \text{ at pH 6.4}$
Figure 8

pH Rate Profile for the Reaction Between p-SO$_3^-$C$_6$H$_4$N$_2^+$
and HP(O)(OCH$_3$)$_2$ in Buffer Solution
DISCUSSION

The base catalyzed nucleophilic reactions of dialkyl phosphonate can be understood according to the general mechanism outlined as follows:

\[
\begin{align*}
\text{HP} + B & \xrightleftharpoons[k_2}{k_1} P^- + BH^+ \\
P^- + S & \rightarrow \text{Product}
\end{align*}
\]

Where HP represents dialkyl phosphonate, which can be ionized by base B to form an ambident anion \( P^- \). The ambident anion can either regenerate dialkyl phosphonate by removing a proton from \( BH^+ \), or react with a substrate \( S \) to form product. The kinetics of (5) and (6) are uncomplicated, if the anion is reactive enough so that steady-state method may be applied for its concentration. This method gives:

\[
[P^-] = \frac{k_1[HP][B]}{k_3[S] + k_2[BH^+]} \tag{7}
\]

and correspondingly,

\[
\frac{d \text{ Product}}{dt} = \frac{k_1k_3[HP][B][S]}{k_3[S] + k_2[BH^+]} \tag{8}
\]

If more than one base is present and effective, then (8) can be written as:

\[
\frac{d \text{ Product}}{dt} = \sum_i \frac{k_3[HP][S][B_i]}{k_3[S] + k_2[B_iH^+]} \tag{9}
\]
Equation (9) can take up one of the two limiting forms depending on whether \( k_3[S] \) is much greater or much smaller than \( k_{2i}[B_i H^+] \) term. The former leads to:

\[
\frac{d \text{Product}}{dt} = [HP] \sum_i k_{1i} [B_i]
\]  

(10)

and the later leads to:

\[
\frac{d \text{Product}}{dt} = k_3[HP][S] \sum_i \frac{k_{1i} [B_i]}{k_{2i} [B_i H^+]}
\]  

(11)

Since an equilibrium between HP and \( P^- \) is established in the steady-state, i.e.,

\[
\frac{k_{1i} [B_i]}{k_{2i} [B_i H^+]} \quad \text{HP} \xrightarrow{\text{P}} \text{P}^- \quad (12)
\]

\[
\frac{[P^-]}{[HP]} = \sum_i \frac{k_{1i} [B_i]}{k_{2i} [B_i H^+]}
\]  

(13)

and the equilibrium constant \( K_{eq} \) for the ionization of dimethyolphosphonate in aqueous solution is related hydroxide ion concentration by:

\[
K_{eq} = \frac{k_{1-\text{OH}} [\text{OH}^-]}{k_{2-\text{H}_2\text{O}} [\text{H}_2\text{O}]} = \frac{[P^-]}{[HP]}
\]  

(15)
Equation (11) can be expressed as follows:

$$\frac{d \text{Product}}{dt} = \frac{k_3 k_{1-\text{OH}}}{k_{2-\text{OH}}[\text{H}_2\text{O}]} \frac{[\text{OH}^-][\text{S}][\text{HP}]}{[\text{H}_2\text{O}]}$$  \hspace{1cm} (16)

Equation (10) corresponds to general base catalysis, and equation (16) corresponds to specific base catalysis.

From the above analysis it is clear that the factor which determines whether (10) or (16) is observed is the relative rate of the anion $P^-$ reacting with substrate $S$ compared to that with $B_1H^+$. A high rate of the anion reacting with the substrate leads to (10), and a high rate of the neutralization or low rate of anion reacting with substrate leads to (16).

Now let us turn our attention to the experimental findings concerning some of the base catalyzed reactions of dialkyl phosphonates. In spite of the fact that dialkyl phosphonates undergo a large variety of base catalyzed reactions, only the halogen oxidation and hydrogen isotope exchange reaction have received kinetic treatment.$^{11}$

The oxidation of dialkyl phosphonates to dialkyl phosphates by halogen was first studied by Nylén$^7$ in 1938. It was found that the reaction in aqueous buffer is subject to general acid and general base catalysis. Under the condition of high halogen concentration, the rate is independent of the nature as well as concentration of the halogen.

These results are readily accommodated by the first limiting case of the general rate law equation (10). It is evident, that the $k_3[S]$ term is only marginally greater than the $k_{24}[\text{BiH}^+]$ term since high halogen concentration is needed for zero order dependence on halogen to be observed.
The base catalyzed deuterium exchange reaction of diethyl phosphonates in deuterium oxide was studied by Silver and Luz, and Hammond. The second order base catalysis constants for the acetate, cacodylate, and deuterioxide ion (1.3 x 10^{-3}, 4.5 x 10^{-2}, and 2.0 x 10^{-5} l. mole^{-1} sec^{-1}) compared favorably with the corresponding second order constant for the iodine oxidation (1.5 x 10^{-2}, 3.0 x 10^{-2} and 1.3 x 10^{-5} l. mole^{-1} sec^{-1}) providing that the medium change and isotope effects are taken into consideration.

The multiple role that deuterium oxide plays in the isotopic exchange reaction made it necessary to modify the appearance of the rate equation. Since deuterium oxide is used as solvent, any labile proton in the buffer system is expected to be replaced by deuterium, therefore, the reversal of anion P^{-} to protium diethyl phosphonate is negligibly small. With this in mind, equation (5) and (6) can be rewritten as:

\[ \text{HP} + \text{B}_i \xrightarrow{k_{1i}} \text{P}^- + \text{B}_i\text{H}^+ \]  \hspace{1cm} (17)

\[ \text{P}^- + \text{B}_i\text{D}^+ \xrightarrow{k_3} \text{Product} \]  \hspace{1cm} (18)

and correspondingly,

\[ [\text{P}^-] = \sum_i \frac{[\text{HP}]k_{1i}[\text{B}_i]}{k_3[\text{B}_i\text{D}^+]} \]  \hspace{1cm} (19)

\[ \frac{d\text{Product}}{dt} = \sum_i \frac{k_3k_{1i}[\text{HP}][\text{B}_i][\text{B}_i\text{D}^+]}{k_3[\text{B}_i\text{D}^+]} = [\text{HP}] \sum_i k_{1i}[\text{B}_i] \]  \hspace{1cm} (20)
Equation (20) is identical with (10), the rate law that is followed by the halogen oxidation reaction. Thus, it can be concluded that any factor which makes the term \( k_{21}[B_1H^+] \) unimportant also ensure the applicability of the first limiting case of the general rate law. In Nylén's work, this is brought about by a higher rate of anion reaction with the substrate with some assistance from the high concentration of the substrate, whereas in the isotopic exchange experiment this is brought about by low concentration of protium donor. The agreement between the results from these two reactions clearly demonstrated that they follow the general mechanism.

While the general mechanism is adequately justified by experimental results corresponding to the first limiting case, its applicability to the second limiting case is at best indirectly inferred. No kinetic evidence which confirms the intervention of the general mechanism in the form of the second limiting case can be found in the literature. Perhaps the lack of interest is in part due to the fact that very little is known about the acid dissociation constants \( k_a \) for these esters. On the other hand, the instability of dialkyl phosphonates in aqueous acid and base may also have discouraged any serious effort.

Without precise knowledge of \( k_a \) the equation (16) is in an insolvable form. However, the similarity between equation (3) and (16) suggests to us that the base catalyzed reaction between dimethyl phosphonate and diazonium salts can be interpreted in terms of the second limiting case of the general mechanism. Assuming indeed this is the case, we obtain from equation (3) and (16):

\[
k' = \frac{k_{\text{obsd}}}{[OH^-][ArN_2^+]} = \frac{k_3k_{11}}{k_2[H_2O]} \tag{21}
\]
Substitute the values of observed rate constant $k_{obsd}$ for the reactions conducted with $1.8 \times 10^{-2}$ M diazonium salt and the appropriate hydroxide ion concentration ($10^{-7}$ for 1e and $10^{-7.6}$ M for 1b) into equation (21) leads to the ratios of 12.6:1 and 6.4:1 for $k_2[H_2O]$; $k_{3-1e}^{[1e]}$ and $k_{2,2}^{[1b]}$ and $k_{3-1b}^{[1b]}$, respectively. Strictly speaking, these ratios are not sufficiently large to allow the $k_3[ArN_2^+]$ term in the denominator of equation (9) to be ignored. In accord with this, we find that the values of $k'$ listed in Table 2 are not substrate independent as defined originally. However, for a given substrate at a given concentration $k'$ is essentially independent of pH. Hence, we believe that specific base catalysis is still a fair description for the role played by the base in this reaction.

Taking these observations into consideration, a more appropriate rate law would be reintroducing the term $k_3[ArN_2^+]$ into denominator of (16) to give:

$$k_{obsd} = \frac{k_1 k_3[ArN_2^+][OH^-]}{k_3[H_2O] + k_3[ArN_2^+]}$$  \hspace{1cm} (22a)

which can be expressed in terms of $k'$, i.e.,

$$\frac{1}{k'} = \frac{k_2[H_2O]}{k_1 k_3} + \frac{[ArN_2^+]}{k_1}$$  \hspace{1cm} (22b).

From equation (22b) it is obvious that a plot of $1/k'$ versus $ArN_2^+$ yields:

$$\text{Slope} = \frac{1}{k'} = \rho$$ \hspace{1cm} (23)

$$\text{Intercept} = \frac{k_2[H_2O]}{k_1 k_3} = \psi$$ \hspace{1cm} (24).
Figures 9 and 10 correspond to $1/k'$ versus $1e$ and $1/k'$ versus $1b$ respectively. The least-square slopes $\rho$ intercepts $\psi$, and the correlation coefficients $c$ are listed as follows:

<table>
<thead>
<tr>
<th>Diazonium Salt</th>
<th>Slope $\rho$</th>
<th>Intercept $\psi$</th>
<th>Correlation Coefficient $c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1e$</td>
<td>$0.7 \times 10^{-5}$</td>
<td>$0.18 \times 10^{-6}$</td>
<td>$0.98$</td>
</tr>
<tr>
<td>$1b$</td>
<td>$0.3 \times 10^{-5}$</td>
<td>$0.58 \times 10^{-8}$</td>
<td>$0.99$</td>
</tr>
</tbody>
</table>

When the values of $k_1$ ($1.4 \times 10^5$ M$^{-1}$ sec$^{-1}$ from $1b$ and $3.3 \times 10^5$ M$^{-1}$ sec$^{-1}$ from $1e$) and the value determined by Nylén ($7.3 \times 10^5$ M$^{-1}$ sec$^{-1}$) are compared, discrepancies in the order of a factor of two to three are found. The poor agreement is probably due to the fact that only a narrow range of the concentration of diazonium salt was suitable for our study. Nevertheless, that these values are at least consistent within one order of magnitude, strongly suggests rate law (21) could in fact be correct.

To provide further support we shall make an effort to establish the range of rate constants and the range of the related acid dissociation constant of dimethyl phosphonate that are internally consistent with equation (22a). Although $k_2$ and $k_3$ in equation (22a) cannot be solved independently, yet if the upper or lower limits of one can be established, the other can be readily computed through equation (24). Since only the order of magnitude of these limits of rate constants are of interest, we shall ignore the error existing in the values of the intercept and use the order of magnitude for computation.
Figure 9

$1/k$ Versus the Concentration of $p$-$SO_3^-$

$C_6H_4N^+$

$2 \times 10^{-2}$ M

$1/k \times 10^7 m^-2$ mole sec$^{-1}$
The upper limit for \( k_3 \) is estimated by considering that the reaction rate between iodine and dimethyl phosphonyl anion is at diffusion controlled limit \( (10^{10} \text{ l. mole}^{-1}\text{sec}^{-1}) \). If the general mechanism applies to both the iodine oxidation and the diazonium salt reaction, then \( k_{3-1b} \) would have to be at least two orders of magnitude lower than \( k_{3-I_2}^* \) in order to account for the differences in rate law. Thus, \( k_{3-1b} \) assumes an upper limit of \( 10^8 \text{ l. mole}^{-1}\text{sec}^{-1} \). The lower limit of \( k_3 \) can be reached by considering the acid dissociation constant \( k_a \) of dimethyl phosphonate which is related to \( k_3 \) by equation (25), i.e.,

\[
k_3 = \frac{k_w}{k_a \psi}
\]  

(26)

A reasonable estimate of the upper limit of \( k_a \) leads to a lower limit for \( k_3 \). After considering the fact that dimethyl phosphonate neither reacts with aqueous base to form salt nor shows any buffer capacity in aqueous solution;\(^{10,11}\) and Hammond's estimated \( k_a \approx 10^{-15} \) for diethyl phosphonate, we assume an upper limit \( k_a \approx 10^{-14} \) for dimethyl phosphonate.

Corresponding to these limits, the order of magnitude of \( k_1, k_2, k_{3-1e}, k_{3-1b} \) and \( k_a \) are calculated and listed as follows:

<table>
<thead>
<tr>
<th></th>
<th>( k_1 )</th>
<th>( k_2 )</th>
<th>( k_{3-1e} )</th>
<th>( k_{3-1b} )</th>
<th>( k_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>upper limit</td>
<td>( 10^5 )</td>
<td>( 10^5 )</td>
<td>( 10^7 )</td>
<td>( (10^8) )</td>
<td>( 10^{-16} )</td>
</tr>
<tr>
<td>lower limit</td>
<td>( 10^5 )</td>
<td>( 10^4 )</td>
<td>( 10^6 )</td>
<td>( 10^6 )</td>
<td>( (10^{-14}) )</td>
</tr>
</tbody>
</table>

* This is a generous assumption since a high concentration of iodine is needed for iodine independent rate law to be observed.
It is noteworthy that the upper and lower limits of $k_{3-1e}$ and $k_{3-1b}$ are within a rather narrow range, and they compared favorably with the rate constants for the acid-base combination reaction between diazonium ions and strong nucleophiles such as hydroxy ion and cyanide ion,\textsuperscript{12} (ca. $10^5$ - $10^6$ M$^{-1}$ sec$^{-1}$).

Finally, it should be pointed out that a crude Hammett $\rho = + 2$ can be estimated for the reaction under investigation. Although the accuracy of this value leaves much to be desired, the fact that it is lower than $\rho = + 2.61$ for the hydroxy ion reaction\textsuperscript{12} and $\rho = + 2.31$ for the cyanide ion reaction\textsuperscript{12} is consistent with the exceptionally high nucleophilic reactivity of dimethyl phosphonoyl anion.\textsuperscript{6,11}

We have shown that the general appearance of the rate law, the agreement in $k_{1-0H}$, the dependence of rate on substrate, and the range of the estimated values of $k_3$, can be best understood by invoking the general mechanism of the base catalyzed nucleophilic reactions of dimethyl phosphonate. Consequently, we conclude it is operative in the reaction under investigation.

An ultimate proof for the intervention of the general mechanism would be a smooth transition from rate determining attack of phosphonyl anion to rate determining generation of the anion as the reactivity of diazonium salt increases. Unfortunately, conventional spectrophotometric methods require that base labile diazonium salts be subjected to relatively high pH for a relatively long period of time. Thus, most diazonium salts would undergo interfering side reactions even before the reaction of interest could be observed.

While there seems little doubt that our result can be best explained by invoking the general mechanism, we believe that a reinvestigation
of this problem (perhaps by a flow technique in which the interference of side reactions could be minimized) would lead to a more complete set of data from which Bronsted $\beta$ and deuterium isotope effect as well as a more accurate Hammett $\rho$ could be determined. With this additional information a better correlation between this reaction and the base catalyzed nucleophile reactions of dialkyl phosphonates with other substrates, as well as the acid-base combination reaction between diazonium salts and other nucleophiles can be achieved.
EXPERIMENTAL

General

Melting points were determined with a Mel-Temp apparatus and were uncorrected; nmr spectra were obtained on a Varian Association A-56/60 spectrometer with TMS as internal standard using approximately 15% v/v solution in CCl₄; and uv spectra were recorded on a Cary 14 spectrophotometer. Unless otherwise noted, spectral grade methanol was employed as solvent.

Material

Reagent grade commercial chemicals were used as received unless otherwise specified.

Dimethyl phosphonate, Matheson, Coleman and Bell, practical, was dried over Drierite and distilled through a 14 in. glass helices packed column. The fraction boiled at 62⁰–63⁰ (15 mm) was collected and used.

Reactions

Arenediazonium salts was prepared according to the procedure of Starkely,¹⁴ from recrystallized or distilled aryl amines and were recrystallized several times from glacial acetic acid and ether until constancy of uv spectra were reached.

Dimethyl arylazophosphonates. To 0.20 mole of the appropriate arenediazonium salts suspended in 30 ml of aqueous solution of dimethyl phosphonate (0.2 mole) at 0⁰ was added one equivalent of NaHCO₃ in small portions over a period of 15 min. After the addition was completed, the reaction mixture was stirred for 15 min. at 0⁰C, and extracted with
several portions of methylene chloride. The combined extracts were
dried over Drierite. Removal of solvent, afforded the desired dimethyl
arylazophosphonate as a red oil in 75-80% yield. These products gave
uv spectra which compared favorably with those reported in the
literature. Nmr spectra showed typical phosphorus bond methoxy
doublets $\delta 4.95$ ($6H J_{P-H} = 10$ Hz) and the signals expected from the
corresponding aryl group. Crystalline products of the $p$-nitro derivative
[mp. $114^\circ - 116^\circ$ Lit.$^1 119^\circ$] and the $p$-cyano derivative mp. $74-75^\circ$ were
obtained from methylene chloride/pentane mixture; However, no difference
was found between the uv and nmr spectra of the crude products and those
of the corresponding recrystallized products. In the case of the
$p$-methoxy derivative, the freshly isolated sample showed time dependent
uv spectra. While other features remained unchanged, the extinction
coefficient of the 475 nm band increased from ca 100 to 243. The uv
spectra of the sample, after a few hours of aging, showed no such time
dependence and gave $\epsilon_{475 \text{ nm}} = 243$.

**Kinetic Measurements.**

Kinetic measurements were carried out spectrophotometrically.
Typically, buffer with a total phosphate concentration of 0.1 M,
made up according to the procedure of Britton,$^{15}$ was chilled to $0^\circ$ and
added to a weighed sample of diazonium salt in a volumetric flask. A
33 ml aliquot of the resulting solution was placed in a 10 cm quartz
cell and allowed to reach thermal equilibrium in the thermostated cell
housing of Cary 14 spectrophotometer over a period of 15 min. A 2 $\mu$l
sample of dimethyl phosphonate was then introduced into the cell by
means of a micro syring and the change in absorbance corresponding
to the formation of the dimethyl arylazophosphonate 485 nm for the
p-SO$_3^-$ derivative (Qa) and 505 nm for the p-CN derivative (Qb) was
recorded.
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PART III

THE TRITIUM ISOTOPE EFFECT IN HYDROGEN TRANSFER
REACTION BETWEEN CARBON AND PHOSPHORUS
INTRODUCTION

The radical addition of phosphorus compounds containing one or more P-H bond to olefins is a general reaction. Numerous examples can be found in the reviews by Walling and Pearson,\textsuperscript{1a} and Stacey and Harries.\textsuperscript{1b} Of all the additions of phosphorus compounds to olefins, those involving dialkyl phosphonates have received most attention. Attempts to add dialkyl phosphonates to unactivated olefins with acid or base catalysts have been unsuccessful.\textsuperscript{2,3} However, addition occurs smoothly in the presence of radical initiator such as peroxides and azonitriles, or upon ultraviolet radiation. The addition of dialkyl phosphonates to terminal olefins yields anti-Markownikoff 1:1 adduct. When the reaction is conducted with a high concentration of olefin, in addition to 1:1 adduct, telomers containing one dialkyl phosphonate and two or more olefin units are produced. Therefore, it seems certain that the reaction occurs by a radical chain mechanism\textsuperscript{1a} as shown in Scheme 1.

\[ (\text{RO})_2\text{P-H} + (\text{RO})_2\text{P} \rightarrow (\text{RO})_2\text{P-C=C} \rightarrow (\text{RO})_2\text{P-C=CH} \rightarrow (\text{RO})_2\text{P-C=CC=C} \]
\[(\text{RO})_2\text{P-C-C-C-C-} + (\text{RO})_2\text{P-H} \rightarrow (\text{RO})_2\text{P-C-C-C-C-H} + (\text{RO})_2\text{P}^*\]  

The addition step, eq. (2), probably is reversible, since the addition of substituted phosphine to cis-2-butene, trans-2-butene was found among the unreacted olefins. This and many other characteristics of the reaction are very similar to the extensively studied radical chain addition of sulfhydroyl compounds to olefins.

Recently, Lewis and Butler have reported the tritium isotope effects in the chain transfer step of the radical chain additions of thiophenol and benzyl mercaptan to various olefins. The variations in these isotope effects are interpreted in terms of transition state symmetry measured by the differences in bond strength to hydrogen in the initial state (RS-H) and the final state (H-C-C-SR). Similar observations were reported on hydrogen transfer from sulfur to carbon radicals generated by a non-chain process.

In order to gain some knowledge of the potential energy surface associated with hydrogen transfer from phosphorus to a carbon radical, the tritium isotope effects of the radical addition of dimethyl phosphonate and dimethyl thiophosphonate to a variety of olefins was studied.

Since our results will be interpreted in terms of the magnitude of the isotope effect, it is appropriate to mention the various factors that might influence isotope effect.
Isotope effects were found experimentally soon after the discovery of deuterium in 1932, and now have become one of the most powerful tools in the study of reaction mechanism. Detailed theoretical treatment can be found in the work of Begleison,7 Johnston,8 Westheimer,9 Melander10 and Bell.11 The origin of isotope effects can be traced back to the substantial differences in mass between protium, deuterium, and tritium. Electronic contributions to the potential energies of A-H and A-D, to a good approximation, are identical regardless of which isotope is present. However, as a consequence of the Heisenberg uncertainty principle the ground state energies for A-H and A-D bonds differ by the difference of the mass dependent zero point vibrational energies (ZPE).

\[ \Delta E = ZPE_{oAD} - ZPE_{oAH} = \frac{1}{2} \hbar (\nu_{AD} - \nu_{AH}) \]  

(6)

where \( \hbar \) is the Planck constant, \( \nu_{A-D} \) and \( \nu_{A-H} \) refer to the vibrational frequencies of A-D and A-H bonds respectively.

In a hydrogen transfer reaction between two large groups A and B,

\[ A-H + B \longrightarrow [A\cdots H\cdots B] \xrightarrow{\neq} A + H-B \]

electronic contributions to the potential energies of \([A\cdots D\cdots B]\xrightarrow{\neq}\) and \([A\cdots H\cdots B]\xrightarrow{\neq}\) are again identical regardless of which isotope is present. The difference between the potential energies of the two activated complexes is the difference in the mass dependent zero point vibrational energies.

\[ \Delta E^{\neq} = ZPE^{\neq}_{ADB} - ZPE^{\neq}_{AHB} \]  

(7)
Therefore, the net difference in activation energies may be expressed as follows:

\[
\Delta E = (ZPE^\text{AD}_\text{O} - ZPE^\text{AH}_\text{O}) - (ZPE^\text{ADB}_\text{O} - ZPE^\text{AHB}_\text{O})
\]  

(8)

Due to the unique nature of the transition state, isotope dependent vibration are not always present. This point can be readily illustrated by a simple model in which we isolate the vibrational and translational freedom along the reaction coordinate for consideration.\(^9\) If we find a three particle system A---H---B in a potential energy well, it would have two vibrational modes, namely, a symmetrical vibration and an antisymmetrical vibration.

\[
\begin{align*}
A \to H & \leftrightarrow B \\
\leftrightarrow A & \leftrightarrow H \to \leftrightarrow B
\end{align*}
\]

symmetrical  
antisymmetrical

When A---H---B is a transition state, one of these two modes or some combination of them, must become translational motion along the reaction coordinate.\(^12\) The antisymmetrical mode with increasing A---H bond length and decreasing H---B bond length would correspond to a successful hydrogen transfer; alternatively, with decreasing A---H bond length and increasing H---B bond length would correspond to an unsuccessful encounter between A---H and B. As the antisymmetrical vibration has no potential minimum, it is therefore, not a real vibration but a reaction mode.

The symmetrical vibration is quite different. Since an increase in potential energy would result whether both A and B moving away or approach H, therefore, it has a positive force constant and it is the real vibration remaining in the transition state.
If A-H and H-B have the same bond strength, then this vibration would be truly symmetrical with respect to hydrogen (i.e., A and B periodically move in the opposite direction and H remains motionless). As this vibration is isotope independent, the term \( \left( \text{ZPE}^{A-D}_{A-H} - \text{ZPE}^{A-H}_{A-H} \right) \) in equation (8) vanishes, and all the difference in ZPE s would be transformed into difference in activation energies. Correspondingly, there will be a theoretical maximum isotope effect, i.e.,

\[
\frac{k_\text{H}}{k_\text{T}} = e^{-\Delta E}.
\]

(9)

where \( \Delta E = (\text{ZPE}^{A-D}_{A-D} - \text{ZPE}^{A-H}_{A-H}) \).

However, when the strength of the partial bonds of hydrogen to A and to B are not equal, the symmetrical vibration will no longer consist merely of the motion of A and B; the hydrogen atom will move too. Therefore, the vibration frequency must depend to some extent on the mass of the central atom (i.e., on whether it is hydrogen or deuterium). To the extent that the difference in ZPE s is maintained in the transition state by this vibration, the observed isotope effect will be reduced from the theoretical maximum.

In a more realistic model for the hydrogen transfer between A and B, the doubly degenerated bending vibration should also be considered.\(^{11}\)

This is a rather difficult task since the frequencies of the isotope dependent bending vibrations in the transition state are not accessible experimentally and they cannot be calculated theoretically by the available methods.
In a linear three center hydrogen transfer, it is generally assumed that the bending vibrations for the ground state and the corresponding transition state are similar and thus do not contribute significantly to isotope effect. However, this is not likely to be so in all reactions, and it is probable that changes in bending frequencies contribute to some unusually large and or unusually small isotopes.\textsuperscript{13}

So far, we have considered the nonclassical behavior (i.e., ZPE) of hydrogen in a potential energy well and the resulting isotope effect. We shall now take up the nonclassical behavior of hydrogen passing across a potential energy barrier. The same uncertainty principle of quantum theory, which led to the formulation of ZPE, predicts that a particle possessing higher energy than that of a barrier has a finite chance of being reflected, and one possessing less energy than that of the barrier has a finite chance of crossing. The later process is commonly known as "tunneling".

Tunneling has been called upon in many hydrogen transfer reactions in which isotope effects in excess of the theoretical maximum were observed. Examples and the theoretical bases have been reviewed by Caldin.\textsuperscript{14} A quantitative evaluation of tunneling in hydrogen transfer reaction requires detailed knowledge of the corresponding potential energy surface which is not obtainable at this time. In order to illustrate qualitatively how various factors may influence tunneling, Bell's parabolic model barrier will suffice here.\textsuperscript{15} Bell characterizes the

\[
\nu_t = \frac{1}{2} \frac{1}{E^2/\pi a(2m)^2}
\]

(10)

parabolic barrier by its high, $E$, half-width, $a$, and the curvature at the top by a frequency, $\nu_t$, which is the frequency a particle of mass $m$
would have if it were vibrating in an energy well having the same shape as the barrier as shown in Figure 1a.

Figure 1a. Bell's Parabolic Barrier

If the barrier were inverted to a well a particle of mass \( m \) in this will have

\[
ZPE = \frac{1}{2} h \nu_t
\]

Figure 1b. Quantum Mechanical and Classical Barrier Permeabilities

The probability for the particle of mass, \( a \), and energy, \( w \), to cross the parabolic barrier is governed by the expression:\(^\text{15}\)

\[
G(w) = \left[ 1 + \exp\left(\frac{2\pi(E-w)}{h \nu_t}\right) \right]^{-1}
\]  

(11)

or,

\[
G(w) = \left[ 1 + \exp\left(\frac{2\pi^2a(E-w)(2m)^{1/2}}{hE^{1/2}}\right) \right]^{-1}
\]  

(12)
A comparison between the quantum mechanical permeability of the parabolic barrier with its classical counterpart is illustrated in Figure 1b. Although Figure 1b indicates that the reflection is at least as important as tunneling, it should be pointed out that a more realistic model barrier, the Erkert barrier,\textsuperscript{16} would show that reflection is relatively unimportant. Furthermore, in a hydrogen transfer reaction the fraction of molecules possessing higher energy than the barrier is negligibly small, thereby, make reflection unnecessary for our consideration.

By evaluation of $G(w)$ in equation (8) in terms of a hydrogen transfer reaction, it can be shown that the permeability vanishes rapidly as the width of the barrier or the mass of the hydrogen isotope increases. The appearance of the total energy of the particle term, $E$ in equation (8), has some very interesting consequences. The implication is that there will be a temperature dependent tunneling correction to reaction rate.\textsuperscript{17} At high temperature, the particle would have sufficient energy to cross the barrier in classical manner; whereas, at low temperature, tunneling correction would become important. Such a temperature
dependence should reveal itself as an upward curvature in the low temperature region of the Arrhenius plot providing that the temperature dependency of the reaction is studied over a wide range.

However, for practical reasons, temperature dependence of hydrogen transfer reactions often cannot be studied over a wide range of temperatures. In case the study is carried out at relatively low temperature, the preexponential factor resulting from the incomplete Arrhenius plot would be lower than the similar reaction without tunneling. 18

It is noteworthy that a recent model calculation pointed out that tunneling is more important in hydrogen transfer reactions involving a symmetrical barrier. 13a

From the above discussion we can conclude that the best chance for observing tunneling in a hydrogen transfer reaction is in a reaction involving protium transfer crossing a thin and symmetrical barrier at relatively low temperature.

We have more or less explored the three principle factors which could influence the magnitude of isotope effect, namely: the loss of stretching vibration, the loss of bending vibration, and tunneling. The relative importance of each factor would largely depend on the particular reaction. To isolate various contributions to the isotope effect for a given reaction is not always possible. This is especially true when the isotope effect is at, or near, the theoretical maximum set by the total loss of stretch ZPE. Apart from the more illusive contribution from the change of bending frequency, the contribution from change of stretching frequency and tunneling can be correlated with transition state symmetry. The best correlation would be expected in the cases
that the loss of stretching ZPE is the most prominent factor.
METHOD AND RESULTS

The tritium isotope effects in radical chain addition of dimethyl phosphonate and dimethyl thiophosphonate to olefins were studied by a competitive method. A ten- to thirteen-fold excess of the phosphorus compound which had previously been exchanged with tritium enriched water was allowed to react with the appropriate olefin in the presence of either benzoyl peroxide or 2,2'-azobis-(2-methylpropionitrile) at the temperature the initiator decomposed at a convenient rate.

Since the conversion of the labeled phosphorus compounds to the 1:1 adducts was very low, the tritium isotope effects were calculated according to the linear approximation method described by Melander. The isotope effect is simply equal to the molar specific activity of the reactant, or divided by the molar specific activity of the product, $\alpha_p$, as shown:

$$\frac{k_H}{k_T} = \frac{\alpha_r}{\alpha_p}$$ (13)

The isotope effects and the yields in the addition of dimethyl phosphonate and dimethyl thiophosphonate to unsaturated compounds are summarized in Table 1, and the nmr and a selected portion of ir spectra of these addition products are reproduced in the Appendix.

The radical addition dimethyl phosphonate and dimethyl thiophosphonate to olefins appears to be a satisfactory method for the synthesis of the corresponding alkylated phosphonates providing that the radical intermediate generated from addition step (i.e., equation (2) of Scheme 1) is not highly resonance stabilized. In general, better than 80% yield
TABLE 1

Tritium Isotope Effects and Yields in the Addition of Dimethyl Phosphonate and Dimethyl Thiophosphonate to Unsaturated Compounds

<table>
<thead>
<tr>
<th>Entry</th>
<th>Unsaturated Compounds</th>
<th>(a) (k_H/k_T) Yield</th>
<th>(b) (k_H/k_T) Yield</th>
<th>Order of Transition</th>
<th>Order of Apparent Bond Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PhCH=CH(_2)</td>
<td>--</td>
<td>e</td>
<td>3.8 .30%</td>
<td>1</td>
</tr>
<tr>
<td>2.</td>
<td>AcOCH(_2)CH=CH(_2)</td>
<td>4.9 (\geq 80%)</td>
<td>5.6 (\geq 80%)</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>3.</td>
<td>CH(_3)OC(O)CH=CH(_2)</td>
<td>--</td>
<td>e</td>
<td>6.7 .47%</td>
<td>1</td>
</tr>
<tr>
<td>4.</td>
<td>AcOCH(_2)(CH(_3))C=CH(_2)</td>
<td>6.0 (\geq 80%)</td>
<td>7.6 (\geq 80%)</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>5.</td>
<td>C(_2)H(_5)OCH=CH(_2)</td>
<td>6.1 .40%</td>
<td>8.7 (\geq 80%)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>6.</td>
<td>AcO(CH(_3))C=CH(_2)</td>
<td>10.0 .78%</td>
<td>7.2 (\geq 80%)</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>7.</td>
<td>AcOCH=CH(_2)</td>
<td>12.4 .27%</td>
<td>8.1 .37%</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>8.</td>
<td>(CH(_3))(_3)SiCH(_2)CH=CH(_2)</td>
<td>11.1 (\geq 80%)</td>
<td>9.6 (\geq 80%)</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>9.</td>
<td>PhOCH(_2)CH=CH(_2)</td>
<td>--</td>
<td>f</td>
<td>8.4 (\geq 80%)</td>
<td>3</td>
</tr>
<tr>
<td>10.</td>
<td>NCCH(_2)CH=CH(_2)</td>
<td>--</td>
<td>f</td>
<td>8.3 (\geq 80%)</td>
<td>3</td>
</tr>
<tr>
<td>11.</td>
<td>PhCH(_2)CH=CH(_2)</td>
<td>11.9 (\geq 80%)</td>
<td>8.1 (\geq 80%)</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>12.</td>
<td>PhCH(_2)(CH(_3))C=CH(_2)</td>
<td>10.0 (\geq 80%)</td>
<td>7.0 (\geq 80%)</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>13.</td>
<td>n-C(_6)(_6)H(_13)CH=CH(_2)</td>
<td>8.7 (\geq 80%)</td>
<td>6.8 (\geq 80%)</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>14.</td>
<td>CH(_2)(CH(_2))(_5)CH=CH</td>
<td>8.4 (\geq 80%)</td>
<td>7.3 (\geq 80%)</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>15.</td>
<td>CH(_2)(CH(_2))(_3)CH=CH</td>
<td>9.1 (\geq 80%)</td>
<td>--</td>
<td>d</td>
<td>4</td>
</tr>
<tr>
<td>16.</td>
<td>CH(_2)(CH(_2))(_2)CH=CH</td>
<td>7.5 (\geq 80%)</td>
<td>--</td>
<td>d</td>
<td>4</td>
</tr>
<tr>
<td>17.</td>
<td>PhC≡CH</td>
<td>--</td>
<td>f</td>
<td>6.5 .43%</td>
<td>5</td>
</tr>
<tr>
<td>18.</td>
<td>n-C(_4)(_4)H(_9)C≡CH</td>
<td>6.4 .52%(^g,h)</td>
<td>--</td>
<td>i</td>
<td>5</td>
</tr>
<tr>
<td>19.</td>
<td>(CH(_3))(_3)CH=CH(_2)</td>
<td>6.1 .60%(^h)</td>
<td>6.4 .53%</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>
(TABLE 1 continued)

a Reactions were carried out at 90±0.1° with benzoyl peroxide as catalyst.
b Reactions were carried out at 80±0.1° with AIBN as catalyst.
c Tentatively assigned (see discussion).
d The balance of material was primarily in the form of telomer unless otherwise noted.
e Failed to isolate any 1:1 adduct due to extensive polymerization of olefin.
f This experiment has not been carried out.
g The 1:1 adducts were isolated as binary mixture of cis- and trans-isomers.
h The balance of material was in the form of unreacted olefin.
i Failed to isolate any 1:1 adduct due to extensive formation of 2:1 adduct.
of the 1:1 adducts were isolated as high boiling colorless oils [90-150° (1 mm)] by reduced pressure distillation. A second distillation afforded samples that were pure according to nmr analysis. That no further improvement could be made on the homogeneity was demonstrated by the lack of change in nmr spectra and in molar specific activity of the sample before and after such an operation. The purified samples gave nmr, ir, and in a few cases mass spectra that are in accord with products which would be expected from the chain transfer step (i.e., equation (3) of Scheme 1).

When the radical intermediate generated by phosphoryl radical addition is stabilized by an adjacent phenyl, carbonyl, or oxygen function, the telomerization (i.e., equation (4) of Scheme 1) competed with chain transfer. Under the conditions employed in this study, telomerization predominated to the extent that little or no pure 1:1 adduct could be isolated in some cases. The reactions involving styrene, β-methylstyren, ring substituted styrene, methyl acrylate, methyl methacrylate and N-vinyl cabazole are typical examples in which this is true. When 1:1-diaryl substituted ethylenes were allowed to react with dimethyl phosphonate, unreacted olefins were recovered in essentially quantitative yield. Apparently, both the telomerization and chain transfer became endothermic.

In addition to the reactions with olefins, attempts were made to react dimethyl phosphonate and dimethyl thiophosphonate with 1-hexyne, and dimethyl thiophosphonate with phenylacetylene. These reactions suffered from the complication that in addition to 1:1 adducts, a significant amount of 2:1 adducts made up of two phosphonate and one acetylene units were also produced. In fact, the reaction between
dimethyl thiophosphonate and 1-hexyne gave 2:1 adducts as major products and no 1:1 adduct could be isolated.

It is interesting to note that the radical addition of dimethyl phosphonate to 1-hexyne and dimethyl thiophosphonate to phenylacetylene gave cis- and trans-1:1-adducts in unequal amounts. Spectral data on the purified binary mixture provided little help in determining which of the two geometric isomers was the major product. For instance, the ir spectra of the binary mixture of cis- and trans-1-dimethylphosphoryl-1-hexene showed that the stretching vibration of the carbon-carbon double bond occurred at 1630 cm\(^{-1}\) which is 28 cm\(^{-1}\) lower than that of a typical cis-disubstituted double bond. The bending absorption of a typical double bond (i.e., \(\nu_{\text{cis}} = 690 \text{ cm}^{-1}\) and \(\nu_{\text{trans}} = 960-970 \text{ cm}^{-1}\)) is completely missing from the spectra. The nmr spectra of the binary mixture of cis- and trans-1-dimethylphosphoryl-1-hexene and that of cis- and trans-1-dimethylthiophosphoryl-2-phenylethylene showed exceedingly complex vinyl proton signals which discouraged a detailed analysis of coupling constants.

Kampmeier\(^{19}\) and Singer\(^{20}\) studied the stereoselectivities of the radical addition reactions of alkyne in some detail. The evidence provided supports the idea that the intermediate vinyl radicals generated from radical addition to simple alkynes, are rapidly equilibrating species. Consequently, the stereoselectivity must arise from the differences in free energies of activation leading to the two isomeric chain transfer products. It has been suggested that steric\(^{20}\) and/or electronic\(^{19a}\) interaction would favor trans addition. Therefore, to
the major isomer in the binary mixtures mentioned earlier, we assigned the cis geometry.

However, it should be pointed out that our assignment is by no means conclusive. In view of the formation of substantial quantities of 2:1 adducts in these reactions, it is conceivable that the kinetic product, the cis isomer, could isomerize to the thermodynamically more stable trans isomer via the addition-elimination mechanism. Such a mechanism was proposed for the isomerization of cis-2-butene to trans-2-butene, a side reaction, in the free radical addition of mercaptan or dialkyl phosphine⁴ to cis-2-butene.

Finally, we noticed that while 2,2'-azobis-(2-methylpropionitrile) was a satisfactory initiator for the dimethyl thiophosphonate reactions, it was not very effective in catalyzing the dimethyl phosphonate addition. In order to achieve a good yield of the desired products, benzoyl peroxide was used in all the dimethyl phosphonate reactions.
DISCUSSION

Before entering into a discussion of the results, the possible sources of error need to be explored. These would include the error introduced by the assumption made in the "linear approximation method" employed in the calculation of isotope effect; errors in the determinations of molar specific activities of reagents and products; and a small uncertainty in the reaction temperature.

The validity of the linear approximation method depends largely on the extent of conversion with respect to the isotopically labeled reagent. In principle, an infinite excess of labeled reagent is required to prevent any error from this source. However, in practice, a ten-fold excess is usually sufficient to apply this method without any significant error.\(^{10}\)

The major errors, most likely, were introduced in the determinations of molar specific activities of reagents and products. First, there are some random errors such as statistical errors in the number of counts, time of counting, and weighing. Care was taken to minimize these errors by using a large number of counts (\(10^4\) to \(10^5\) counts), long counting time (10 to 20 minutes), and triplicate samples in each molar specific activity determination. The fact that the extreme deviations were no greater than 3% for each of these measurements, indicates that the random errors are insignificant.

However, there are some bias errors associated with the uncertainty of the homogeneity of the sample which could be important. For instance, dimethyl phosphonate is found to be very hygoscopic and dimethyl thiophosphonate, to a lesser extent, is also found to be
hygroscopic. In the preparation of the tritium labeled phosphonate esters, dimethyl phosphonate and dimethyl thiophosphonate were exchanged with tritium enriched water. To remove water after each exchange, the phosphorus compounds were dried over Drierite and fractionated several times until constancy of molar specific activity was reached. Although these samples were kept away from atmospheric moisture as much as possible, no special precaution was taken during transfer into the reaction vessel. By virtue of the small equivalent weight of hydrogen in water, an inclusion of 0.1%, w/w, of inactive water is equivalent to a 1.3% increase of exchangeable hydrogen in the sample. If exchange between water absorbed from the atmosphere and the labeled material had not taken place before and during the radical addition reaction, little or no error would be introduced. On the other hand, if extensive exchange had taken place before or during the reaction, some of the tritium would be washed into water, and the activity of the labeled reagent would be over-estimated by the amount lost in the exchange.

The 1:1 adducts, especially those derived from dimethyl phosphonate addition to olefins with oxygen-containing functional groups, are hygroscopic. This is evident from the fact that these samples, after exposed to atmospheric moisture showed OH band in their ir spectra and the intensity of the band depended on the length of exposure. Since freshly distilled samples with minimum exposure to atmospheric moisture were employed in counting, any error from this is quite insignificant.

As the 1:1 adducts are high boiling materials, attempts to determine their purity by glpc method were unsuccessful. The purity of each sample was checked by its nmr spectrum and in a few cases by mass spectra.
Although there was no evidence of contamination, the possibility that samples were contaminated by a few percent of the 1:2 adducts cannot be excluded. To a good approximation the reaction leading to the 1:2 adduct would involve an isotope effect similar to the reaction generating the 1:1 adduct. Therefore, to the extent that samples were contaminated by the higher molecular weight impurity of the same molar specific activity there would be an uncertainty in molecular weight employed in the calculation. Since the molecular weight of the 1:1 adduct was actually used, the molar specific activity would be slightly underestimated.

There was some uncertainty in the reaction temperature because of a time elapse from the moment the reaction vessel was immersed in the oil bath until the reactants reached thermal equilibrium. We believe that the error from this source is quite small because a heating rate test showed that only two minutes were required for the contents of the reaction vessel to reach a temperature ca.5° from thermal equilibrium, while an additional three minutes were sufficient for the reaction temperature to be within one degree of bath temperature.

In summary, other than the errors derived from contamination of the phosphorus compounds by water, for which no firm estimate could be established, the combined errors derived from other sources is unlikely to be much greater than ± 3%. The reproducibility established by several repeated reactions involved errors not significantly greater than ± 3%; thus, the results listed in Table 1 can be used for meaningful discussion.

To establish some basis for discussion, let us first consider the theoretical limit of isotope effects if all of the stretching vibration for the P-H bond is lost. The stretching vibration for dimethyl phosphonate and dimethyl thiophosphonate show a small concentration and
solvent dependency, therefore, values reported in the literature vary slightly. Some of the reported numbers are listed in Table 2.

Since the deviations are not significantly large, we arbitrarily took the value 2444 cm\(^{-1}\) for the phosphonate\(^{23a}\) and 2416 cm\(^{-1}\) for thiophosphonate\(^{23b}\) as probably most free from hydrogen bonding effects. From these values, the maximum isotope effects 7.74 and 8.00 were calculated for phosphonate reaction at 90\(^0\) and thiophosphonate reaction at 80\(^0\) respectively.

**TABLE 2**

<table>
<thead>
<tr>
<th>Condition</th>
<th>(\text{HP(0)(OCH}_3\text{)}_2)</th>
<th>(\text{HP(0)(OCH}_3\text{)}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor(^{23b})</td>
<td>2435 cm(^{-1})</td>
<td>-</td>
</tr>
<tr>
<td>0.025-1.0M(^{23a,b}) in CCl(_4)</td>
<td>2439 cm(^{-1})</td>
<td>-</td>
</tr>
<tr>
<td>Neat(^{23a})</td>
<td>2427 cm(^{-1})</td>
<td>2406 cm(^{-1})</td>
</tr>
<tr>
<td>0.010-0.015M(^{23a}) in CCl(_4)</td>
<td>2444 cm(^{-1})</td>
<td>2416 cm(^{-1})</td>
</tr>
<tr>
<td>Neat(^{23a})</td>
<td>2432 cm(^{-1})</td>
<td>2400 cm(^{-1})</td>
</tr>
</tbody>
</table>

When these theoretical maximum isotope effects are compared with the values listed in Table 1, it is readily recognized that two-thirds of the experimentally established isotope effects either exceed or come very close to the theoretical limit. The exceptional cases are reactions involving carbon radicals that belong to one of the
following four classes: (1) carbon radicals stabilized by resonance (i.e., entries 1b, 2a, 2b, 3b, 5a and 5b); (2) carbon radicals that are SP$^2$ hybridized; (3) carbon radicals generated from allyl esters (i.e., entries 2a, 2b, 4a and 4b); and (4) carbon radicals that are sterically hindered (i.e., entries 19a and 19b).

The large isotope effects as well as those relatively smaller ones in class (1) and (2) radicals are comprehensible in terms of bond strength. If we assume that H-P bond strength is very similar to H-C$_{SP^3}$ bond, then the large isotope effect in the hydrogen transfer to the majority of secondary radicals is entirely reasonable. The reduction of isotope effects due to resonance stabilization of carbon radical as well as the reduction in isotope effect due to destabilization of carbon radical by a change from SP$^3$ to SP$^2$ hybridization are also perfectly consistent with the theory presented in the introduction.

However, there are some features of the data which defy a simple interpretation. At least in part, the problem is that the isotope effects under consideration may respond to subtle changes in bending vibration and tunneling. Unfortunately, the existing theories are entirely inadequate to allow a meaningful correlation between changes in bending vibration in transition state and tunneling with structure modification. Therefore, a discussion along this line will not be attempted.

In principle, it is possible to correlate qualitatively the effects of substituent on transition state structure.$^{24}$ In the following, we shall tentatively account for the unusual features by invoking ionic and steric contributions to transition state symmetry in order to offer a more or less self consistent interpretation of the data.
One of these unusual features is the anomalously low isotope effects for allyl esters, and another is the fact that olefins with a polar $\gamma$-substituent gave higher isotope effect than those without substituent (i.e., compare 10a, 11a, 12a with 13a and compare 9b, 10b, and 11b with 13b). Perhaps if we consider the transition state in the hydrogen transfer step to be some what polar in nature then these anomalies may become understandable.

Often radical reactions are insensitive to polar changes. Nevertheless, exceptions to this rule are found in the literature. For example, when substituted toluenes were brominated with molecular bromine, or chlorinated\(^{25}\) by protonated N-chloroamine,\(^{26}\) substituent effects indicated by substantial values of the Hammett rho were found. Dipolar transition states have been invoked in the free radical addition of thioacetic acid to trans-2-chloro-2-butene in order to rationalize the prepondance of the threo isomer.\(^{27}\) It was assumed that the largest negative dipole on the saturated carbon was oriented away from the developing dipole in the transition state, thus leading to the threo product, i.e.,

\[
\begin{array}{c}
\text{(Ac)} \\
\text{\(\delta^+\)} \\
\text{H} \\
\text{\(\cdot\cdot\cdot\)} \\
\text{C} \\
\text{\(\cdot\cdot\cdot\)} \\
\text{CH}_3 \\
\end{array}
\]

\[
\begin{array}{c}
\text{\(\delta^-\)} \\
\text{H} \\
\text{\(\cdot\cdot\cdot\)} \\
\text{C} \\
\text{\(\cdot\cdot\cdot\)} \\
\text{CH}_3 \\
\end{array}
\]

\[
\begin{array}{c}
\text{\(\delta^-\)} \\
\text{H} \\
\text{\(\cdot\cdot\cdot\)} \\
\text{C} \\
\text{\(\cdot\cdot\cdot\)} \\
\text{Cl} \\
\end{array}
\] 

\[
\begin{array}{c}
\text{\(\delta^-\)} \\
\text{H} \\
\text{\(\cdot\cdot\cdot\)} \\
\text{C} \\
\text{\(\cdot\cdot\cdot\)} \\
\text{Ac} \\
\end{array}
\]

\[\rightarrow\]

threo product.
On account of the highly polarizable nature of the phosphorus atom, it is possible that a neighboring polar function can induce some polar contribution to the transition state and thereby produce a shift in transition state symmetry. In the cases of the γ-substituted olefins, the shift appears to be in the direction of approaching a more symmetrical transition state and giving rise to a higher isotope effect.

The anomalously low isotope effects which were found in the reactions involving allylic esters cannot be accounted for by the inductive effect alone. However, in these cases the acetyl function is suitably situated to participate in the manner illustrated as follows:

\[ \text{R} = \text{H or CH}_3 \]

Since an ionic contribution may cause a shift away from product like transition state, anchimeric assistance could produce a further shift in the same direction, possibly, to the extent that the transition state becomes reagent-like. If this is indeed what happens, the
low isotope effects for these reactions are no longer a puzzle.

It should be pointed out that acetyl participation is most certainly unimportant in the ground state radical, at least, bond formation between the carbonyl oxygen and $\beta$-carbon does not take place, i.e.,

with formation of a ketalyl radical intermediate. Failure to detect products such as the corresponding ketal and $\beta$-acetyl derivatives, which could arise from the ketalyl radical argues against the presence of such an intermediate.

In addition to the electronic effect, the steric effect may also play a significant role in the hydrogen transfer reaction. It has been shown in the proton transfer from nitropropane to substituted pyridines that steric effects influence the isotope effect strongly, possibly by introducing a steep and thin barrier where tunneling becomes important. It may also raise the activation energy so that reaction has to proceed further along the reaction coordinate before the transition state is reached. Most likely, this was what happened in the cases where neopentyl radicals were at the reception end of hydrogen transfer (i.e., entries 19a and 19b).

As expected, the variations in isotope effect between most cyclic olefins and 1-octene are quite small. A noticeably lower value for
the cyclopentene reaction is probably accountable by the increases in angle strain and I-strain as the cyclopentyl radical approaches the transition state.\textsuperscript{29} i.e.,

\begin{center}
\includegraphics[width=0.5\textwidth]{cyclopentene_transition_state.png}
\end{center}

increase in eclipsing C-H bonds

The resulting increase in activation energy could cause the transition state to shift towards the product-like direction and correspondingly product a lower isotope effect.

The changes in isotope effects resulting from a change from a secondary radical to a tertiary radical probably also stem from steric origin. The effect appears to be obscured because the pairs of reactions in which such comparison can be made are: those giving isotope effects that are very near or significantly above the theoretical maximum (i.e., entries 6a vs 7a, 6b vs 7b, 11a vs 12a, and 11b vs 12b) and those in which neighboring group effect of the acetyl function may be important (i.e., entries 2a vs 4a and 2b vs 4b).

In the former case, where tunneling is most likely to intervene, the influence of the addition methyl group is difficult to assess. However, for the later case an explanation which is consistent with the steric argument presented for the neopentyl radical can be offered.
The additional methyl group at the reaction site could cause an increase in steric compression or a reduction in the effectiveness of the acetyl participation. By either view the transition states involving radicals derived from 8-methylallyl acetate is expected to be closer to symmetrical than that of allyl acetate and giving rise to a higher isotope effect.

We have more or less explored the noticeable trends as well as some special features of our data. In summary, while the bond strength is still the major factor influencing transition state symmetry, modifications of the transition state symmetry by polar or steric effects probably should not be overlooked. If appropriate adjustment for polar and steric influences are superimposed on the bond strength consideration, a tentative ordering of transition state symmetries such as the one presented in Table 1 can be accomplished.

From this correlation, it is interesting to note that for the entries, which have been given transition state symmetry of order 1, the isotope effect is greater for the thiophosphonate reaction than the phosphonate reaction; whereas, for the remaining entries the reverse is true. The implication is that the maximum isotope effect for the thiophosphonate reaction occurs at an earlier position of the order. If we recall that the phosphorus hydrogen bond in dimethyl thiophosphonate is weaker than that in dimethyl phosphonate, as indicated by their stretching vibration absorbtions, then the fact that the maximum isotope effect for dimethyl thio-phosphonate reaction is found in the earlier position in the order, should come as no surprise.

Finally, it cannot be overemphasized that much of the interpretation presented in this discussion is at best an educated guess. Nevertheless,
we believe that our results have pointed out some of the limitations of the existing theories concerning the interpretation of isotope effect, and certain complications which could be associated with the application of a radical addition reaction in the investigation of isotope effect. We hope that these results will on one hand prompt the development of new theories, especially those concerning bending vibration and tunneling; and on the other hand will help us to find more suitable systems in which a better control of the various important factors can be achieved.

We are far from mastering the seemingly simple potential energy surface of the hydrogen transfer reaction. Much theoretical work, as well as experimental work, is needed before such a claim can be made. A study of isotope effect in the radical addition of hydrogen halides to olefins which is already in progress in our laboratory, may soon provide information pertaining to the importance of polar effect in hydrogen transfer from hetero atom to carbon radical. An investigation of the radical addition of secondary phosphines with suitably chosen polar substituents also appears to be promising in this connection.
EXPERIMENTAL

General

Nmr spectra were recorded on a Varian Associates A-56/60 spectrometer with TMS as internal standard, using approximately 15% v/v solution in CCl₄; ir spectra were recorded on a Beckman IR-8 spectrophotometer using neat liquid placed between sodium chloride plates; glpc analysis were performed on a Perkin-Elmer 800 gas chromatograph (flame ionization detector) using a 10 ft. x 1/8 in. column packed with 10% Carbowax on Chromosorb W; mass spectra were obtained on a CEC 21-110C mass spectrometer; and radioactivity measurements were made with a Packard Tri-Carb Model 3365 liquid scintillation spectrometer.

Materials

Reagent grade commercial materials were used without further purification except for the following: Olefins either purchased from commercial source or prepared according to known procedures were dried over Drierite and fractionated to glpc purity before used; phosphorus trichloride was purified by distillation; and triethylamine was distilled from calcium hydride.

Reactions

Tritium enriched dimethyl phosphonate. To 440 g (4 moles) of dimethyl phosphonate was added 2 ml tritium enriched water (1 µCi/g), and a few drops of acetic acid. The solution was stirred for 24 hours and then dried over Drierite. Reduced pressure distillation through a 14 in.
glass helices packed column yielded a center fraction 395 g [bp. 64-65° (15 mm)]. Fractionation was repeated one or two times until constancy in molar specific activity was reached.

**Dimethyl thiophosphonate.** The dimethyl thiophosphonate was synthesized via the dimethyl chlorophosphinate according to the literature procedure. Trimethyl phosphonate 248 g (2 moles) was added slowly to phosphorus trichloride 173 g (1 mole) over a period of 1 hour with stirring. At the time the addition was completed, the mildly exothermic reaction had caused the reaction mixture to rise to ca. 45°. The reaction was allowed to proceed at 45 to 50° for an additional hour and the resulting mixture was distilled through a 6 in. Vigreux column. A fraction 238 g [bp. 32-40° (40 mm)] consisting of a mixture of 70-80% dimethyl chlorophosphinate and 30-20% methyl dichlorophosphinate was collected. The above mentioned procedure was repeated several times and the mixtures of methyl chlorophosphinates were combined and fractionated through a 14 in. glass helices packed column to give 1000 g [bp. 32-34° (40 mm) Lit.31 bp. 103-105° (760 mm)]; nmr δ 3.57 (d, J=11 Hz. methoxy).

A stream of dried hydrogen sulfide was passed into a vigorously stirred mixture consisting of dimethyl chlorophosphinate 46 g (0.3 mole), trimethylamine 33 g (0.3 mole), and 1 l. of anhydrous ether at -15° to -10° until it was no longer being absorbed. To isolate the product, the reaction mixture was filtered and the filtrate was washed with portions of water, dried over Drierite, and concentrated with the aid of a rotary evaporator. Typically 28 g (74%) of dimethyl thiophosphonate [bp. 52-54° (12 mm) Lit.32 bp. 52-54° (12 mm)], nmr δ 3.82 (6H, d, J = 14 Hz, methoxy), δ 4.87 (1H, d, J = 664 Hz, phosphoryl) was
separated by reduced pressure distillation. The above mentioned procedure was repeated nineteen times in order to produce 530 g of dimethyl thiophosphonate.

Tritium Enrichment of Dimethyl Thiophosphonate. Tritium enrichment of dimethyl thiophosphonate was carried out in the same manner as that described for the dimethyl phosphonate.

General Procedure for the Addition of Dimethyl Phosphonate and Dimethel Thiophosphonate to Unsaturated Compounds. The appropriate olefin (0.03 m), benzoyl peroxide (1.50 mmole) and a large excess (0.40 mole) of tritium enriched dimethyl phosphonate was placed in a thick wall ampule (1 in. I.D. x 8 in. length). After being properly degassed, the ampule was sealed and placed in a thermostated oil bath at 90.0±1\,^\circ\text{C} for eight hours. The reaction mixture was cooled to room temperature and the 1:1 addition product was isolated by reduced pressure distillation through either a 6 in. glass helices packed column or a 4 in. Vigreux column. A second or even a third distillation was often needed to obtain 1:1 adduct free of contamination by decomposition products derived from initiator and 1:2 adducts. The 1:1 adduct and pot residue were characterized by their nmr and ir spectra. Nmr spectra and a selected portion of ir spectra of these compounds are reproduced in Appendix 1.

The reactions involving dimethyl thiophosphonates were carried out in the same manner as that described for the dimethyl phosphonate, except for three minor changes: (1) only a 10-fold excess of dimethyl thiophosphonate over olefin was employed; (2) 2,2'-azobis(2-methyl-propionitrile) was used in place of benzoyl peroxide and (3) the reaction was carried out at 80.0±0.1\,^\circ\text{C}. 
Counting Procedure. Weighed samples were added to 20 ml of a solution containing 5 g of 2.5 diphenyloxazole and 0.1 g of p-bis[2-(5-phenyloxazoyl)] benzene per liter of toluene and counted for 20 min. Background corrections and efficiency corrections using external standardization were applied to all results. All counting efficiencies were about 28-33%. Since no sample quenched badly, no effort was made to maximize the efficiency. Samples of dimethylphosphonate and dimethyl thiophosphonate gave molar specific activities in the order of $2 \times 10^8$ decomposition mole$^{-1}$ min$^{-1}$ with an extreme deviation of less than 3%.

Determination of Heating Rate for Reaction Mixture to Reach Thermal Equilibrium with Oil Bath. A thermometer was inserted into the reaction vessel containing 33 g of dimethyl phosphonate or 30 g of dimethyl thiophosphonate. As soon as the vessel was immersed into the thermostated oil bath, the temperature was taken at 15 sec. intervals until thermal equilibrium was reached. The procedure was repeated three times for each phosphonate and in all cases, the temperature rose to $5^\circ$ from equilibrium temperature in 2 min. and reached within $1^\circ$ of the oil bath temperature in 5 min.
REFERENCES


APPENDIX
(CH₃)₃SiCH₂CH₂CH₂P(OCH₂)₂

CH₃OCH₂CH₂CH₂P(OCH₂)₂

CNCH₂CH₂CH₂P(OCH₂)₂
\[(\text{CH}_3)_2\text{CHCH}_2\text{P(OCH)}_2\]  
\[(\text{CH}_3)_2\text{CCH}_2\text{P(OCH)}_2\]