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by

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PART I. INTRODUCTION

Although the intermediacy of a divalent carbon species was postulated[1] as early as 1862, only within the last 20 years has the existence of highly electrophilic carbenes been firmly established by experimental observation.[2,3]

In a series of papers originating in 1950, Hine, et al.,[2] employed kinetic techniques to effectively demonstrate the formation of dihalocarbenes in the basic hydrolysis of a number of haloforms. The pronounced electrophilic behavior of carbenes was illustrated by Doering and coworkers[3a,3b] when dichlorocarbene, generated from chloroform and potassium t-butoxide via α-elimination, was shown to add to olefins producing dichlorocyclopropanes. A fascinating example of high reactivity presents itself in the indiscriminate insertion into carbon-hydrogen bonds by methylene produced by the photolysis of diazomethane.[3b]

One of the most popular means of generating carbenes has been through α-elimination. In recent years the exact nature of the electrophilic intermediates involved has come under close scrutiny. Some divalent carbon species derived from different precursors react in the same fashion qualitatively but differ enough quantitatively to make a common intermediate very suspect.

An extensive study was conducted by Closs and Moss who prepared a series of arylcyclopropanes from α-elimination on benzal bromides and from the photolysis of aryldiazomethanes in the presence of olefins.[4] Although both intermediates yielded more syn cyclopropane than anti and both were consumed faster by olefins of increasing nucleophilicity, the electrophilic species produced in the photolysis reaction proved to be

$$X = H, \ p - CH_3, \ p - Cl, \ m - Cl, \ p - OCH_3$$
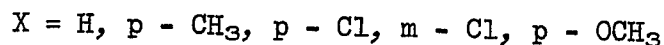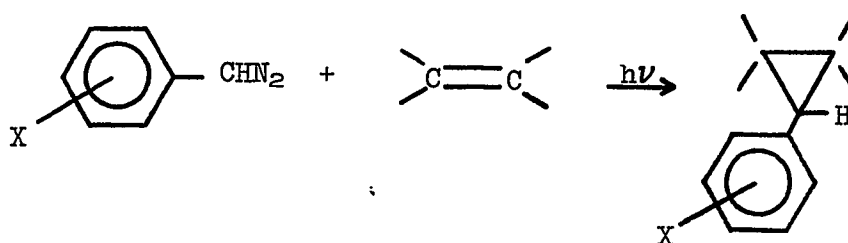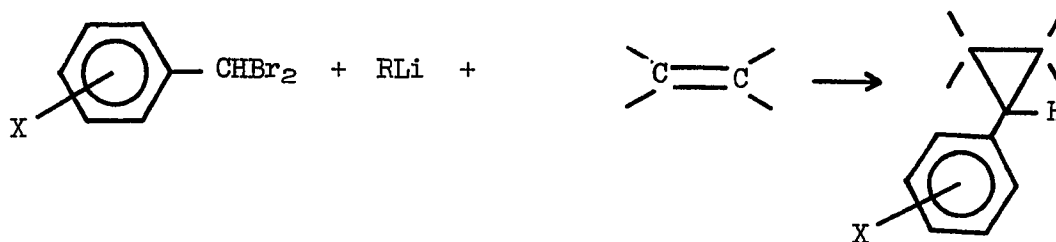
a more reactive intermediate in both categories. Since a considerable body of information strongly suggests that the photolysis of diazoalkanes gives true divalent carbon intermediates,[5] the α-elimination intermediate was designated a "carbenoid." The term is used to describe "intermediates which exhibit reactions qualitatively similar to those of carbenes without necessarily being free divalent carbon species.[4]"

Currently, much interest has centered around distinguishing between a free carbene (2) and a carbenoid (1) as the cyclopropane producing intermediate in α-elimination reactions. Conditions which might be expected to play a role in this reaction include the nature of the leaving groups, the stability of the free carbene, the type of olefin, and the solvent.
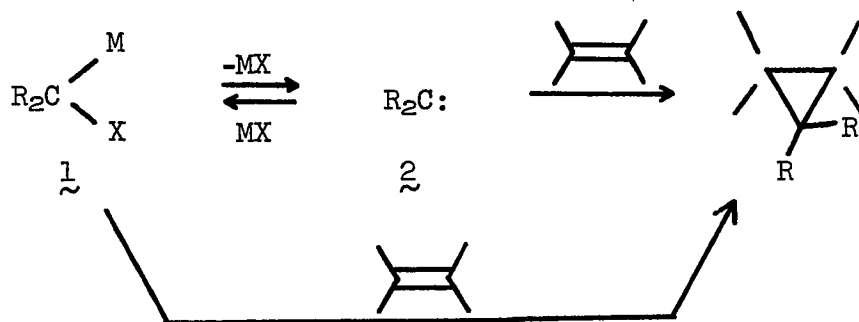
An ingenious piece of work exemplifying the influence of different leaving groups and discounting the intermediacy of a free carbene is illustrated in the deuterium isotope effect for intramolecular insertion in the formation of hexadeuterated 1,1-dimethylcyclopropanes from 1-halo-2,2-di(methyl-$\underline{d}_3$)propyllithium reagents.[8] The isotope effect was shown to vary with different halide leaving groups: k_H/k_D = 2.43 ± 0.02 for
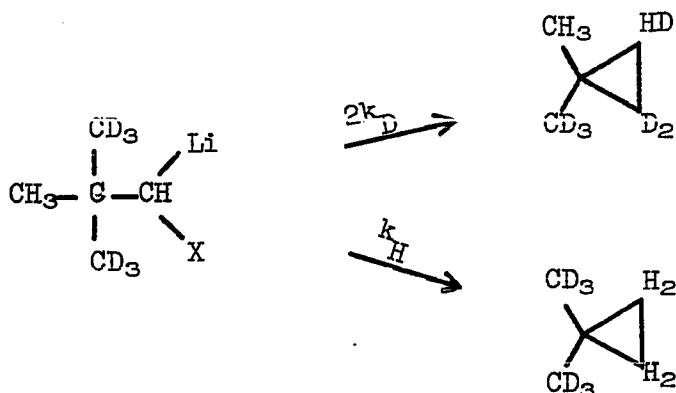
X = I ($-44°$); k_H/k_D = 2.06 ± 0.10 for X = Br ($-44°$); and k_H/k_D = 1.71 ± 0.06 for X = Cl ($-68°$). These results imply that the halide be present in the transition state for insertion and that a common intermediate, namely a free carbene, is bypassed. This conslusion was strengthened by a comparison of the inter- and intramolecular isotope effects for this

system which indicated that there was no intermediate separating the
initially formed organometallic reagent from product. Other studies in
which the metal moiety was varied lead to similar conclusions.[9]

The nonbonding electrons of methylene can have antiparallel spins
(singlet state) or parallel spins (triplet state). Spectroscopic and
theoretical studies[15,16] indicate that triplet methylene is a linear
molecule (3) and singlet methylene possesses a bent configuration (4).
As a consequence of spin conservation, singlet methylene is formed

3   4

initially although triplet methylene is now considered to be the ground
state species[17] (a singlet ground state is favored for difluorocarbene
however).[18]

As judged from the selectivity exhibited by carbenes in reactions
with olefins to form cyclopropanes, the relative stabilities of a series
of carbenes follow the order $CF_2 > CCl_2 > CBr_2 > CHCl > CH_2$.[3c,6,7,27]
Halogens appear to stabilize the carbene by overlap of the unshared
electrons of halogen with the vacant carbon p-orbital.

To date, every method of generating dichlorocarbene has been shown
to produce the free carbene. A very lucid example is available in the
kinetic work of Seyferth and coworkers.[10] The reaction rate of phenyl-
(bromodichloromethyl) mercury with olefin proved independent of olefin
concentration and was first order in organomercury reagent. More highly
substituted olefins hastened the reaction while the addition of phenyl-

mercuric bromide retarded cyclopropane formation. The quantitative

analysis of these effects fit perfectly the following mechanistic scheme:

$$\phi HgCCl_2Br \quad \underset{k_{-1}(fast)}{\overset{k_1(slow)}{\rightleftarrows}} \quad \phi HgBr + :CCl_2$$

$$:CCl_2 \quad + \quad \underset{}{\bigg\rangle \!\!=\!\! \bigg\langle} \quad \xrightarrow{k_2(fast)} \quad \triangle$$
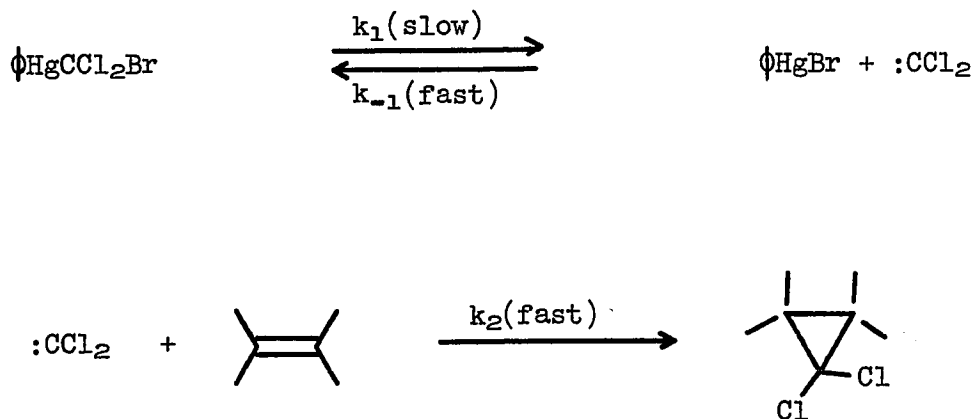
Since the relative reactivities of a series of olefins of varying

nucleophilicities (ranging from 2,3-dimethyl-2-pentene to 1-heptene)

with dichlorocarbene generated from ϕ HgCCl$_2$Br,[10] CCl$_3$CO$_2$Na,[11] CHCl$_3$/

KOC(CH$_3$)$_3$[12,7b], LiCCl$_3$,[13] and the thermolysis of HCCl$_3$ give the same

quantitative results within experimental error, a free dichlorocarbene

intermediate is believed formed in each case. These results follow from

the high degree of stability which halogens impart to the carbene center.

The least stable and most reactive of all the carbenes is methylene.[3b,7c]

When created by photolysis or pyrolysis of diazomethane in the presence

of a hydrocarbon, methylene inserts into C-H bonds in an approximate

statistical manner[3b,7c] and adds to olefins to yield cyclopropanes.

Methylene generated in this manner is truly a free carbene.

From chemical evidence the stereospecific addition of a carbene to

a double bond appears to be a singlet reaction.[3c,3e,19,20] Every addition

to a double bond involving α-elimination has proceeded completely stereo-

specifically cis, whereas nonstereospecific addition has occurred in some

cases where the divalent electrophilic intermediate was generated from a

diazo compound.[21,22]

The complex which forms in the reaction of methylene iodide with zinc-copper couple is stable in ether and reacts slowly with olefins yielding cyclopropanes.[23] In contrast to the diazomethane results, no C-H insertion products appear. Kinetic studies verified that the reaction rate is first order in olefin concentration and that the intermediate exhibits electrophilic character.[24] The reaction also shows a steric preference, with norbornene giving only exo adduct.[25]

The accumulation of all this information leads to the conclusion that a carbenoid, formally designated ICH_2ZnI, transfers methylene directly to an olefin without ever going through a free carbene.

Many such methylene transfer agents are now recognized which evince a wide range of halide and metal leaving groups.[26] Due to the selectivity of these reagents the emergence of free methylene appears dubious.

Of intermediate stability between methylene and dichlorocarbene rests monochlorocarbene. Evidence has been amassed which supports the carbenoid pathway in α-elimination reactions involving the transfer of monochloro-carbene to olefin. Closs and Coyle[6] compared the reactivities of free chlorocarbene produced by photolysis or pyrolysis of chlorodiazomethane with the intermediate generated in the reaction of methylene chloride and

$$\ce{>C=C<} + \overset{Cl}{\underset{H}{>}}C=\overset{+}{N}=\overset{-}{N} \quad \xrightarrow[\text{pentene}]{\begin{array}{c}\Delta\ (-30^\circ)\\ \text{or } h\nu\ (-50^\circ)\end{array}} \quad \triangle-Cl \quad (1)$$

$$\ce{>C=C<} + CH_2Cl_2 + BuLi \quad \xrightarrow[\text{pentene}]{-35^\circ} \quad \triangle-Cl \quad (2)$$
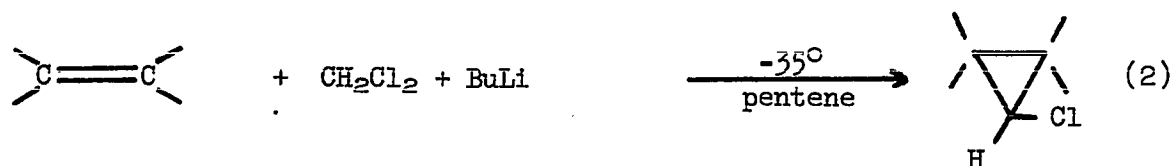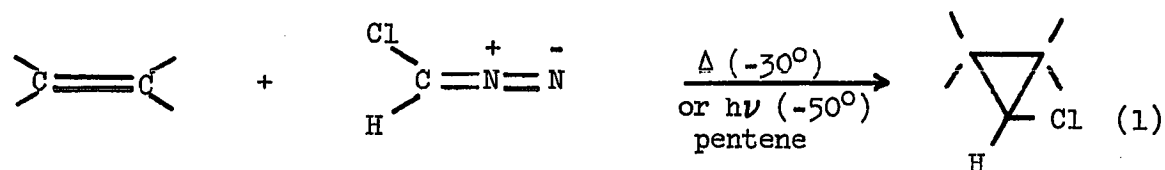
butyllithium. In both cases the addition to _cis_ and _trans_ butene is
stereospecific. Presumably, singlets are responsible. Olefins more
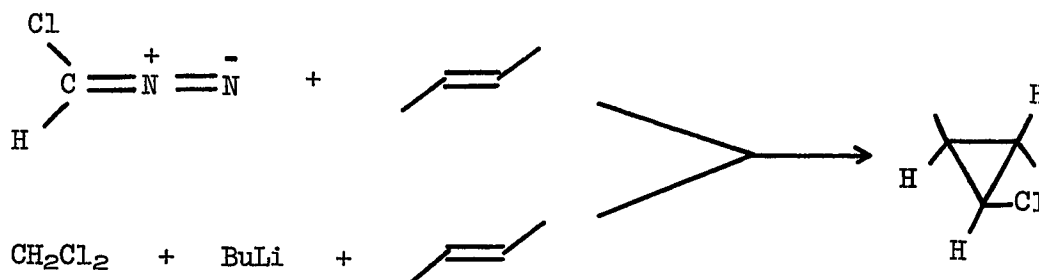
highly substituted with alkyl groups react faster, but less selectivity
is observed for the intermediate generated from chlorodiazomethane. In
reaction 1 tetramethylethylene is consumed 1.6 times faster than 1-butene.
In reaction 2 this value rises to 12.2.

The ratio of _syn_ to _anti_ products varies in the two systems. The
free chlorocarbene (reaction 1) shows no preference at all, giving equal
amounts of _syn_ and _anti_ products, whereas in reaction 2, _cis_-butene
yields cyclopropanes with _syn_/_anti_ = 5.5.
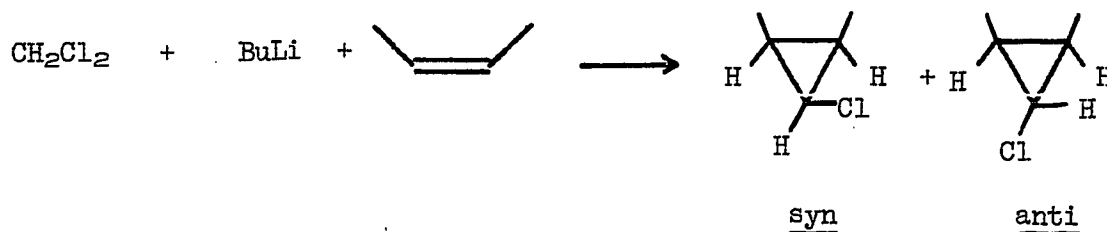
Preferential formation of the less thermodynamically stable _syn_ product
occurred in all cases where chlorocarbenoid was the intermediate.
Although the reason for this behavior remains obscure, it would appear
that _syn_/_anti_ selectivity for this particular system is a property of
the carbenoid and not the free carbene.

Obvious empirical differences dictate that the two reactions
.contribute nonidentical electrophilic intermediates. Photolysis or

pyrolysis of chlorodiazomethane also leads to insertion of chlorocarbene into the C-H bonds of the hydrocarbon solvent. This behavior is not witnessed in the reaction of methylene chloride and butyllithium.

An argument might be advanced which accuses the chlorodiazomethane decomposition of producing a "hot" carbene (i.e., excess vibrational and translational energy). Such a species would be expected to react a bit more indiscriminately than ground state chlorocarbene. Such "hot" intermediates are not long-lived in solution because they are readily relieved of their excess energy through collisions with solvent molecules. Although it holds true that the intermediate differentiates between olefins only to a small degree, the ratio of addition to a double bond to insertion into secondary C-H bonds of the solvent is 600. Having so many collisions with solvent molecules it seems difficult to imagine that the intermediate does not attain thermal equilibrium.

Although a portion of reaction 2 may traverse the free carbene route, the syn/anti ratios combined with the relative rates of olefin reactivity strongly suggest that the major reaction pathway is through the carbenoid.

A remarkable observation was made by Katz and Garratt[28a] when they treated methylene chloride and cyclooctatetraene with methyllithium solutions containing different lithium halides. When the methyllithium included lithium iodide, only one product, syn-9-methylbicyclo[6.1.0] nonatriene (5), was observed. However, in the presence of lithium bromide the major products isolated were syn- (6a) and anti-9-chloro-bicyclo[6.1.0]nonatriene (6b) with only a small amount of 5. Control experiments proved that 5 was a primary product of the reaction and did not arise from a coupling of 6a or 6b with methyllithium.

$$\text{(cyclooctatetraene)} \quad + \quad CH_3Li \quad + \quad CH_2Cl_2 \quad \xrightarrow{Et_2O} \quad \text{(product)} \; CH_3$$
(LiI)

5

$$\text{(cyclooctatetraene)} \quad + \quad CH_3Li \quad + \quad CH_2Cl_2 \quad \xrightarrow{Et_2O} \quad \text{(product)} \; Cl \quad + \quad 5$$
(LiBr)

6
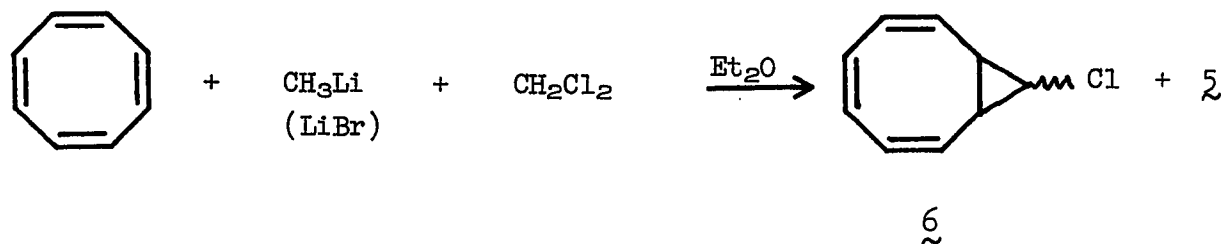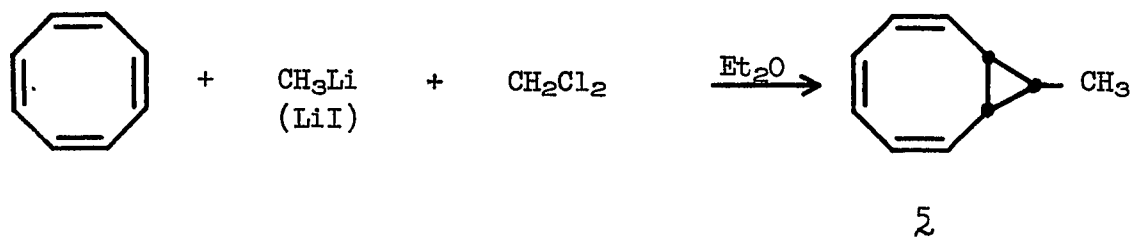
Since this initial discovery, the "salt effect" in α-elimination

reactions has received a moderate degree of attention.[28] Jefford,

et al.,[28d] studied the products obtained in the reaction of norbornene,

methylene chloride, and methyllithium. With the use of methyllithium

prepared from methyl chloride and lithium metal, the only products

isolated were exo, anti-3-chlorotricyclo[3.2.1.0^{2,4}]octane (7) and

exo-4-chlorobicyclo[3.2.1]oct-2-ene (8). The same reaction, but with

$$\text{(norbornene)} \quad + \quad CH_2Cl_2 \quad + \quad CH_3Li \; \xrightarrow{Et_2O} \quad \text{(products 7 and 8)}$$
(LiCl)

7   **8**
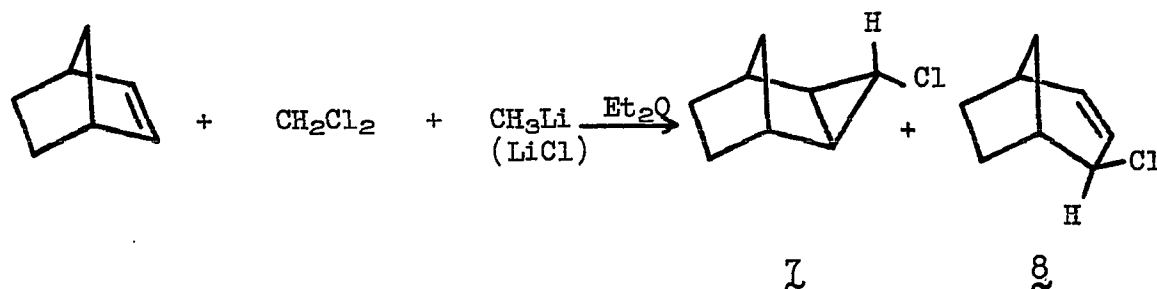
methyllithium prepared from methyl bromide and lithium metal, gave 7 and

8 along with exo, anti-3-bromotricyclo[3.2.1.0^{2,4}]octane (9) and exo-4-

bromobicyclo[3.2.1]oct-2-ene (10).
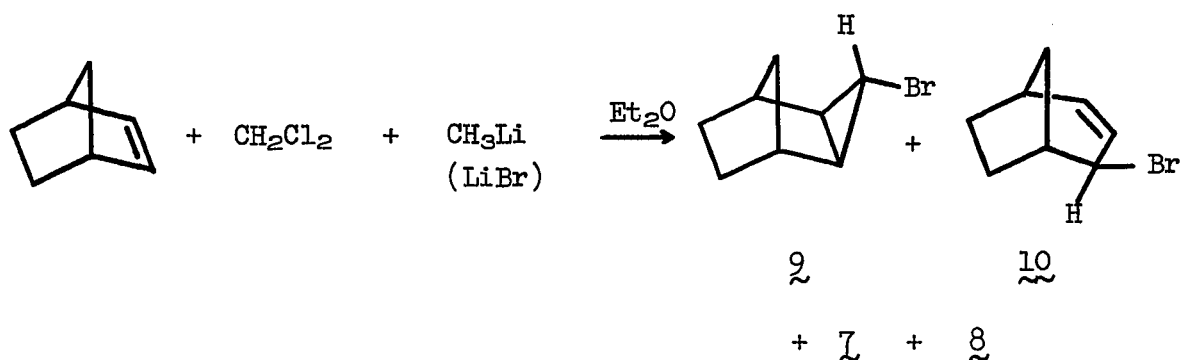
The appearance of $\underset{\sim}{8}$ and $\underset{\sim}{10}$ can be handily explained by an orbital

symmetry-allowed ring opening process of initially formed exo,syn-3-

halotricyclo[3.2.1.0^{2,4}]octane ($\underset{\sim}{11}$).[37,41] A mechanistic scheme for the

$\underset{\sim}{8}$ X = Cl

$\underset{\sim}{10}$ X = Br
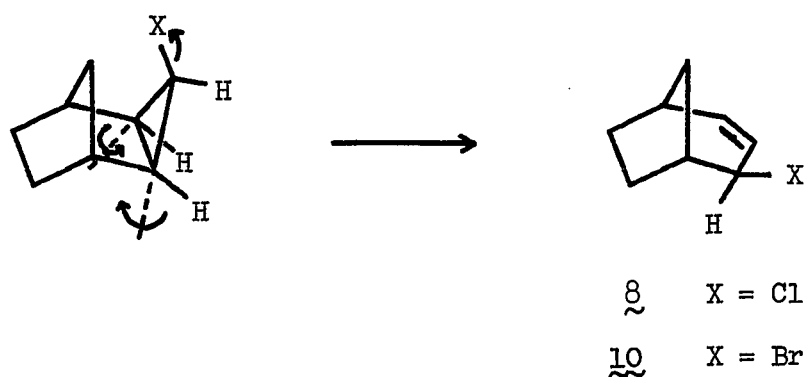
formation of the bromo derivatives was not suggested.

The first attempt at rationalization of the salt effect was due to

Closs and Coyle[28c] who studied the reaction of benzal chloride, methyl-

lithium (LiCl, LiBr, LiI), and olefin. The major products (65 to 95%

yields) were 1-phenyl-1-chlorocyclopropanes ($\underset{\sim}{12}$) and 1-phenyl-1-methyl

cyclopropanes ($\underset{\sim}{13}$).

In order to make intelligible all the findings of their experiments,

the authors thought it convenient to postulate an initial formation of

phenyldichloromethyllithium ($\underset{\sim}{14}$) which then underwent three reactions,

two of which were irreversible. Being an electrophile, $\underset{\sim}{14}$ could react

with olefin, lithium halide, or methyllithium. The methylcyclopropanes

would stem from intermediates of type $\underset{\sim}{16}$. Carbenoid $\underset{\sim}{15}$ would be expected

$$\phi CHCl_2 \;+\; CH_3Li \;\longrightarrow\; \phi - \overset{\overset{\text{Li}}{|}}{\underset{\underset{\text{Cl}}{|}}{C}} - Cl$$

$$\underset{\sim}{14}$$

olefin →

$$\xrightarrow[\text{LiCl}]{\text{LiX}}\quad \phi - \overset{\overset{\text{Li}}{|}}{\underset{\underset{\text{X}}{|}}{C}} - Cl$$

$$\underset{\sim}{15}$$

CH₃Li ↘

$$\phi - \overset{\overset{\text{Li}}{|}}{\underset{\underset{\text{Cl}}{|}}{C}} - CH_3$$

$$\underset{\sim}{16}$$
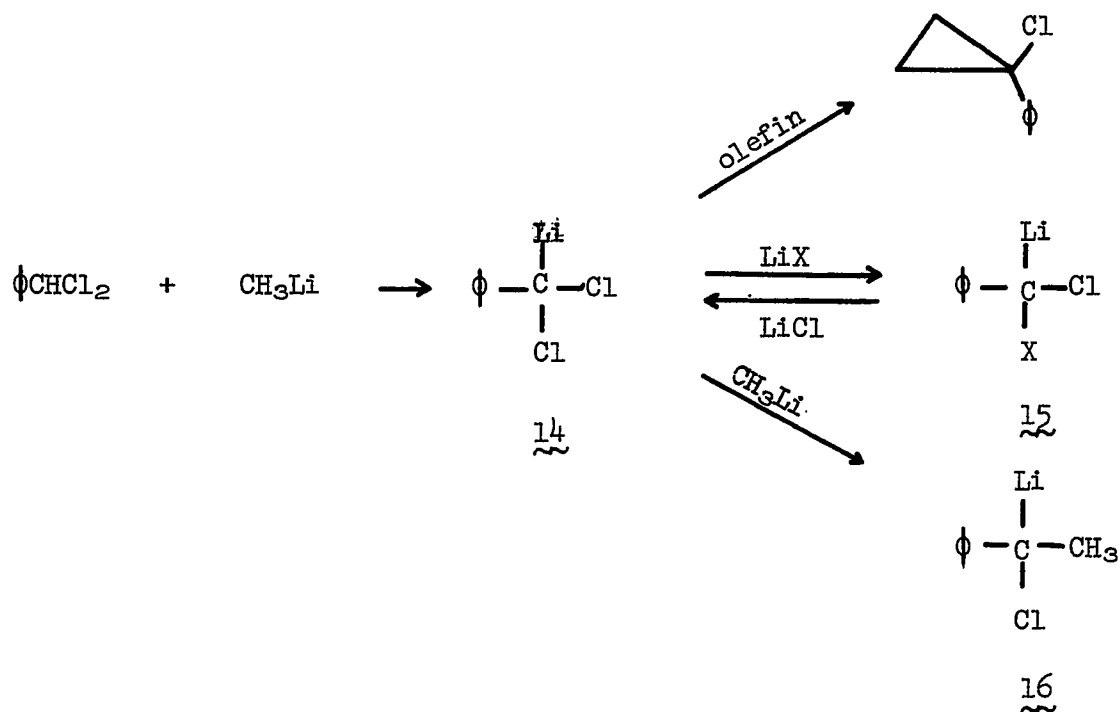
to undergo all the reactions attributed to $\underset{\sim}{14}$, and, therefore, the appearance of the mysterious bromo compounds as observed by Jefford and coworkers[28d] finds an explanation. A further requirement, needed to explain changes in product ratios, states that the ratio of the reaction rate of the carbenoid with methyllithium to the rate with olefin increases in the order chloride, bromide, iodide as leaving group.

In 1964 Dilling[28b] reported that the reaction of styrene, methylene chloride, and methyllithium containing lithium iodide provided only two products: phenylcyclopropane ($\underset{\sim}{17}$) and cis-1-methyl-2-phenylcyclopropane ($\underset{\sim}{18a}$). However, repetition of this same experiment by Magid and Welch[28j] revealed the presence of four products (ignoring cis/trans isomers): $\underset{\sim}{17}$, $\underset{\sim}{18}$, 1-chloro-2-phenylcyclopropane ($\underset{\sim}{19}$), and 1-iodo-2-phenylcyclopropane ($\underset{\sim}{18}$). When methyllithium (LiCl) was employed, only $\underset{\sim}{19}$ was isolated in 18% yield ($\dfrac{\text{cis } (\underset{\sim}{19a})}{\text{trans } (\underset{\sim}{19b})} = 2.3$). Use of methyllithium (LiBr)

$$\phi\text{-CH=CH}_2 \quad + \quad CH_2Cl_2 \quad + \quad \underset{(LiI)}{CH_3Li} \quad \xrightarrow{\ Et_2O\ } \quad \underset{17(44\%)}{\triangle} \quad + \quad \underset{18(16\%)}{\triangle\text{-CH}_3} \quad +$$

$$\frac{cis}{trans} = 1.0$$

$$\underset{19(4\%)}{\triangle\text{-Cl}} \quad + \quad \underset{20(8\%)}{\triangle\text{-I}}$$

$$\frac{cis}{trans} = 1.6 \qquad\qquad \frac{cis}{trans} = 1.0$$
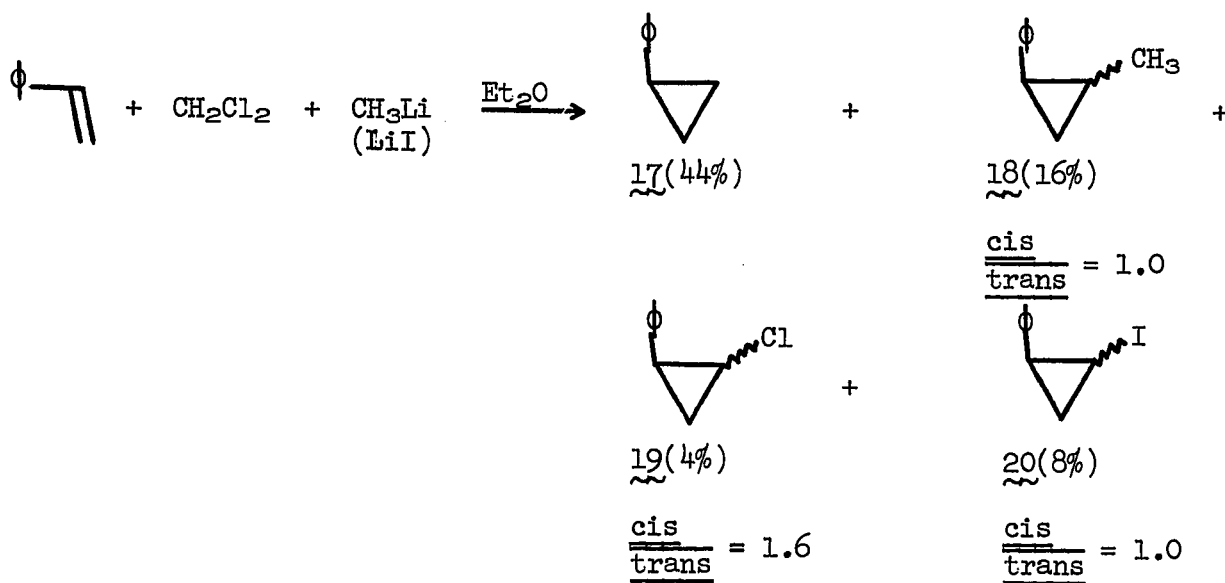
resulted in formation of 19 (42% yield) ($\frac{19a}{19b}$ = 1.7), cis-(21a) and trans-1-bromo-2-phenylcyclopropane (21b) (3% yield), and only a trace of 18. Solely in the case of lithium iodide presence were substantial amounts of 17 and 18 isolated.

Furthermore, reacting in a stereospecific retentive manner with excess methyllithium, 20a and 20b were shown to produce 18a and 18b respectively along with about an equal amount of 17.[28j] The reaction was

$$\underset{20a}{\triangle\text{-I}} \quad \xrightarrow[\text{2) H}_2\text{O}]{\text{1) CH}_3\text{Li(LiI)}} \quad \underset{\underset{49\%}{17}}{\triangle} \quad + \quad \underset{\underset{51\%}{18a}}{\triangle\text{-CH}_3}$$

$$\underset{20b}{\triangle\text{-I}} \quad \xrightarrow[\text{2) H}_2\text{O}]{\text{1) CH}_3\text{Li(LiI)}} \quad \underset{\underset{59\%}{17}}{\triangle} \quad + \quad \underset{\underset{41\%}{18b}}{\triangle\text{-CH}_3}$$
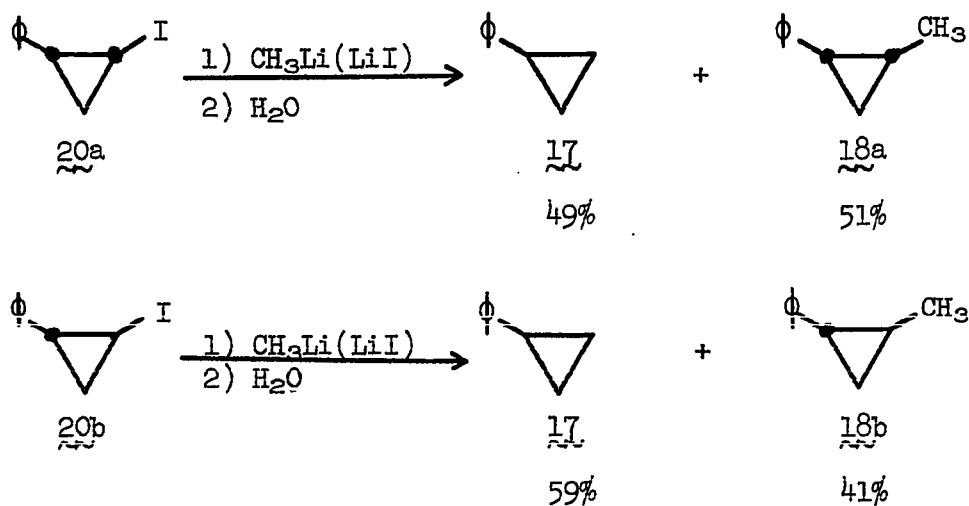
complete within five minutes at room temperature.

The coupling process was envisioned as advancing through a one-step (route b) or a two-step Wurtz reaction (route a) involving four-centered transition states (illustrated for the cis isomer Figure 1). Neither 19 nor 21 underwent this reaction.

Figure 1
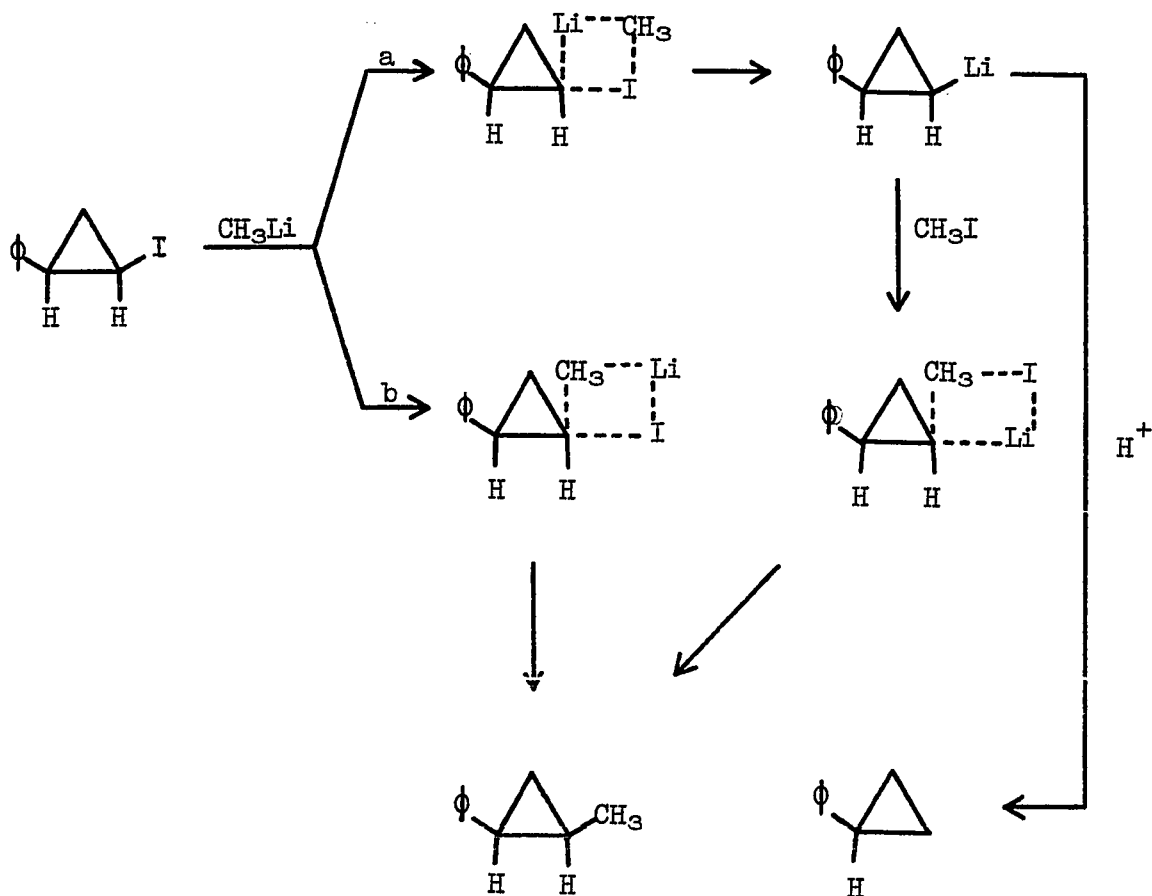
Figure 2 incorporates the reactions originally proposed by Closs and Coyle[28c] to account for the products. The dashed lines represent processes which may occur but which were deemed less likely than the solid line reactions.[28j] In the case where LiX = LiI, a possible pathway to 17 and an alternative route to 18 were depicted as secondary reactions of methyllithium with the primary product 20.

Figure 2

Mechanistic Scheme for Formation of Products[27c]
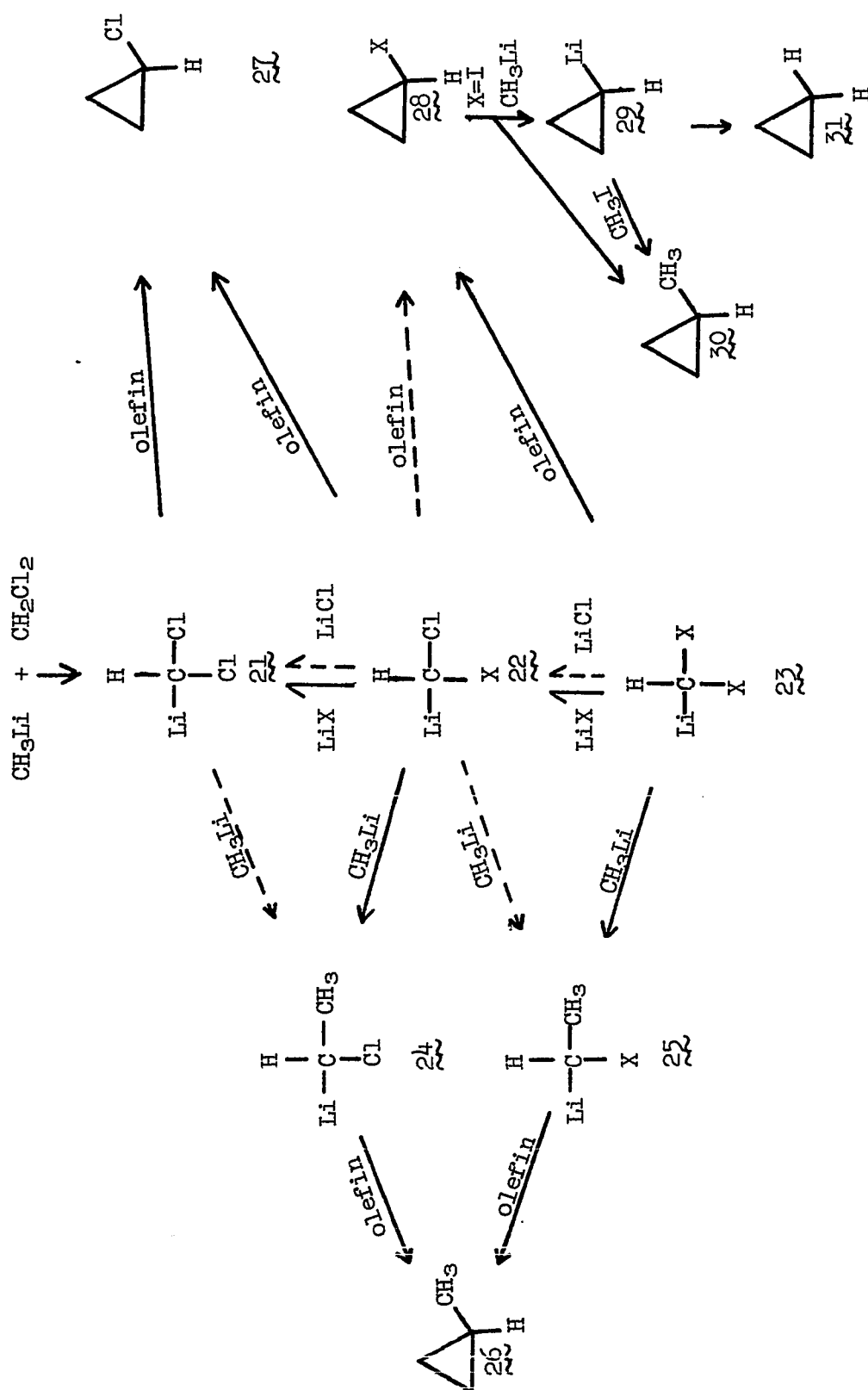
It should be noted that intermediate $\underset{\sim}{23}$ was believed a more likely

precursor of $\underset{\sim}{28}$ than intermediate $\underset{\sim}{22}$ because the latter would tend to

eject LiX (LiBr or LiI), which is a better leaving group than LiCl.[28j]

With cyclohexene as olefin the same qualitative results were ob-

tained as in the styrene example.[28g,28k,28h] A thorough investigation

of the reaction by Magid and Welch[28k] revealed the following product

distribution utilizing methyllithium prepared from methyl iodide:

$$\underset{\sim}{32} \qquad \underset{\sim}{33a}$$
$$0.9\% \qquad 1.7\%$$

$$\underset{\sim}{33b} \qquad \underset{\sim}{34a} \qquad \underset{\sim}{34b} \qquad \underset{\sim}{35a} \qquad \underset{\sim}{35b}$$
$$0.8\% \qquad 5.6\% \qquad 3.2\% \qquad 4.6\% \qquad 2.9\%$$
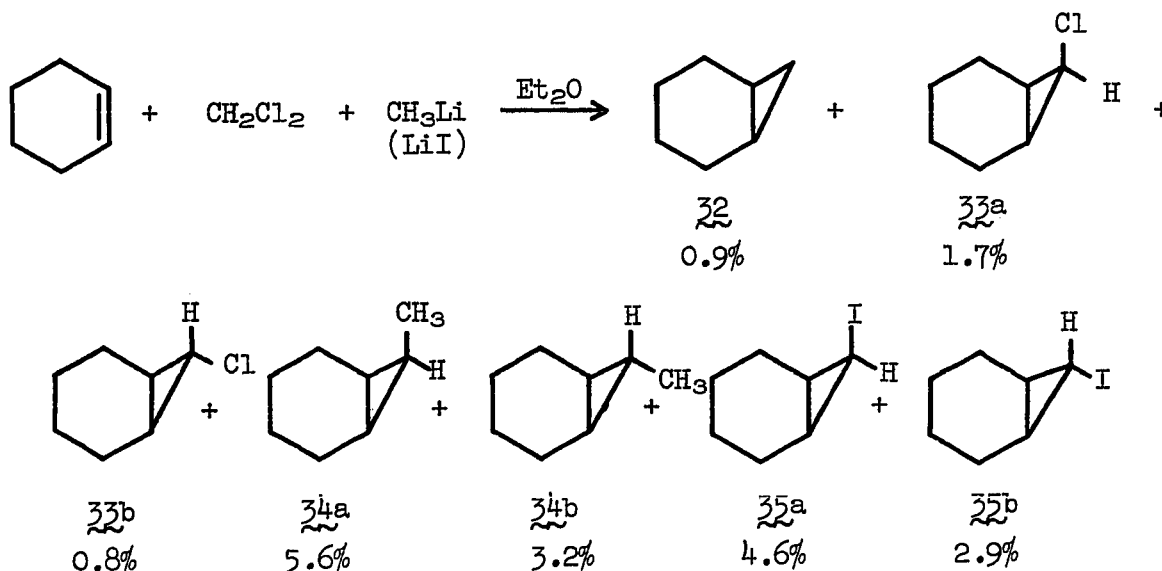
As before, cis- ($\underset{\sim}{35a}$) and trans-7-iodonorcarane ($\underset{\sim}{35b}$) coupled with methyl-

lithium in a retentive manner forming cis- ($\underset{\sim}{34a}$) and trans-7-methyl-

norcarane ($\underset{\sim}{34b}$) respectively along with an approximately equivalent amount

of norcarane ($\underset{\sim}{32}$). The same sort of mechanistic maze as illustrated in

Figure 2 was again advocated by the authors.

In an earlier study of this system, Dilling and Edamura,[28g] who had

overlooked the formation of $\underset{\sim}{35}$, proposed yet another pathway to norcarane.

As shown in Figure 3, this mechanistic route depends on the creation

in situ of chloroiodomethane. An adequate methylene transfer agent $\underset{\sim}{36}$

Figure 3

$$CH_2Cl_2 + CH_3Li \longrightarrow LiCHCl_2 \xrightarrow{LiI} LiCHClI$$

$$LiCH_2Cl + CH_3I \xleftarrow{CH_3Li} CH_2ClI + LiCHCl_2$$

32   36
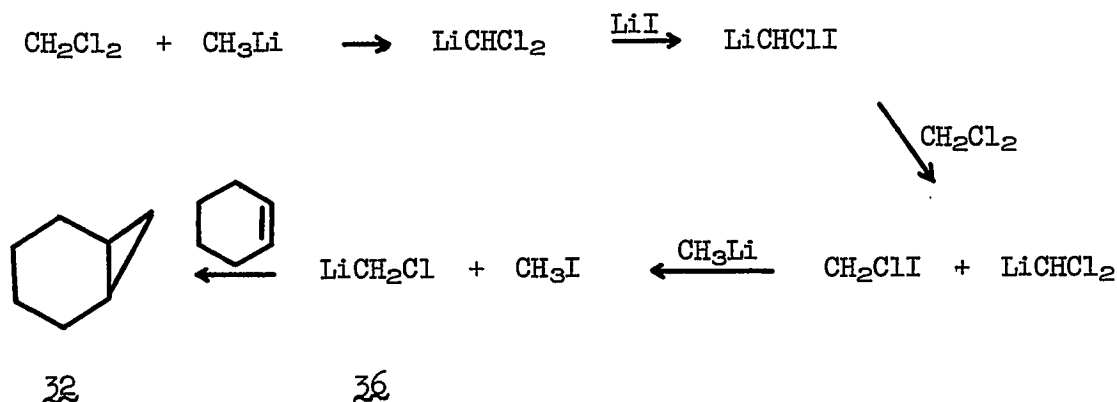
could be generated by halogen-metal exchange between chloroiodomethane and methyllithium.

In support of this scheme, these same workers detected a small amount of chloroiodomethane in the reaction of tetramethylethylene, methylene chloride, and methyllithium (LiI). The only other products which they reported were 3-chloro-1,1,2,2-tetramethylcyclopropane (37) and pentamethylcyclopropane (38).

Gardner and Hatch[28i] presented convincing evidence that 7-methyl-norcarane (34) is a primary product of the reaction of cyclohexene, methylene chloride, and methyllithium (LiI). In a control reaction in which 7-iodonorcarane (35) was treated with methyllithium (LiI) in the presence of methylene chloride, only 3% of norcarane formation was detected along with 97% of unreacted 35. Magid and Welch conducted this reaction without methylene chloride present. None of the methyl-cyclopropane 34 appeared. Significant support for the carbenoid mechanism was provided by the finding that 1,1-di-iodoethane reacts with methyllithium in the presence of cyclohexene to give the methylcyclopro-panes 34a and 34b in the same ratio as observed in the reaction of

cyclohexene, methylene chloride, and methyllithium (LiI).

Since it is known that the iodonorcarane $\underset{\sim}{35}$ reacts much slower with methyllithium than does the iodophenylcyclopropane $\underset{\sim}{20}$,[28j,28k] at least a portion of the methylphenylcyclopropane $\underset{\sim}{18}$ could result from a secondary reaction of $\underset{\sim}{20}$ with methyllithium. Perhaps all of the phenylcyclopropane $\underset{\sim}{17}$ could be produced by such a reaction.

PART I. DISCUSSION AND RESULTS

The abnormal products resulting from the presence of lithium iodide seemed to be at a maximum in the styrene case. The initial phase of research was directed at determining the efficiency with which lithium iodide diverted the electrophilic intermediates from formation of the normal products. This was accomplished by varying the proportion of lithium iodide to methyllithium.

In order to avoid complications arising from the presence of two lithium halides in the methyllithium, the course of action followed involved the preparation of halide-free methyllithium.[82] The reaction of dimethylmercury with excess lithium metal in anhydrous ether produces practically a quantitative yield of halide-free methyllithium. The

$$(CH_3)_2Hg \quad + \quad 2Li \quad \xrightarrow{Et_2O} \quad 2CH_3Li \quad + \quad Hg$$
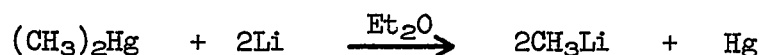
lithium amalgam settles to the bottom of the reaction flask.

Anhydrous lithium iodide is conveniently prepared by the addition of halide-free methyllithium to an ethereal iodine solution. The addition is halted when the dark iodine color vanishes. No methyl iodide remains after removal of volatile materials under vacuum. Only a white solid is

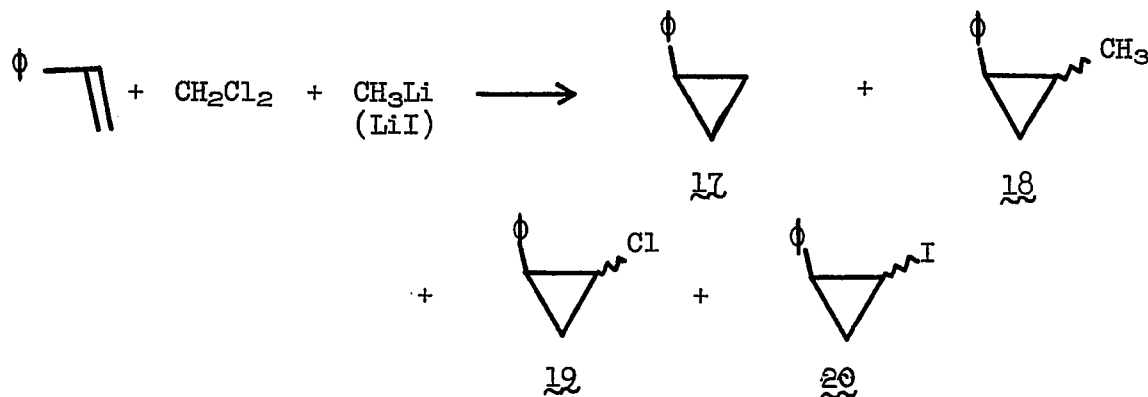$$CH_3Li \quad + \quad I_2 \quad \xrightarrow{Et_2O} \quad CH_3I \quad + \quad LiI$$
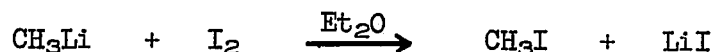
present. Lithium iodide prepared in this manner under an inert atmosphere free from moisture is very soluble in diethyl ether.

The efficiency of lithium iodide was determined by adding 0.02 mole of methyllithium containing varying amounts of anhydrous lithium iodide to a stirred solution of 0.08 mole of styrene and 0.04 mole of methylene

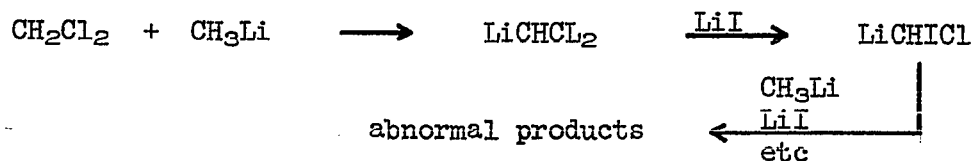chloride at room temperature. The results of these experiments are presented in <u>Table 1</u>.

In most cases four products (ignoring <u>cis</u> and <u>trans</u> isomers) were formed. The identification and glpc retention times of these products

$$\phi\text{—}\diagdown\text{||} + CH_2Cl_2 + \underset{(LiI)}{CH_3Li} \longrightarrow \phi\text{-}\triangledown + \phi\text{-}\triangledown\text{-}CH_3$$

$$\underset{17}{} \qquad \underset{18}{}$$

$$+ \phi\text{-}\triangledown\text{-}Cl + \phi\text{-}\triangledown\text{-}I$$

$$\underset{19}{} \qquad \underset{20}{}$$

had been accomplished by others in this laboratory and all the necessary information was available.[29] The yields were determined by quantitative glpc analysis.

Halide-free methyllithium gives the same results as does methyllithium prepared from methyl chloride.[28j] Only the chlorophenylcyclopropane 19 is formed in both instances with <u>cis</u>/<u>trans</u> = 2.3, and the total yields are nearly equivalent.

One of the most striking findings as seen in <u>Table 1</u> is that even a very meager amount of lithium iodide (LiI/CH_3Li = 0.10) diverts 68% of the reaction to abnormal products. Thus it would appear that lithium iodide very effectively intercepts the initially formed carbenoid. This is a result consistent with the observed rapid rate of reaction of lithium iodide with

$$CH_2Cl_2 + CH_3Li \longrightarrow LiCHCL_2 \xrightarrow{\text{LiI}} LiCHICl$$

$$\text{abnormal products} \xleftarrow{\underset{\text{etc}}{\overset{CH_3Li}{\text{LiI}}}}$$

other carbenoids.[30]

Table 1

Relative Yields %[a]

Mole Ratio LiI/CH$_3$Li	Phenyl-cyclopropane (17)	1-Methyl-2-phenyl-cyclopropane (18)	1-Chloro-2-phenyl-cyclopropane (19)	1-Iodo-2-phenyl-cyclopropane (20)[e]	Total Yield %[a]
0	--	--	100	--	23[b]
0.10	20	48	32	trace	18[c]
0.40	25	51	18	6.2	19
0.66	27	52	13	8.4	19
1.11	24	55	11	9.9	21
1.95	30	43	10	17	29
4.0	0	0	0	0	0

a   All yields based on the limiting reagent, methyllithium. Formation of all of the products requires one

equivalent of methyllithium, except for 18 which requires two equivalents.

b   Methyllithium solution added over 45 min.

c   Methyllithium solutions for all reactions containing LiI were added over 25-35 min.

d   cis/trans = 1.5 for all reactions containing LiI.

e   cis/trans = 1.0 for all reactions containing LiI.

A glance at Table 1 reveals some general trends in going from LiI/CH$_3$Li = 0.10 to LiI/CH$_3$Li = 1.95. The relative contribution of the iodocyclopropane 20 to the product distribution increases with increasing amounts of lithium iodide. The trend is similar for cyclopropane 17 but reversed for the chlorocyclopropane 19. These results fit the mechanism outlined in Figure 2.

A very drastic change takes place when the ratio of lithium iodide to methyllithium is raised to 4.0. Although the reason for this sudden turn of events is not entirely clear, one can begin to pose questions as to what exactly constitutes the structure of the carbenoid.

Köbrich and coworkers[70,71] have prepared a number of stable α-halo-organolithium reagents at low temperatures in tetrahydrofuran solvent. One such stable reagent was dichloromethyllithium (39).[70] This substance behaved in a nucleophilic manner at low temperatures, undergoing reactions characteristic of organolithium reagents. Under conditions at which 39 is stable to reaction with olefin, it readily undergoes reaction with butyllithium giving a mixture of hydrocarbons.[71] This transformation was viewed as beginning with a direct displacement of chloride ion by butyl=lithium (40).
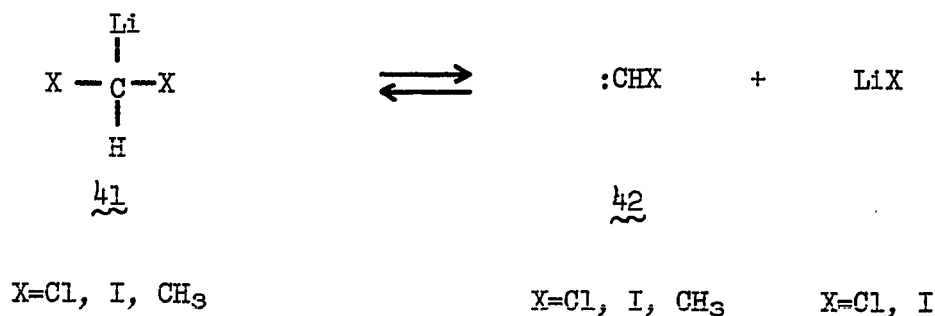

40
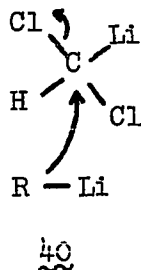
At higher temperatures or in less polar solvents, the proposed reagent 39 behaves in a highly electrophilic manner, being far less selective than free dichlorocarbenes toward addition to double bonds.[6,81] It would

appear that 39 is capable of exhibiting both nucleophilic and electro-
philic character.[71]

As will be seen later the methylcyclopropane 18 is indeed a primary
product of the reaction. In the original explanation of the salt effect,
Closs and Coyle[28c] suggested that the ratio of the rate of reaction of the
carbenoid with methyllithium to the rate with olefin increases in the order
chloride, bromide, iodide as leaving group. It is not altogether clear,
however, why a presumably better leaving group (LiI) should make the
highly electrophilic carbenoid more selective in favor of a better nucleo-
phile.

A plausible rationalization of these and other facts proposes the
existence of at least two intermediates: one would relinquish divalent
carbon only grudgingly, being subject to displacement more favorably by
strong nucleophiles such as lithium iodide and methyllithium; the second
intermediate would exhibit far less selectivity, being capable of reacting
with olefins even in the presence of much better nucleophiles.

There exists at least three situations which fulfill the above
requirements, but not all are in tune with every experimental finding.
The first obvious possibility pictures a rapid equilibrium between a
disubstituted methyllithium reagent (41) and the free monosubstituted

$$
\begin{array}{ccc}
\overset{\displaystyle Li}{\underset{\displaystyle H}{X-\overset{|}{\underset{|}{C}}-X}} & \rightleftharpoons & :CHX \quad + \quad LiX \\[1em]
41 & & 42 \\[1em]
X=Cl,\ I,\ CH_3 & & X=Cl,\ I,\ CH_3 \qquad X=Cl,\ I
\end{array}
$$

carbene (42). Naturally the free carbene would exhibit less selectivity.

The effect of a huge concentration of lithium iodide would be to displace the equilibrium far to the left forcing depletion of 41 via reaction with methyllithium as in 40.

Due mainly to the objections raised by Closs, et al.,[6] it seems highly unlikely that a free carbene intervenes in this reaction. These workers have adequately demonstrated that a free chlorocarbene does not form in the reaction of methylene chloride, butyllithium, and olefin (discussed in the introduction). By comparing syn/anti ratios in the cyclopropane products, they have also proven that free methylphenylcarbene is not the precursor of methylphenylcyclopropanes in the reaction of benzal chloride, methyllithium (LiI), and olefin.[28c]

Another arrangement which complies with the requirements depicts an equilibrium between 41 and a monosubstituted carbene—lithium halide complex (43). Without further elaboration, however, such a system does

$$
X-\overset{\overset{\displaystyle Li}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-X \quad \rightleftharpoons \quad LiX\cdot CHX
$$

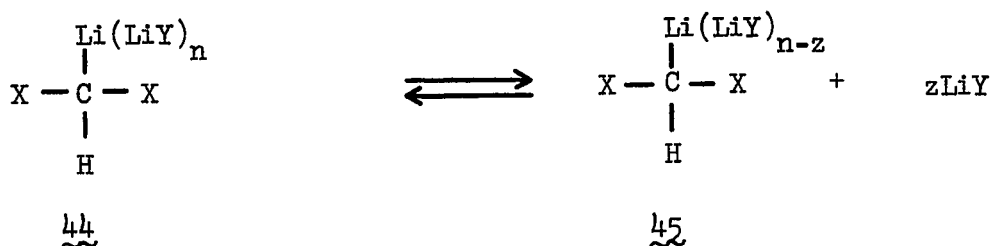41   43
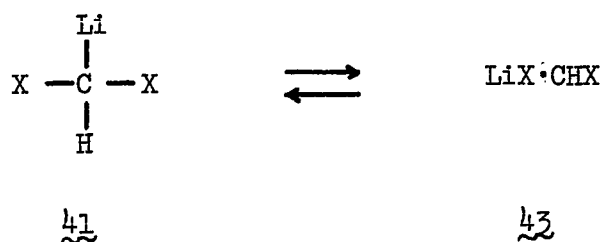
not explain the total lack of cyclopropane products in the presence of huge amounts of lithium iodide.

The final attempt at rationalizing the results deals with the well-documented propensity of organolithium reagents to autocomplex in solvents of relatively low polarity.[76] Methyllithium is known to exist mainly as a tetramer in diethyl ether.[76] Much data has been collected revealing equilibria among complexes of different aggregation of organolithium compounds.[77,78,80] Generally, the more stable the carbanion, the less the

organolithium reagent tends to aggregate: i.e., benzyllithium exists

primarily as a monomer in diethyl ether and tetrahydrofuran presumably

due to delocalization of the negative charge throughout the aromatic

system.[76]

Consonant with the experimental information so far known, an equili-

brium between complexes involving disubstituted methyllithium is proposed.

The larger complex 44 would be less selective since the lithium atom is
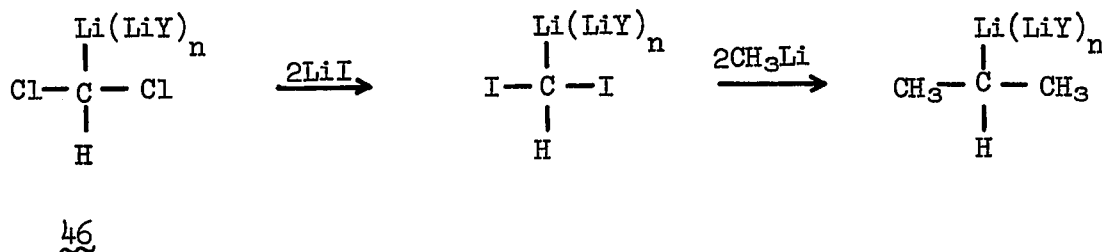
$$
\begin{array}{ccc}
\overset{\displaystyle \text{Li(LiY)}_n}{\underset{\displaystyle H}{\overset{\displaystyle |}{\underset{|}{X - C - X}}}} & \rightleftharpoons & \overset{\displaystyle \text{Li(LiY)}_{n-z}}{\underset{\displaystyle H}{\overset{\displaystyle |}{\underset{|}{X - C - X}}}} \quad + \quad z\text{LiY} \\
44 & & 45
\end{array}
$$

Y = CH$_3$, CHX$_2$, Cl, I

X = Cl, I, CH$_3$

bound to other atoms in the complex and, therefore, is not very available

for coordination with the halide leaving group. The effect would be

similar to the strong lithium atom solvation by tetrahydrofuran to which

Köbrich, et al.,[71] attribute the low temperature stability of dichloro-

methyllithium. The second complex (45) may actually exist as a monomer

with the lithium atom far less committed to complex bonding and much more

available for coordination with the halide leaving group in carbene transfer

reactions. The effect of a huge excess of lithium iodide would be the same

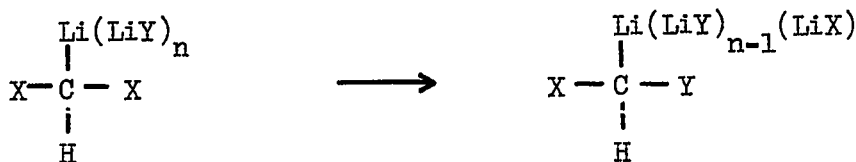as discussed for the free carbene.

In agreement with this scheme we observe that when methylene chloride

is added dropwise to a solution of methyllithium (LiI) and styrene, no

cyclopropane products can be detected after work-up. However, when the

identical reaction is repeated using methyllithium (LiCl), on 8% yield

of the chlorocyclopropane $\underset{\sim}{19}$ is realized. In the former case lithium

iodide acts as a catalyst to facilitate carbon-carbon bond formation in

a series of rapid reactions in an excess of lithium iodide and methyllithium.

These reactions could proceed through the more highly complexed intermediate

$\underset{\sim}{46}$. In the latter system, however, lithium chloride on $\underset{\sim}{46}$ is not so easily

$$Cl-\underset{\underset{H}{|}}{\overset{\overset{Li(LiY)_n}{|}}{C}}-Cl \quad \xrightarrow{2LiI} \quad I-\underset{\underset{H}{|}}{\overset{\overset{Li(LiY)_n}{|}}{C}}-I \quad \xrightarrow{2CH_3Li} \quad CH_3-\underset{\underset{H}{|}}{\overset{\overset{Li(LiY)_n}{|}}{C}}-CH_3$$

$\underset{\sim}{46}$

displaced by methyllithium, permitting a portion of the reaction to proceed

via the less selective intermediate of type $\underset{\sim}{45}$.

It is somewhat amusing to note the possibility of an intramolecular

displacement within the complex harboring the carbenoid.

$$X-\underset{\underset{H}{|}}{\overset{\overset{Li(LiY)_n}{|}}{C}}-X \quad \longrightarrow \quad X-\underset{\underset{H}{|}}{\overset{\overset{Li(LiY)_{n-1}(LiX)}{|}}{C}}-Y$$

The next phase of the research aimed at determining the mechanistic

pathway responsible for the creation of phenylcyclopropane ($\underset{\sim}{17}$) and

1-methyl-2-phenylcyclopropane ($\underset{\sim}{18}$) in the presence of lithium iodide.

Figure 4 shows how $\underset{\sim}{17}$ and $\underset{\sim}{18}$ could arise from legitimate primary processes

(see Figure 3).

Figure 4
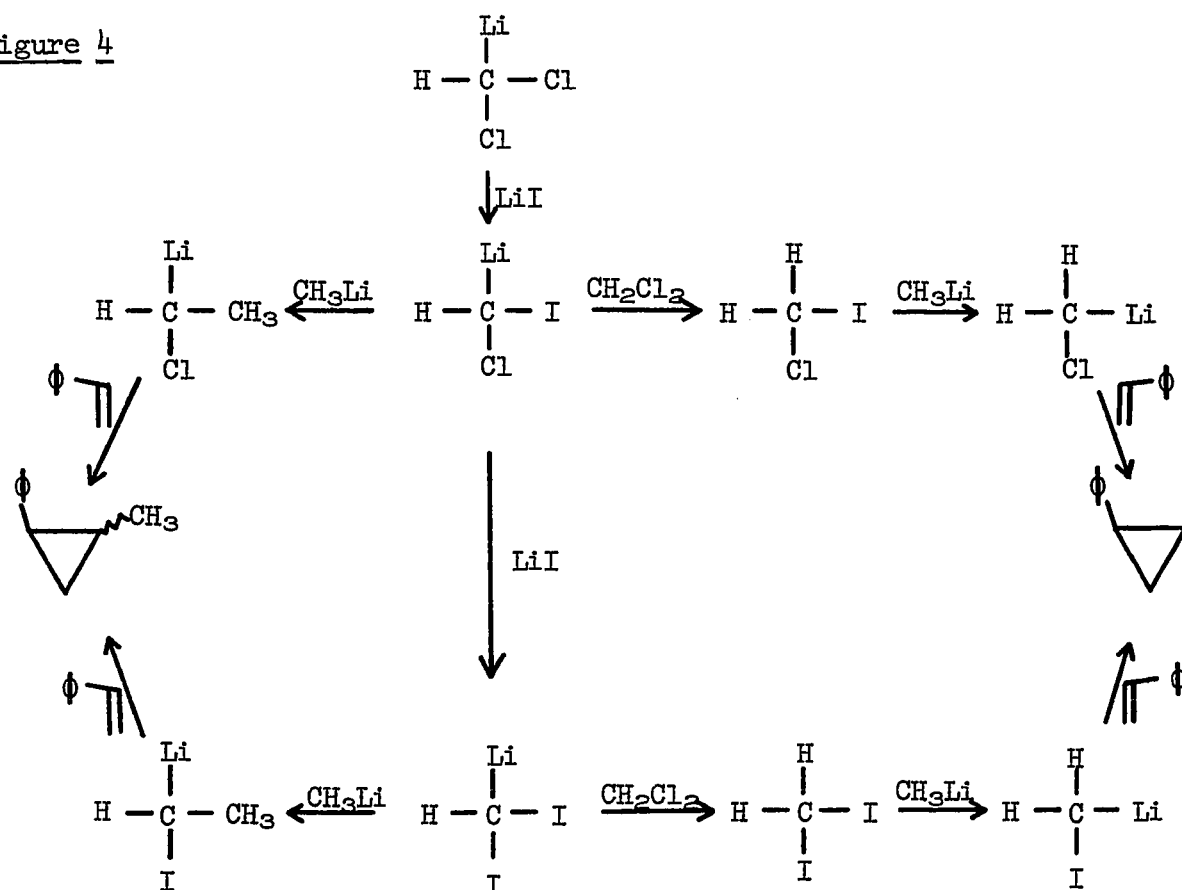
The second possibility results directly from the occurrence of 1-iodo-2-phenylcyclopropane (20) in the reaction. It has been shown that 20 reacts with excess methyllithium to give about equal amounts of 17 and 18 in a very rapid and quantitative operation.[28j] This reaction, however, was not conducted under the reaction conditions since no methylene chloride was present.
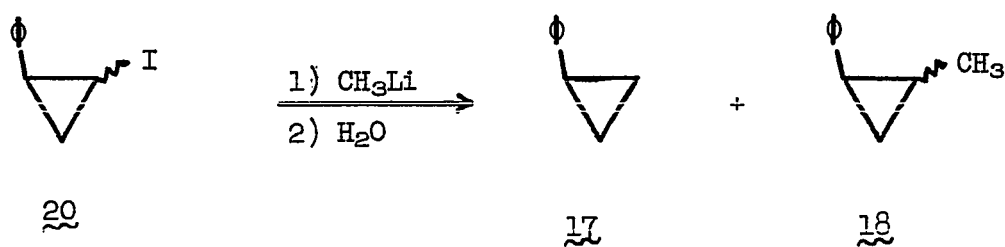
A mixture of the <u>cis</u> and <u>trans</u> iodocyclopropanes 20a and 20b was

prepared in 35% distilled yield by the conversion of the <u>cis</u> and <u>trans</u>

chlorocyclopropanes 19a and 19b into 2-phenylcyclopropyllithium with

lithium (1% sodium) shot in diethyl ether followed by quenching in

ethereal iodine solution. The nmr spectrum corresponded to that already

published for 20.[28j]

When 20 (0.0045 mole) is treated with 0.01 mole of methyllithium

(LiI) under approximate reaction conditions [0.04 mole of methylene chloride,

9.1 ml of hexane (equal in volume to 0.08 mole of styrene), 15 ml of ether],

none of 18 is detected, but 17 is produced quantitatively based upon iodo

compound consumed; 20% of 20 remains unreacted. When 0.01 mole of methyl

iodide is present under identical conditions, the same result is observed.

Therefore the methylcyclopropane 18 represents a primary product of the
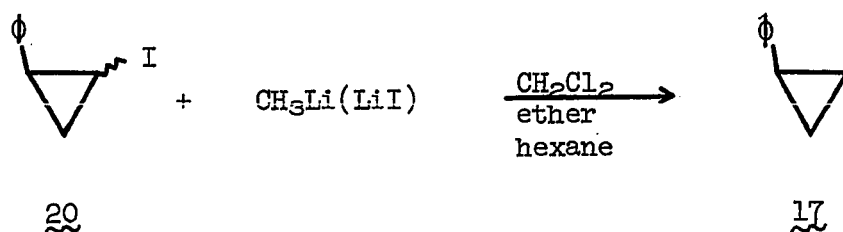
reaction and does not utilize the iodocyclopropane 20 as a precursor;

phenylcyclopropane (17), however, could possibly arise solely by this route.

Inspection of <u>Figure</u> 4 reveals the necessary transitory existence

of chloroiodomethane or diiodomethane before the synthesis of 17 can be

realized.[28g] Halogen-metal exchange with methyllithium could produce

LiCH$_2$Cl or LiCH$_2$I which would be satisfactory methylene transfer reagents

to olefin. In control experiments both chloroiodomethane and diiodomethane

are found to react with methyllithium (LiCl) in the presence of styrene

to give 17 in low yield (6-7%). The presence of a two-fold excess of
methylene chloride does not alter the results in any way. Thus, although
chloroiodomethane and diiodomethane are very facile methyllithium
scavengers, the resulting carbenoids are not very efficient in transferring
methylene to styrene.

The yield of methyl iodide in the reaction of diiodomethane (0.02
mole), methylene chloride (0.04 mole), styrene (0.08 mole), and methyl-
lithium (LiI) (0.02 mole) is 76% based on glpc and nmr analysis. When the
same reaction is conducted without diiodomethane, only a 12% maximum yield
of methyl iodide is found. With styrene and diiodomethane absent, methyl
iodide is formed in 6% maximum yield. Since it is unlikely that much
methyl iodide is consumed in the reaction, it is apparent that the combina-
tion of low methyl iodide yield and inefficient transfer of methylene to
olefin by LiCH$_2$Cl and LiCH$_2$I dictate that only a fraction of 17 could be
formed as outlined in **Figure** 4.

Further evidence that the iodocyclopropane (28 in **Figure** 2) is necessary
for the appearance of the unsubstituted cyclopropane (31 in **Figure** 2) can
be located in the cyclohexene case. Although the iodophenylcyclopropane
20 reacts quite rapidly with methyllithium (complete in less than five
minutes)[28j] both the iodonorcaranes 35a and 35b react much slower (50-70%
after two hours).[28k] Consequently, the yield of norcarane when cyclohexene
is employed as olefin is less than 1%,[28k] whereas the yield of phenylcyclo-
propane (17) using styrene under identical conditions is 22%.[28j]

We have performed another experiment which substantiates this same
sort of reasoning. Contrary to the report of Dilling and Edamura,[28g]
tetramethylethylene, methylene chloride, and methyllithium (LiI) react to
give three products: 3-chloro-1,1,2,2-tetramethylcyclopropane (37),

pentamethylcyclopropane (38), and 3-iodo-1,1,2,2-tetramethylcyclopropane

(47). From quantitative glpc analysis the maximum possible yield of

	37	38	47
	6.0%	9.8%	1.0%
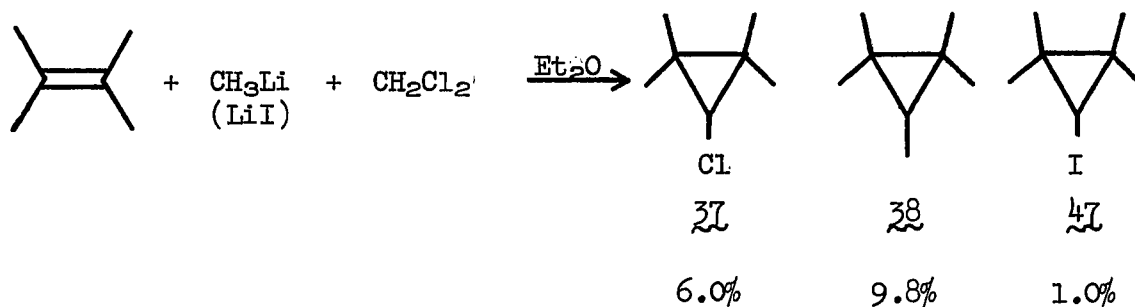
1,1,2,2-tetramethylcyclopropane (48) is 0.07%.

Preparation of authentic samples of 38, 47, and 48 begins with the

isolation of 37 and subsequent treatment with lithium (1% sodium) shot in

diethyl ether yielding the very versatile cyclopropyllithium reagent 49.

Quenching of 49 with water leads to 48 in high yield. Compound 47 is easily

prepared by treating 49 with either iodine/ether or methyl iodide.

Interestingly enough the methyl iodide quench produces only ca. 3% 38, with
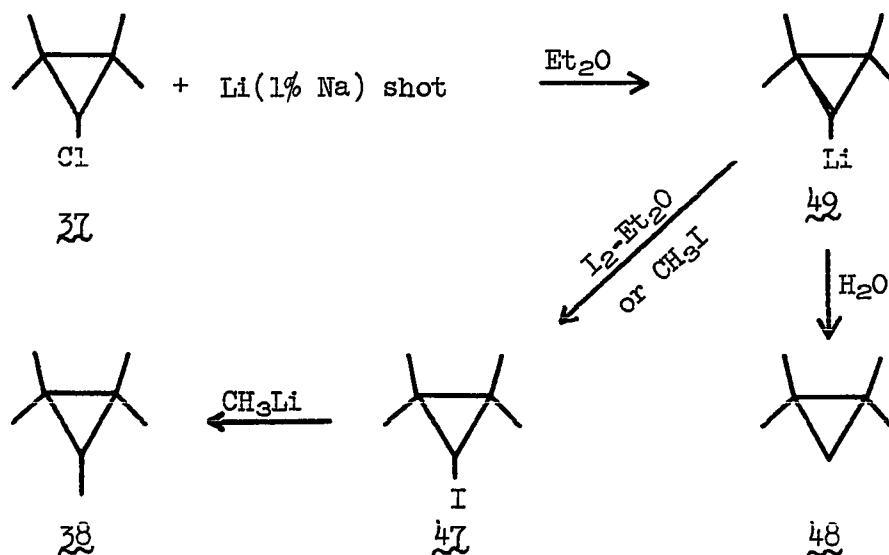
the paramount proportion going to 47.

The reaction of 47 with methyllithium is extremely slow. Only after

22 hrs in refluxing ether is 47 converted into 38 in 60% yield. A minor

product, probably 48 (same glpc retention time) is also formed in 6%

yield. The nmr spectra of all these materials, as reported in the

experimental, are consistent with the structures shown.

The reason why little if any 48 is formed in the tetramethylethylene

experiment is readily explicable on the assumption that the iodocyclo-

propane is the major precursor of the unsubstituted cyclopropane. Thus

for substantial unsubstituted cyclopropane formation, the iodocyclopropane

must also be formed and must be highly reactive toward methyllithium.

Although the methylcyclopropane 18 is a primary product of the

reaction and does not arise from the coupling of the iodocyclopropane 20

and methyllithium, we decided to investigate this coupling process in a

little more detail.

The coupling reaction of the iodocyclopropane 20 and methylithium

was known to be completely stereospecific, going with retention of

configuration: 20a yielded 18a while 20b gave 18b.[28j]

When the iodocyclopropane 20 (0.002 mole) (mixture of 20a and 20b)

is treated with excess methyllithium (LiI) (0.013 mole) in diethyl ether

and quenched in water, the ratio of phenylcyclopropane 17 to methyl-

phenylcyclopropane 18 is 1.3:1. However, when the same reaction is

quenched in iodine/ether, this ratio drops to 0.16:1 with the major pro-

duct being the iodocyclopropane 20.

The simplest interpretation of this behavior envisions at least a

portion of the iodocyclopropane 20 undergoing halogen-metal exchange

with methyllithium to produce 2-phenylcyclopropyllithium (50). This

material is stable in ether and remains intact until quenched with water

or iodine. The lithium reagent 50 could also undergo reaction with any

methyl iodide that had escaped depletion by contact with excess

methyllithium. Simple reverse reaction would regenerate the iodocyclopro-

pane 20 and methyllithium whereas coupling would result in irreversible

formation of the methylcyclopropane 18.

Two combinations appear plausible in the coupling process as out-

lined in <u>Figure 5</u>. Mechanism (a) unites the iodocyclopropane 20 and

<u>Figure 5</u>
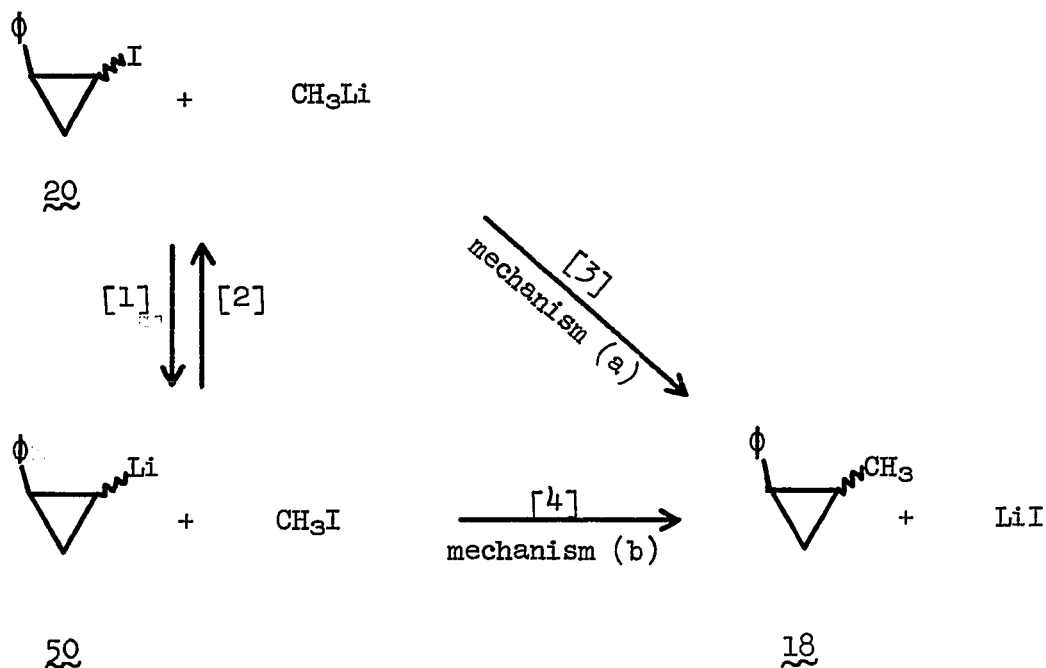
methyllithium in a one-step Wurtz type reaction. Mechanism (b) requires

prior halogen-metal exchange followed by a combination of the cyclopropyl-

lithium reagent 50 with methyl iodide. The immediate task is to

distinguish between these two possibilities.

As described earlier, when the iodocyclopropane 20 is treated with

excess methyllithium in the presence of methylene chloride, only phenyl-

cyclopropane 17 is produced quantitatively. None of the methylcyclopropane

is seen. The same result holds even with additional methyl iodide in

solution.

The most likely explanation is that the iodocyclopropane 20 and

methyllithium combine and undergo reaction [1] giving the cyclopropyl-

lithium 50 and methyl iodide. In the presence of excess methylene

chloride, 50 is protonated faster than it can react with methyl iodide.

Therefore, the partitioning factor k_1/k_3 (the partitioning of 20 and

methyllithium between reactions [1] and [3]) is a huge number

$(k_1 \gg k_3)$.

The next step is to assign a creditable number to the partitioning

factor k_4/k_2 (the partitioning of 50 and methyl iodide between reactions

[2] and [4]). Reaction [4] is irreversible and if reaction [2] could

be made irreversible, then the problem would be solved.

Treatment of the iodocyclopropane 20 (0.002 mole) with excess methyl-

lithium (0.0077 mole) in the presence of a huge excess of methyl iodide

(1.0 mole) in diethyl ether gives only ca. 5% reaction of 20. The only

product is the methylcyclopropane 18. A gas evolves during the addition

indicating that the major source of depletion of methyllithium is via

reaction with methyl iodide. Since the irreversibility of reaction [2]

depends upon methyllithium being consumed once formed, the condition of

a huge excess of methyl iodide is ideal.

The cyclopropyllithium 50 is prepared as already described and added

dropwise to a huge excess of methyl iodide in diethyl ether. Quantitative

glpc analysis shows that 41% of the reaction follows pathway [2] giving

the iodo compound 20 while 59% couples (reaction [4]) to produce the

methylcyclopropane 18. Therefore the partitioning factor k_4/k_2 is ca. 1.4.

With $k_1 > > k_3$ and $k_4 > k_2$, mechanism (b) (reactions [1] and [4]) is

virtually the sole route followed in the coupling of 20 with methyllithium.

The stereochemistry of most of the processes involved can easily

be deduced. It has been shown that the overall stereochemistry is one

of retention of configuration: 20a gives 18a and 20b gives 18b. This means that reactions [1] and [4] must either go both with inversion or both with retention. Since halogen-metal exchange involving organolithium reagents and cyclopropylbromides proceeds with nearly complete retention of configuration on the cyclopropyl fragment,[31] the double retention mechanism assumes a commanding preference. Reaction [2] is also occurring and it must advance with retention on the cyclopropyl moiety.

This one reaction provides an example of halogen-metal exchange occurring with retention on a cyclopropyl iodide as well as retention on a cyclopropyllithium and a coupling reaction proceeding with retention on a cyclopropyllithium. Unfortunately no information can be derived on the stereochemical outcome of the alkyl iodide in the coupling process.

Increasing evidence supports the assertion that coupling products arising from reactions of certain organolithium reagents with organic halides are the result of a radical or radical cage process. Esr signals for both the butyl radical and the methyl radical have been detected in the reaction of butyllithium with methyl iodide in the presence of diethyl ether.[33] Recent studies on chemically induced dynamic nuclear polarization corroborates the formation of radicals in the coupling, exchange, and disproportionation reactions of alkyllithium with alkyl iodides.[34]

The coupling reaction of the cyclopropyllithium 50 with methyl iodide probably occurs via a radical cage. The radicals must collapse to product faster than the cyclopropyl radical can invert. A considerable number of examples of cyclopropyl radicals resistent to inversion have been discovered.[35]

radical cage
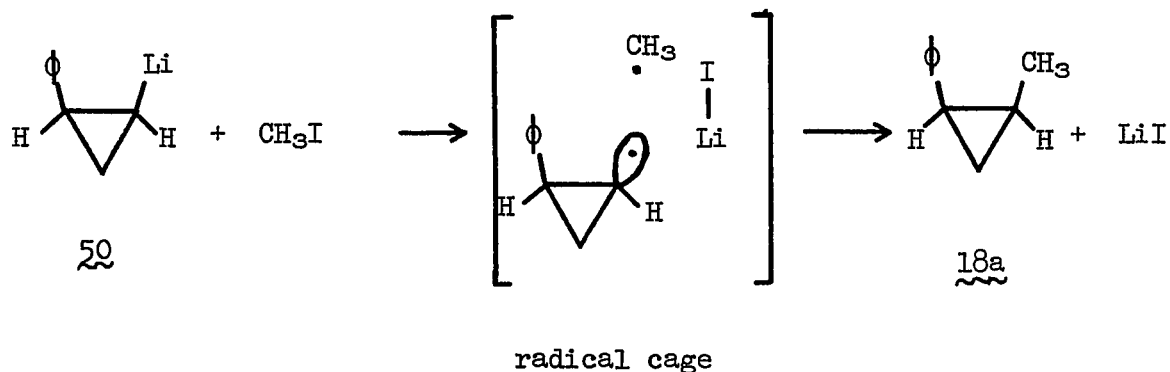
A possible explanation for the failure of reaction [3] to compete effectively with reactions [1] and [4] stems from the aggregation of methyllithium in diethyl ether solution.[76] If it is assumed that tetrameric methyllithium partakes in the halogen-metal exchange reaction with the iodocyclopropane 20, the resulting radical cage could possibly contain a methyl radical still bound to the organolithium aggregate.[34a]
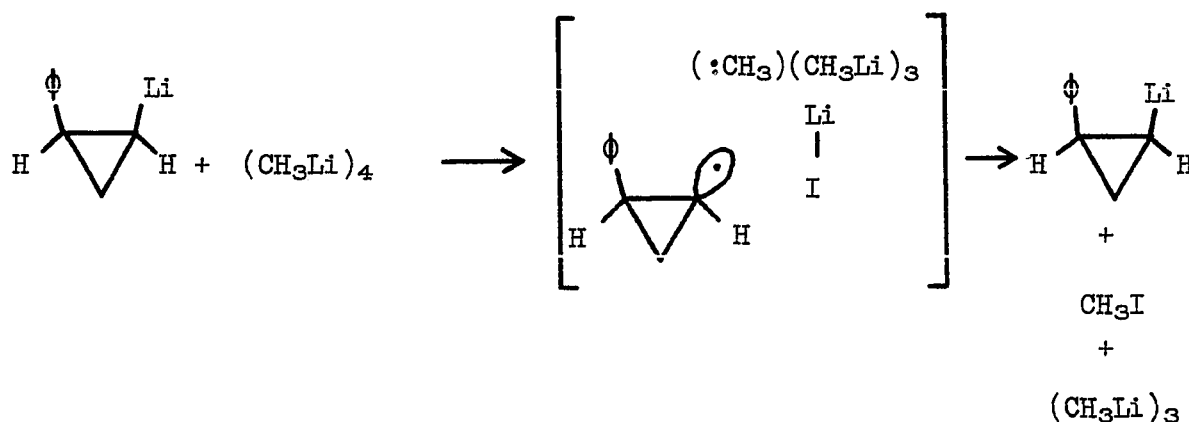

Such a bulky species would be more likely to experience halogen-metal exchange rather than coupling.

PART II. INTRODUCTION

Since the initial communications of Woodward and Hoffmann,[36] the stereochemistry and selectivity of a huge reservoir of concerted reactions have proven to be controlled by the conservation of orbital symmetry. Although the majority of the studies have concerned neutral molecules, a growing number of ionic transformations also have been demonstrated to obey the restrictions imposed by orbital symmetry.[37]

One interesting concerted ionic process recently published deals with the [4 + 2] cycloaddition of cyclopentadiene and 2-methylallyl cation.[38] Using liquid sulfur dioxide as solvent, Hoffmann and coworkers treated 2-methylallyl iodide with silver trichloroacetate in the presence of cyclopentadiene. The creation of four products was realized: 51a, 51b, 52, and 53. The esters represented 25% of the isolated products.
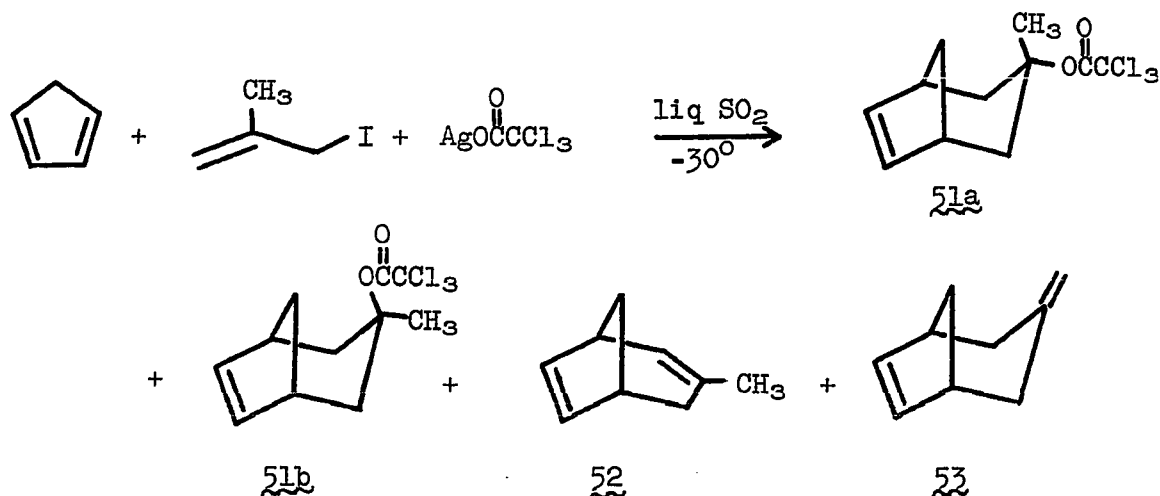

When the reaction was conducted in dichloromethane-acetonitrile solvent using silver tetrafluoroborate only one product, N-(3-methyl-bicyclo[3.2.1]oct-6-en-3yl)acetamide (54) (one isomer), could be recovered after work-up.

54
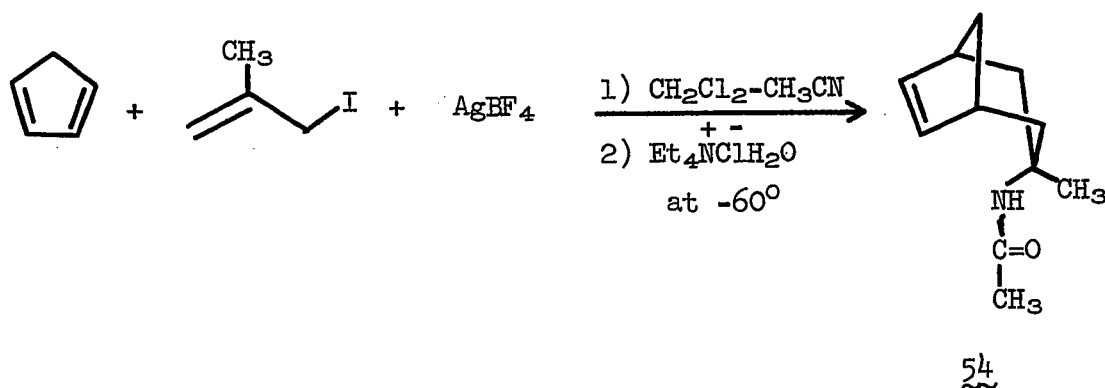
The mechanistic rationale offered by the authors in the first reaction entails initial formation of the solvent separated ion-pair 55.[39] Possessing a considerable lifetime in an excellent cation-

55
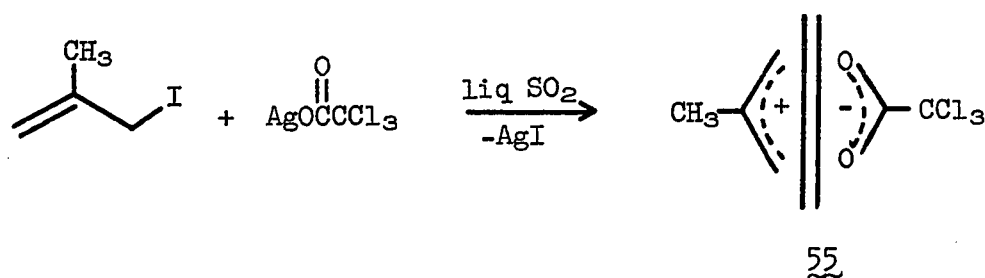
stabilizing solvent such as sulfur dioxide, a wholesome portion of 55 survives to react with cyclopentadiene in a [4 + 2] cycloaddition. A


56a
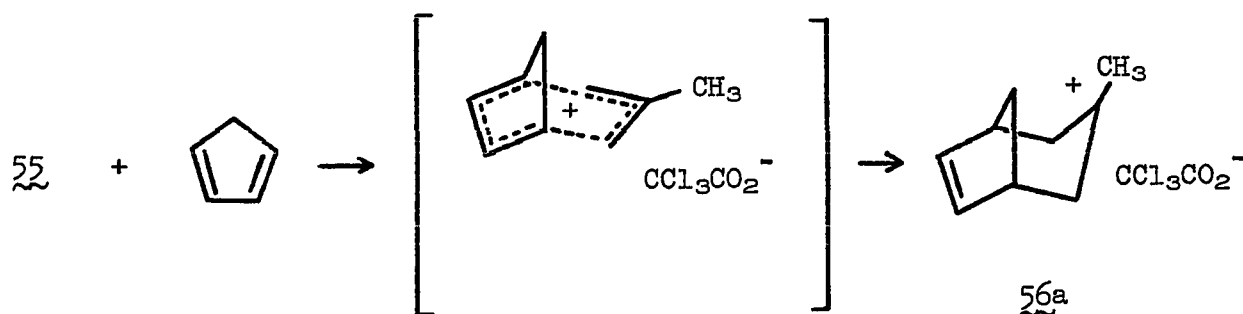
chair-like (referring to the seven-membered ring) transition state was favored. With the assumption that 56a undergoes rapid equilibration to to 56b, all of the products possessed reasonable precursors.
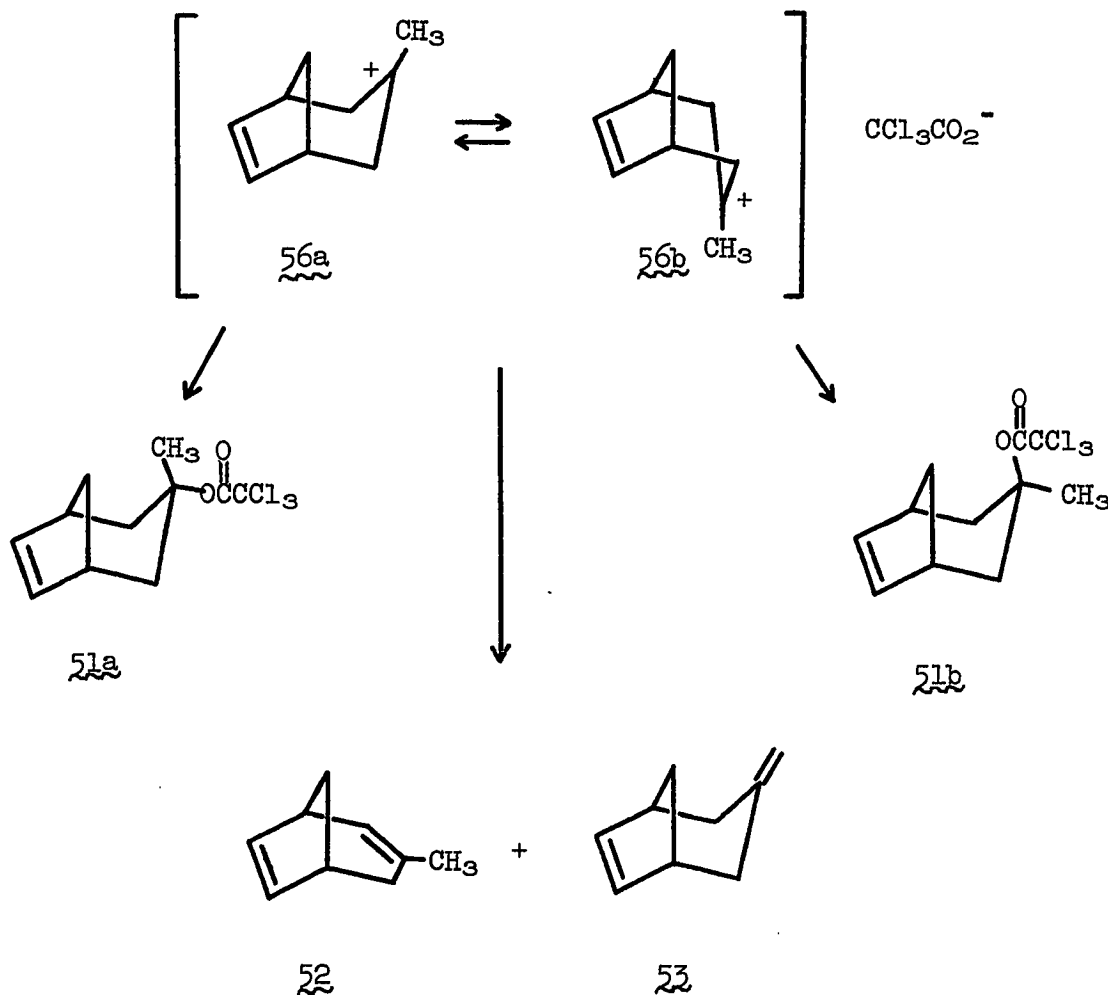
The empirical reasoning for proposing the chair-like transition
state stemmed from the second experiment. In the presence of acetonitrile
56a would not be expected to enjoy a very significant lifetime before
combining with solvent; apparently union with acetonitrile occurs much
faster than ring flipping to give 56b. Thus only one product, 54,
corresponding to reaction of the nucleophile with 56a (not 56b), could be
identified.

Theoretically, the chair-like transition state is likewise favored
because of secondary orbital interactions in the transition state.[37]
In considering the orbital symmetry requirements of a [4 + 2] cycloaddition,
one views the interaction of the diene's highest occupied molecular

orbital with the lowest unoccupied molecular orbital of the dienophile

(57a) (boat-like transition state); and the lowest unoccupied molecular

orbital of the diene with the dienophile's highest occupied molecular

orbital (57b). It is noted that the terminal orbitals in both 57a and

57b possess the correct symmetry for overlap and subsequent bonding.

The secondary orbital interactions in 57a would be expected to be

secondary
interactions

57a   57b
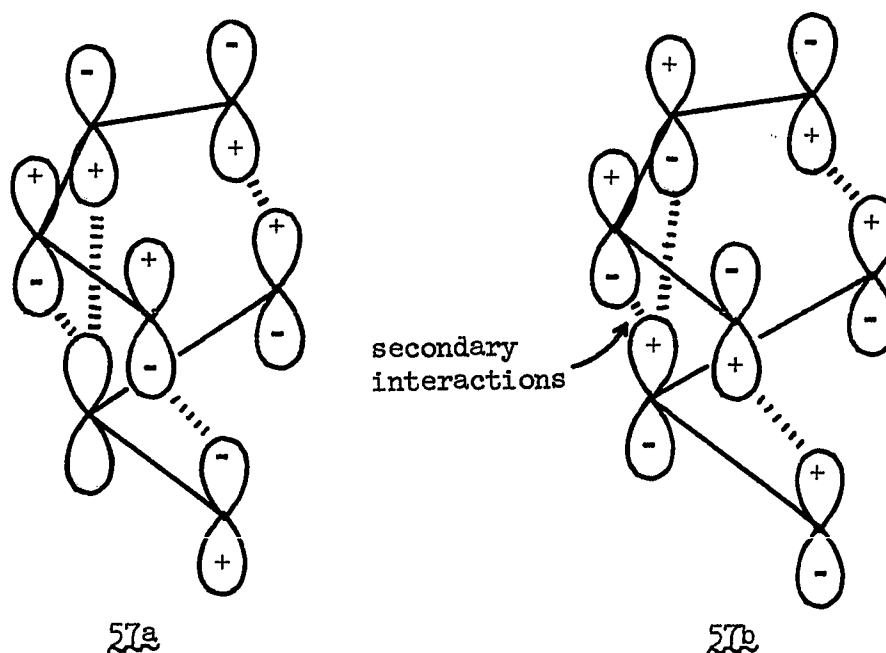
negligible, whereas 57b depicts adverse nonbonding secondary orbital

interactions which would tend to raise the energy of the boat-like

transition state relative to the chair-like arrangement (58). Arguments

other than secondary orbital interactions have been advanced to ration-

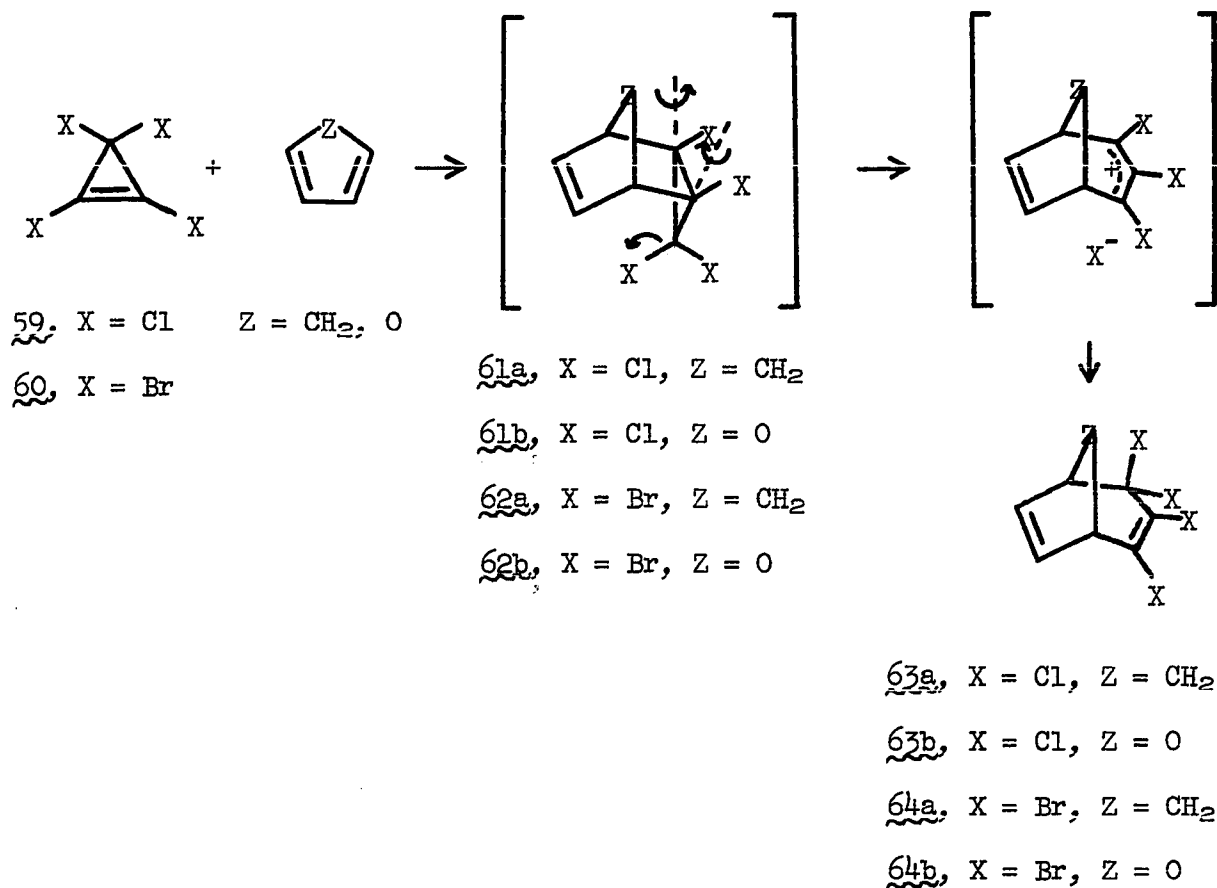alize the stereochemical preference in cycloaddition reactions.[55]

58
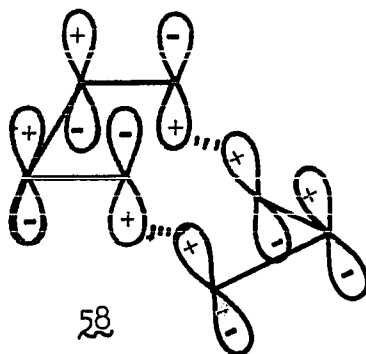
We felt that more subtle examples of such ionic reactions might also appear in the literature.

Law and Tobey[40] have reported the Diels-Alder reaction of tetra-halocyclopropenes with several dienes. The combination of tetrachloro-cyclopropene (59) or tetrabromocyclopropene (60) with cyclopentadiene or furan lead to ring opened products, 63 and 64, in nearly quantitative yields. This reaction was pictured as passing through intermediate 61 (or 62), which undergoes concerted cyclopropyl ring opening.[41] The endo geometry as shown in 61 and 62 finds ample precedence in Diels-Alder reactions of cyclopropenes with cyclopentadiene.[44]

In a competitive experiment these workers discovered that 60 reacted
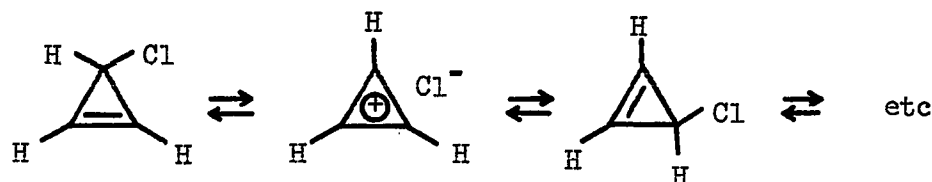
Figure 6

59. X = Cl   Z = CH₂, O

60, X = Br

61a, X = Cl, Z = CH₂

61b, X = Cl, Z = O

62a, X = Br, Z = CH₂

62b, X = Br, Z = O

63a, X = Cl, Z = CH₂

63b, X = Cl, Z = O

64a, X = Br, Z = CH₂

64b, X = Br, Z = O

1.42 times faster with furan than did 59. Since this behavior is
opposed to "Alder's rule"[42] as well as any steric considerations,[44b]
the authors suggested that replacing chlorine by bromine atoms raises
the ground-state energy of the cyclopropene, thus making it more
reactive. The argument depends upon the diminution of internal ring
σ bond strain in the cyclopropene with decreasing molecular weight of
the halogen attached to the methylene carbon. Further support for this
hypothesis was provided by a number of fluorine substituted cyclopropenes.

Although the argument seemed plausible for such minor differences
in rate, we felt an alternative explanation could also account for this
unexpected behavior.

The order of reactivities of the tetrahalocyclopropenes (60 > 59)
is similar to the order of leaving group abilities (Br > Cl). Breslow,
et al.,[43] have shown that chlorine atoms migrate from carbon to carbon
in monochloro-, dichloro-, and trichlorocyclopropenes in both polar and
nonpolar solvents. As exemplified in the case of monochlorocyclopropene,
this phenomenon is believed to occur via the cyclopropenyl cation-
chloride ion-pair 65.

65

By combining the probable formation of the cyclopropenyl cation with
the ability of allyl cations to undergo Diels-Alder reactions, Figure 7
presents a conceivable pathway to products with cyclopentadiene.

Figure 7
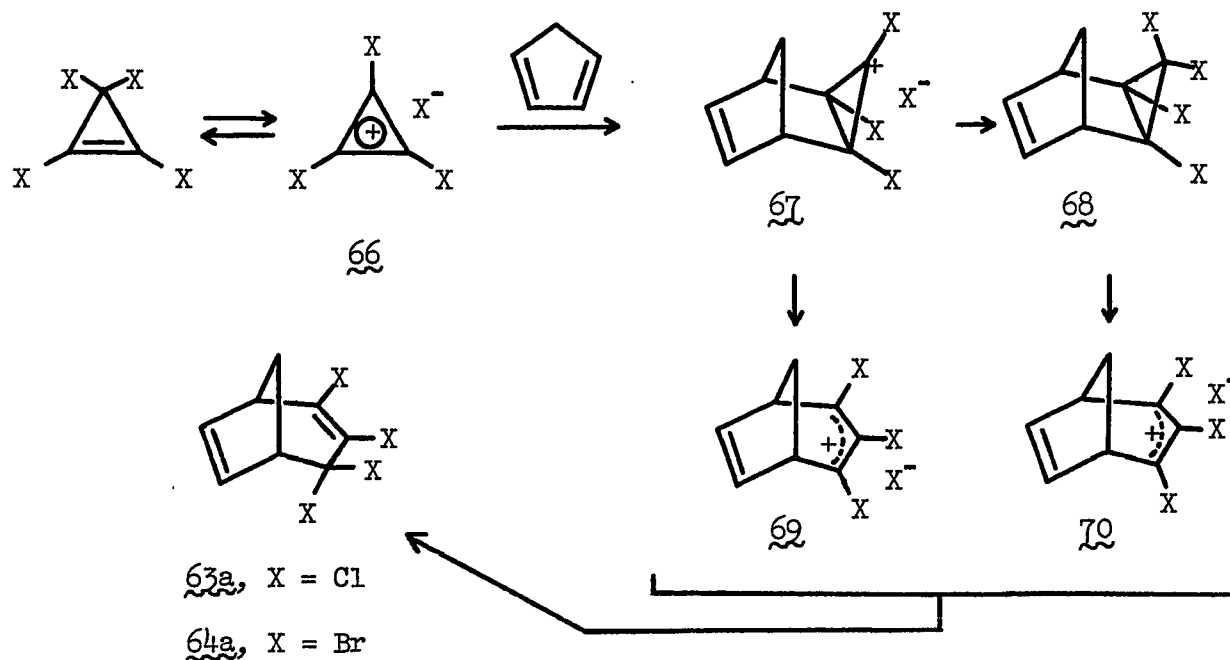
The exo adduct 67 follows from the secondary orbital considerations as outlined for the 2-methylallyl cation. The intermediate 67 could open to the allyl cation 69 or collapse to the momentarily stable cyclopropane 68. Compound 68 would decompose to product in a similar fashion as discussed for the endo isomer (61a and 62a).

An attractive feature of Figure 7 is the virtual lack of steric retardation with varying X moieties. That steric considerations cannot be ignored in the neutral process (Figure 6) is demonstrated by the facts that 3-methylcyclopropene reacts with cyclopentadiene to give only the less sterically hindered endo isomer 71; and 3,3-dimethylcyclopropene does not add even at 100°C.[44b]
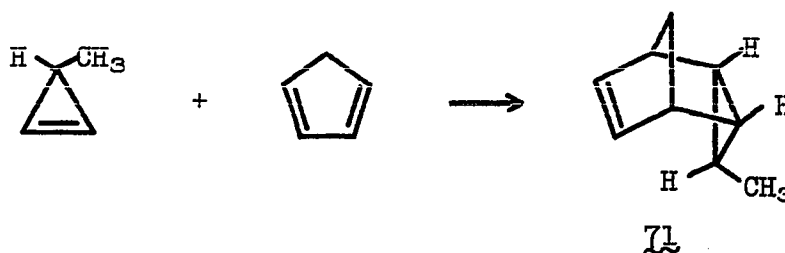
Another concerted ionic process about which little experimental

data has been collected is the symmetry-allowed suprafacial [1,4]

anionic shift.[37] Such a reaction is illustrated in the hypothetical

equilibrium $\underset{\sim}{72} \rightleftharpoons \underset{\sim}{73}$.

$$\underset{\sim}{72} \qquad \underset{\sim}{73}$$
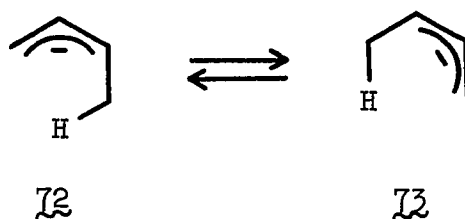
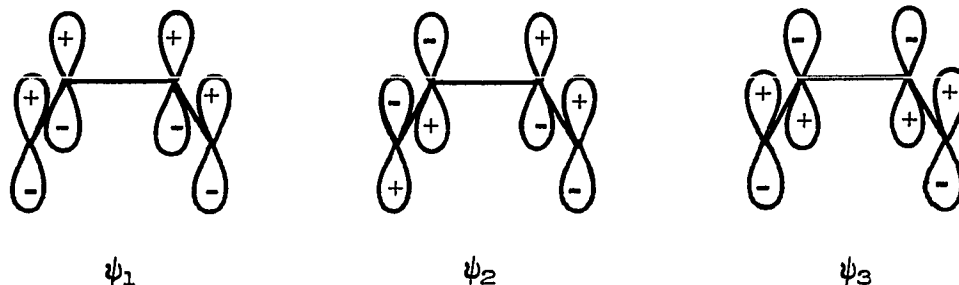Application of the conservation of orbital symmetry reveals that

the stereochemistry of this transformation should be controlled by the

third highest molecular orbital of butadiene ψ_3. Thus, like the

uncharged [1,5] sigmatropic shift, the [1,4] anionic shift is an allowed

$$\psi_1 \qquad\qquad \psi_2 \qquad\qquad \psi_3$$

suprafacial concerted process. For a carbon migration, retention at the

migrating center is required.

The literature provides a single example of a possible [1,4]

anionic hydrogen shift. Chapman and Eian[45] have performed the photo-

chemical cyclization of the amine $\underset{\sim}{74}$. The intermediate $\underset{\sim}{75}$ results from

an excited state electrocyclic reaction which pursues a conrotatory

closure. After reverting to the ground state, $\underset{\sim}{75}$ is free to engage in
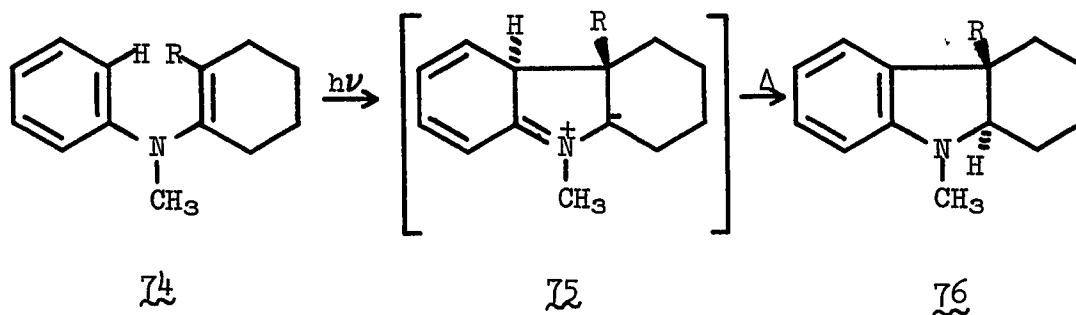
a [1,4] anionic hydrogen shift which returns aromaticity to the molecule (76).

Recent nmr studies[46] have revealed that both allyllithium (77) and 1-phenylallyllithium (78) can best be represented in tetrahydrofuran solution as essentially delocalized structures (AA'BB'C pattern for 77). This is in contrast to the interpretation of the nmr spectra
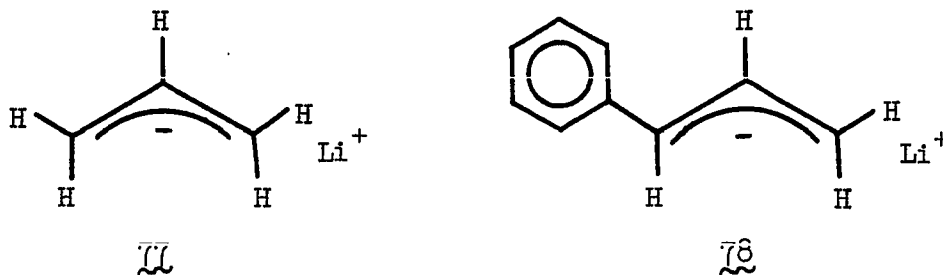
(AB$_4$ pattern) of other allylmetallic compounds containing less electropositive metals.[47] The structures assigned in these cases are usually equilibrating covalent species.

Bates and coworkers[48] investigated a series of pentadienyllithiums (79, 80, 81, 82 and 83) by nmr techniques. In tetrahydrofuran solution all of these species proved to be greater than 90% ionic.
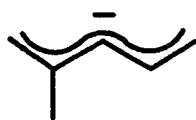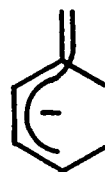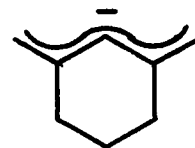
79   80   81   82   83

With an adequate arsenal of stable allyl anions available, appropriate substitution could produce systems theoretically capable of [1,4] anionic shifts.

PART II. DISCUSSION AND RESULTS

A twofold approach was employed in determining if halocyclopropenes follow the cyclopropenyl cation route (Figure 1) in the Diels-Alder reaction with cyclopentadiene. The first approach involved a stereochemical study of the adducts formed from the reaction of monochloro- and dichlorocyclopropenes with cyclopentadiene.

As outlined in Figure 1, the initially formed adduct of the cyclopropenyl cation with cyclopentadiene is the ion-pair 67 which exhibits an exo structure. One option of the ion-pair 67 is collapse to the cyclopropane 68. By use of suitable starting materials, compound 68 could be made a stable molecule.

Following such a sequence with monochlorocyclopropene a stable compound 85 results. If the normal steric course for cyclopropene Diels-Alder reactions were operative, the endo isomer 86 would be formed (assuming the steric considerations true for 3-methylcyclopropene[44b]).
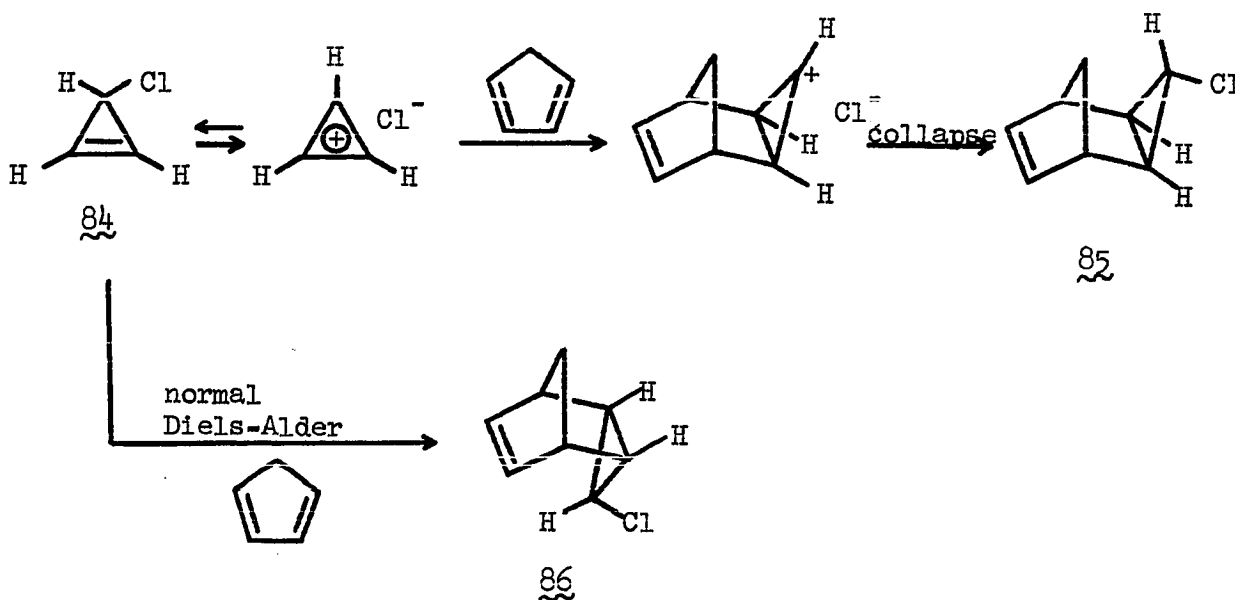
The preparation of monochlorocyclopropene (84) begins with the synthesis of tetrachlorocyclopropene (59). As in the procedure of Tobey

West,[49] 59 is prepared by the addition of dichlorocarbene to trichloro-
ethylene giving pentachlorocyclopropane; this is followed by elimination
of hydrogen chloride with base.

59
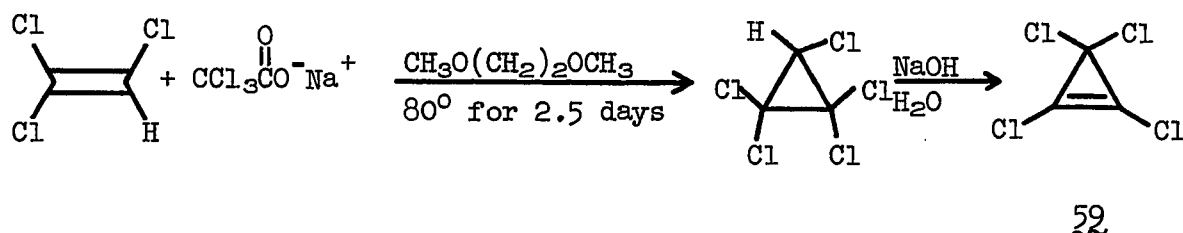
In a recent publication Breslow, et al.,[50] described the procedure
followed in converting 59 into 84. Tri-n-butyltin hydride[51] reacts with
59 in paraffin oil affording a mixture of 59% 84, 14% 3,3-dichlorocyclo-
propene (87), and 27% 1,3-dichlorocyclopropene (88) as judged by nmr
analysis. Isomers 87 and 88 readily interconvert.

84   87   88
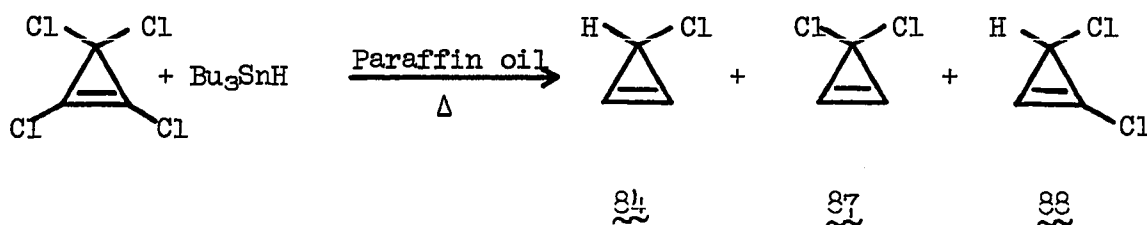
Without separation compounds 84, 87, and 88 are allowed to be consumed
by cyclopentadiene in carbon tetrachloride. Two major products can be
isolated by preparative glpc. The nmr analyses (Table 2) reveal these
compounds to be the Diels-Alder adducts of 84 and 88 with cyclopentadiene.

Chemical correlation of the monochlorocyclopropene adduct is achieved
by the treatment of norbornadiene with methylene chloride and methyllithium.
After treatment with aqueous silver nitrate solution, the major component
is collected by preparative glpc. The nmr spectrum (Table 2) of the
resulting material indicates the presence of two monochlorocarbene adducts

Table 2

H8a H8b H3 H4 H6 H2 H7 H3 Cl H1
86

H8a H3 H8b Cl H5 H6 H4 H7 H1 H2
85
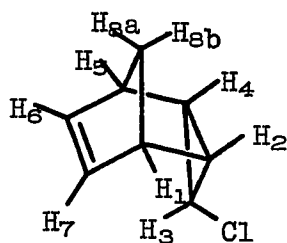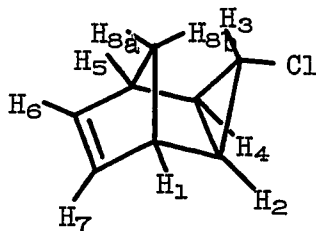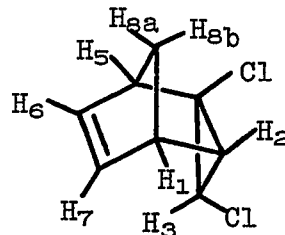
H8a H8b Cl H5 H6 H2 H7 H3 Cl H1
89

Compound	Chemical Shifts (δ units)[*]				
	H_1+H_5	H_2+H_4	H_6+H_7	H_8	H_3
86	3.03 (m)	ca.1.73 (m)	5.85 (t)	ca. 1.73 (m)	2.48 (t)
85	3.03 (m)	1.38 (m)	6.45 (t)	0.95 (m)	3.68 (t)
89	3.19 (m)	2.20 (m)	6.01 (m)	1.81 (m)	2.95 (d)

d = doublet

t = triplet

m = multiplet

* All spectra were taken in carbon tetrachloride.

of norbornadiene. Although these adducts prove resistant to separation

by glpc, the nmr spectrum of the mixture can be easily interpreted. The

mixture consists of 74% exo, anti-3-chlorotricyclo[3.2.1.0^{2,4}]oct-6-ene

(85) and 26% endo, anti-3-chlorotricyclo[3.2.1.0^{2,4}]oct-6-ene (86).

Others have found that carbene additions to norbornadiene affords mainly

1) CH$_2$Cl$_2$, CH$_3$Li

2) AgNO$_3$, H$_2$O-acetone

85   86

74%   26%
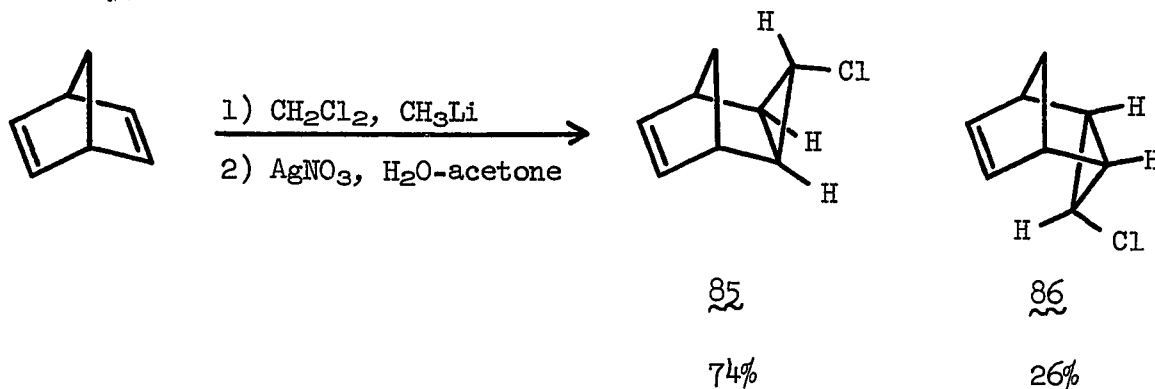
exo adducts.[52]

The Diels-Alder adduct of 3-chlorocyclopropene (84) and cyclopenta-
diene yields an nmr spectrum which coincides exactly with that for structure
86. None of 85 could be detected.

Several considerations of chemical shifts and splitting lead to the

structure assignments shown in Table 2. The same shaped narrow triplet

is observed for H$_3$ in both 85 and 86. The coupling constant value

$J_{3,2} = J_{3,4} = 1.5$ is consistent with the trans arrangement of H$_3$ relative

to H$_2$ and H$_4$ on the cyclopropane ring.[53] The cis configuration would be

expected to give a coupling constant of higher magnitude.[53a] The chemical

shifts of H$_3$ are the most instrumental values in differentiating 85 and

86. Molecular models indicate that H$_3$ in 86 nestles directly under the

π cloud of the double bond connecting C$_6$ and C$_7$. It is anticipated that

H$_3$ in 86 would experience considerable diamagnetic shielding from the

double bond resulting in an upfield shift relative to H$_3$ in 85. Exam-

ination of the chemical shifts in Table 2 reveals H$_3$ in 86 is shifted

1.2 ppm upfield from H_3 in 85. A number of other criteria have found acceptance in the literature as being able to differentiate exo and endo forms of tricyclo[3.2.1.0^{2,4}]oct-6-ene derivatives.[54] Due to the magnetic anisotropy of the cyclopropane ring[57] the vinyl protons on the parent olefin endo-tricyclo[3.2.1.0^{2,4}]Oct-6-ene[44a] are shifted 0.66 ppm upfield from those on exo-tricyclo[3.2.1.0^{2,4}]oct-6-ene.[25] Overwhelming evidence substantiates the view that the cyclopropane ring shields the vinyl protons in the endo configuration but deshields them in the exo form;[54] consequently H_6 and H_7 on 86 are shifted 0.60 ppm upfield from H_6 and H_7 on 85 indicating that 85 and 86 possess the structures assigned.

The final criterion concerns the effect of the cyclopropane ring on the chemical shift of H_8. Available examples of similar systems support the assertion that the cyclopropane ring shields H_8 while exo but deshields these protons while endo.[54,58] This effect appears in the present instance with H_8 on 85 being shifted 0.78 ppm upfield from H_8 on 86.
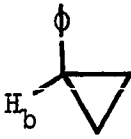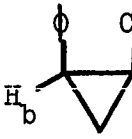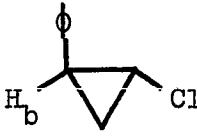
Chemical confirmation of the structure of the Diels-Alder adduct is achieved by the reduction of 86 with sodium and alcohol[56] to give the parent hydrocarbon endo-tricyclo[3.2.1.0^{2,4}]oct-6-ene (90). The nmr spectra of the reduction product and the adduct obtained from cyclopro-

86   90
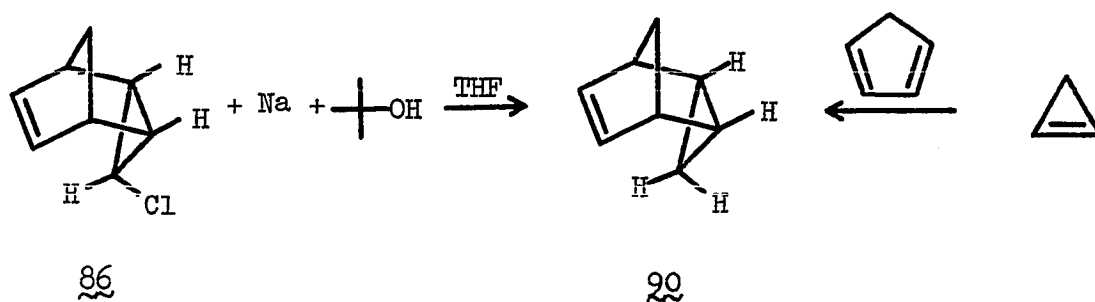
pene plus cyclopentadiene are identical. Since the cyclopropene Diels-Alder reaction with cyclopentadiene is known to give only the endo

isomer $\underset{\sim}{90}$,[44a] the structure of $\underset{\sim}{86}$ is well substantiated.

On the basis of the nmr spectrum (Table 2) the structure of the product obtained in the reaction of 1,3-dichlorocyclopropene ($\underset{\sim}{88}$) with cyclopentadiene is assigned endo, anti-3,4-dichlorotricyclo[3.2.1.0^{2,4}]-oct-6-ene ($\underset{\sim}{89}$). Even though the splitting patterns differ for $\underset{\sim}{89}$ and $\underset{\sim}{86}$, useful structural information can be acquired by comparing the chemical shifts of key hydrogens in the two spectra. The major differences in chemical shifts relative to $\underset{\sim}{86}$ occur with H_3 and H_2 (downfield shifts of 0.47 and 0.48 ppm respectively). This pattern can safely be attributed to the presence of an extra chlorine atom on the cyclopropyl function. Chemical shifts of comparable magnitude have been observed for the benzyl protons in going from phenylcyclopropane ($\underset{\sim}{17}$) to cis- ($\underset{\sim}{19a}$) or trans-1-chloro-2-phenylcyclopropane ($\underset{\sim}{19b}$).[29] Since the chemical shifts of H_6, H_7, and

Compound	$\underset{\sim}{17}$	$\underset{\sim}{19a}$	$\underset{\sim}{19b}$
δ_{H_b}	1.80	2.12	2.21

H_8 on $\underset{\sim}{89}$ resemble more closely $\underset{\sim}{86}$ values than those of $\underset{\sim}{85}$, the shielding phenomena of the cyclopropyl ring in $\underset{\sim}{89}$ coincide with the endo geometry.

If the exo approach is a legitimate criterion for the ionic mechanism (Figure 7) then it appears that both $\underset{\sim}{84}$ and $\underset{\sim}{88}$ follow the normal Diels-Alder route (Figure 6) in reaction with cyclopentadiene. However, since tetrachlorocyclopropene ($\underset{\sim}{59}$) possesses greater steric factors opposing the normal pathway,[44b] the ionic mechanism could yet be operative in the tetrahalocyclopropene reactions.

The kinetic schematic for the ionic process is outlined in <u>Figure</u> <u>8</u>.

<u>Figure</u> <u>8</u>
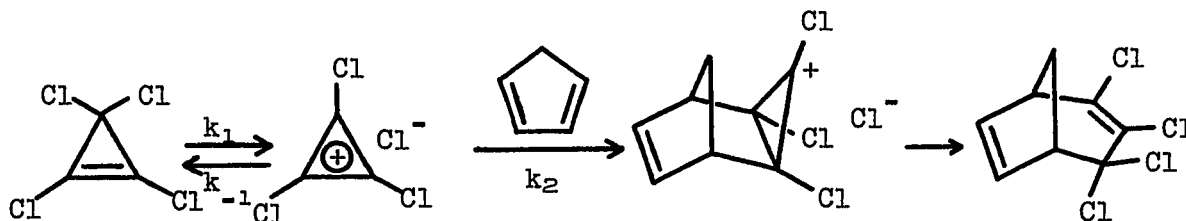
Two kinetic extremes are available to this system.[59] If the assumption

is made that $k_2[C_5H_6] >> k_{-1}$, the reaction would exhibit a rate expression

which is first order in <u>59</u> and independent of diene concentration. This

resembles S_N1 behavior, which is well-known in nucleophilic substitution

reactions. The other extreme, $k_2[C_5H_6] << k_{-1}$, would yield normal

bimolecular kinetics, being first order in both <u>59</u> and diene. The latter

possibility actually includes the equilibrium constant for <u>59</u> $\rightleftharpoons$ <u>81</u> in the

rate expression. Increasingly polar solvents would shift this equilibrium

$$\frac{d[63a]}{dt} = k_2 K_{eq}[59][\text{☐}]$$

to favor more <u>91</u> and thus raise the value of K_{eq}.[43] Although k_2 would be

expected to vary somewhat with change in solvent, the overall rate should

increase with increasing solvent polarity.

It can be safely assumed that this reaction is quantitative since <u>63a</u>

can be isolated in a pure state in 95% yield after one recrystallization

from petroleum ether.[40] The reaction is conveniently monitored by

following product formation using quantitative glpc procedure with an

internal standard. The reactions are conducted with at least a twenty-fold

excess of cyclopentadiene over $\underset{\sim}{59}$. A competing side reaction, the dimerization of cyclopentadiene, causes depletion of 7% of the diene during the course of following the slowest reaction studied for $\underline{ca}$. one half-life.

In every solvent system tried the rates prove to be first order in both $\underset{\sim}{59}$ and cyclopentadiene, $\underline{i.e.}$, equation 3 is obeyed. A pseudo first order plot of log $\left(\dfrac{[\underset{\sim}{63a}]_f}{[\underset{\sim}{63a}]_f - [\underset{\sim}{63a}]}\right)$ vs. time provides a straight line, the

$$\frac{d[\underset{\sim}{63a}]}{dt} = k_{obs}[59]\left[\bigcirc\hspace{-1.1em}\diamond\right] \tag{1}$$

$$\log \frac{[\underset{\sim}{63a}]_f}{[\underset{\sim}{63a}]_f - [\underset{\sim}{63a}]} = k_{obs}\left[\bigcirc\hspace{-1.1em}\diamond\right]t \tag{2}$$

$[\underset{\sim}{63a}]_f$ = final concentration of $\underset{\sim}{63}$a at end of reaction

slope of which, when divided by diene concentration, relinquishes the observed rate constant (k_{obs}) for the reaction. The rate constants obtained in several different solvents are listed in Table 3. The linear dependence on diene concentration, as determined in benzene and acetone, is demonstrated by the doubling of the rate constant with doubling the concentration of diene.

The rate constants are shown to increase only slightly with increasing polarity of solvent. Since the dimerization of cyclopentadiene itself is three times faster in ethanol than benzene[60] and other normal Diels-Alder

Table 3

Solvent	$k_{obs}(\frac{e}{m\text{-}sec})$	temp
CCl_4	2.0×10^{-4}	25°
C_6H_6	4.3×10^{-4}	25°
$(CH_3)_2CO$	5.3×10^{-4}	25°
$(CH_3)_2NCHO$	7.0×10^{-4}	25°
$(CH_3)_2CO$	1.8×10^{-3}	47°

reactions exhibit rate constant changes as high as a factor of ten with change in solvent polarity,[42] this result seems consistent with the normal Diels-Alder process.

By means of the Erying equation,[65] the activation parameters for the reaction in acetone can be easily calculated: $\Delta F_{25^o}^{\ddagger} = 22$ kcal/mole, $\Delta H_{25^o}^{\ddagger} = 11$ kcal/mole, and $\Delta S_{25^o}^{\ddagger} = -36$ eu. The small enthalpy of activation and the large negative entropy of activation closely resemble the values obtained in other Diels-Alder reactions.[42,61] Synchronous bond formation in the transition state is evidenced by the strong negative value of $\Delta S^{\ddagger}$.

An attempt at witnessing catalysis for this reaction was also made. The presence of as high as $0.1N$ mercuric chloride in tetrahydrofuran (THF) exhibits no effect on the observed rate constant.

Breslow and Groves[62] have very recently shown that the cyclopropenyl

cation is 18 kcal/mole more stable than the allyl cation. The aromaticity inherent in the cyclic three-membered system far outweighs the strain energy involved in its formation. Combined with the fact that the cyclopropyl cation (Figure 7) is not expected to be a very stable species as far as carbonium ion stability is concerned,[63] the ionic Diels-Alder involving the cyclopropenyl cation may not be energetically feasible. Attempted cycloaddition reactions of trichlorocyclopropenium tetrachloro-aluminate[64] with a number of dienes in liquid sulfur dioxide did not meet with success in our hands.

The vanguard experiments in studying the possibility of [1,4] anionic shifts center on attaching substituents to 1-phenylallyllithium (78), a substance known to exist largely in the ionic form in tetrahydrofuran.[46a] Compound 78 seems to behave somewhat differently in its two-forked affinity toward hydrogen and carbon. Slight predisposition toward terminal protonation is demonstrated in the water quench of 78. Glpc analysis indicates

	78		92	93	94
			39%	9%	52%
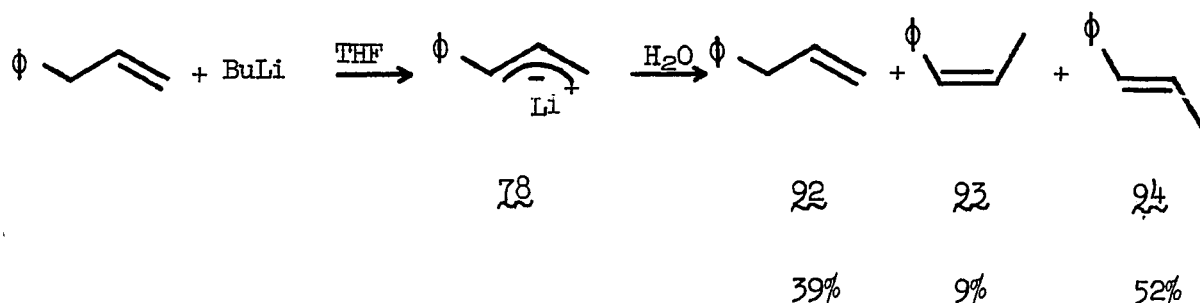
terminal protonation to be about 1.5 times faster than protonation at the benzyl position. Cram, et al.,[66] arrived at a slightly higher value for kinetic protonation of the 1-phenylallyl anion in a different medium.

The benzyl position proves more reactive toward nucleophilic substitution than the terminal position as demonstrated in the quantitative coupling of 78 and allyl chloride. Here 3-phenyl-1,5-hexadiene (95)

$\phi \diagup\diagdown \quad + \quad \diagup\diagdown Cl \quad \xrightarrow[-30°]{THF}$

78   19%   81%

95
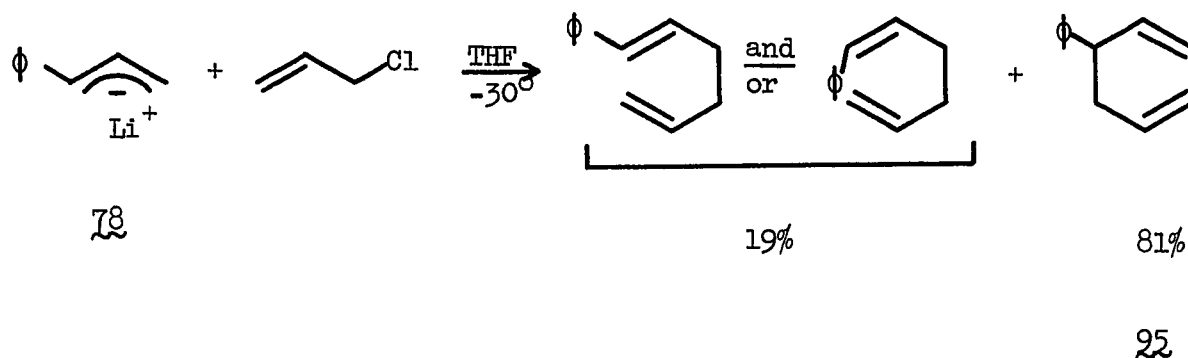
represents 81% of the products.

It was decided to employ the higher nucleophilic tendency of the benzyl position in 78 to generate compounds capable of undergoing [1,4] shifts of both hydrogen and carbon.

The first attempt at spotting [1,4] hydrogen shifts begins with the synthesis of 3,4-diphenyl-1-butene (96) (Table 4) in ca. 80% yield. When

$\phi \diagup\diagdown \quad + \quad \phi CH_2Cl \quad \xrightarrow[-30°]{THF}$

78   96
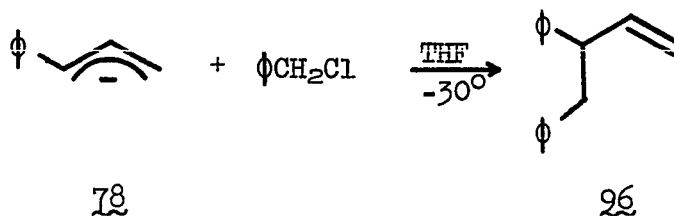
96 is treated with one equivalent of butyllithium in hexane-THF (50:50) or hexane-tetramethylethylenediamine (TMEDA) (50:50), a dark red color develops, which is also characteristic of 78 as well as many other de-localized anions.[67] The resulting solution is quenched in water to return 17% of the starting material as well as 78% of 1,2-diphenyl-cis-butene (97) and 5% of uncharacterized material. A deuterium oxide quench results in incorporation of one deuterium at C_4 in at least 80% of 97. The stable ionic intermediate 98 is suggested as a logical progenitor of 97 and
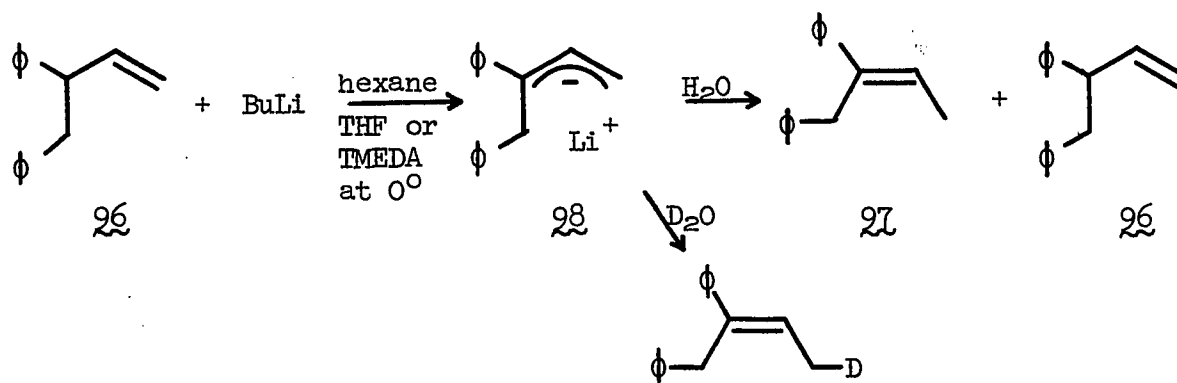
at least 80% monodeuterated

perhaps the starting material found in the product. The amount of ionic character in 98 was not determined; but judging from anology with 78 at least the ionic species should be available on the potential energy surface. Also the use of a better lithium cation solvating medium such as TMEDA would be expected to bolster the stability of the ionic structure.
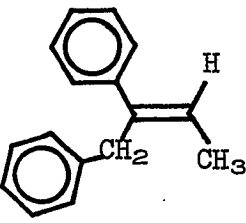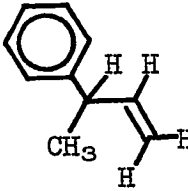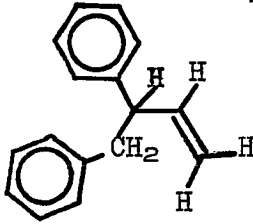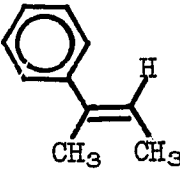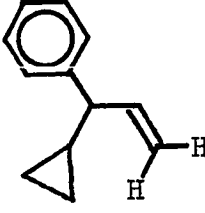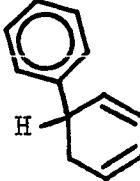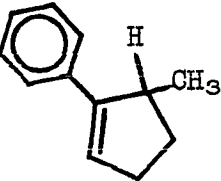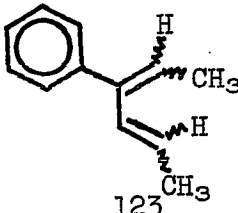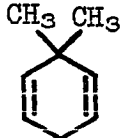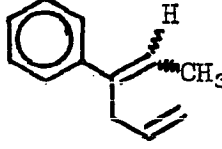
The nmr spectrum is consistent with the cis-butene structure for 97 and not the trans geometry (99). This is based mainly on the calculated
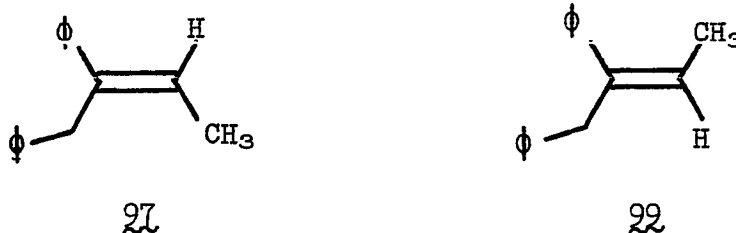
chemical shifts for the vinyl protons in 97 and 99 compared with the actual chemical shift of this quartet. By the use of additive increments for functional groups,[68] the chemical shifts for the vinyl protons in 97 and 99 are easily calculated to be 5.74δ and 5.34δ respectively. The experimentally observed value is 5.94δ. Since these calculations have been shown to yield chemical shifts within 0.50 ppm of the actual value 99.7% of the time (over 4000 cases), one is compelled to choose 97 as the

Table 4

Chemical Shifts and Proton Integration

Structure	Chemical Shift (δ)	Number of Protons	Structure	Chemical Shift (δ)	Number of Protons
97	1.72(d)	3	121	1.32(d)	3
	3.77(s)	2		3.38(m)	1
	5.94(q)	1		4.95(m)	2
	7.05(m)	10		5.95(m)	1
				7.10(s)	5
96	2.92(m)	2	122	1.58(m)	3
	3.50(m)	1		1.82(m)	3
	4.87(m)	2		5.74(m)	1
	5.97(m)	1		7.16(m)	5
	7.00(m)	10			
104	ca.0.34(m)	4	95	2.46(m)	2
	ca.0.92(m)	1		3.32(m)	1
	2.57(m)	1		4.98(m)	2
	5.03(m)	2		5.85(m)	2
	5.96(m)	1		7.19(s)	5
	7.12(m)	5			
106	1.09(d)	3	123	1.48(m)	3
	ca.1.91(m)	2		1.73(m)	3
	ca.2.47(m)	2		ca.5.83(m)	3
	3.19(m)	1		7.19(m)	5
	6.01(m)	1			
	7.35(m)	5			
109	1.02(s)	6	124	1.78(d)	3
	2.57(m)	2		3.21(m)	2
	5.50(m)	4		ca.5.00(m)	2
				ca.5.76(m)	2
				7.18(m)	5

major water quench product of 98. If kinetic quenching may be assumed,
this also suggests that the structure shown for 98 represents the
cardinal conformer of the anion.

The question of interest concerns whether an equilibrium of the
type 98 ⇌ 100 could be realized at higher temperatures. The solution to
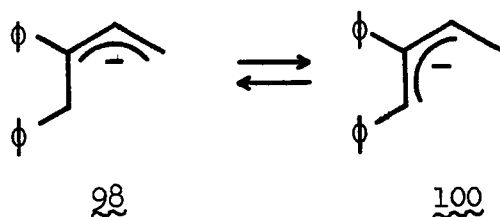
this problem is approached by deuterium labeling.

Figure 9 outlines a series of reactions which eventually produces
3,4-diphenyl-1-butene-4,4-d_2 (101). The nmr spectrum discloses 101 to be

Figure 9
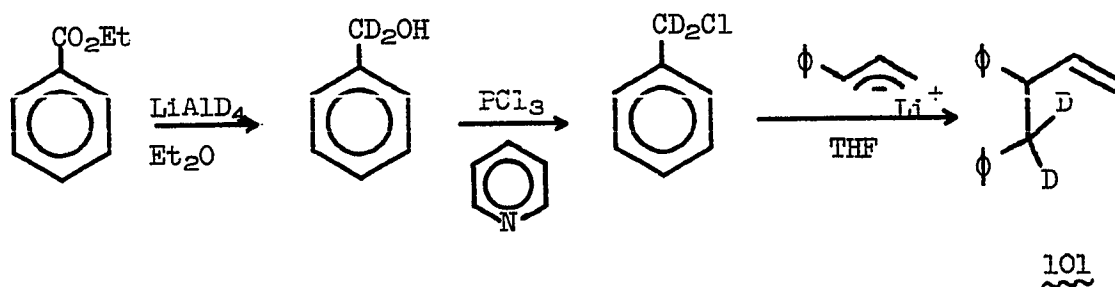
90% dideuterated in the position shown.

When 101 is treated with one equivalent of butyllithium in hexane-
THF, the resulting solution refluxed (ca. 64°) overnight and then quenched
in water, no deuterium scrambling can be detected in the major product
103. The solution remains deep red during the reflux period and the
product ratio upon quenching is very nearly the same as that at 0°,
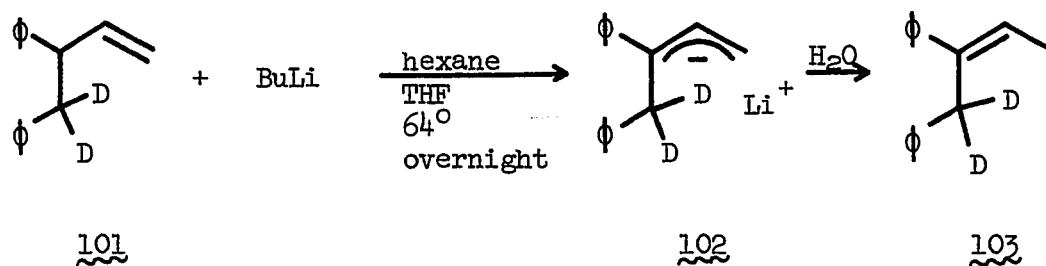
indicating that the ion 102 is not protonated by solvent to a very large

extent.

Although higher temperatures can be attained using hexane-TMEDA,

an unusual reaction course seems to be available to such systems which

will be discussed in part later in the thesis.

An endeavor to witness a [1,4] carbon shift was also made with a

cyclopropane system. When cyclopropene[69,31a] is allowed to bubble through

a solution of 78 in THF, the major product is isolated by preparative glpc

and assigned the structure of the cyclopropane 104 (Table 4).
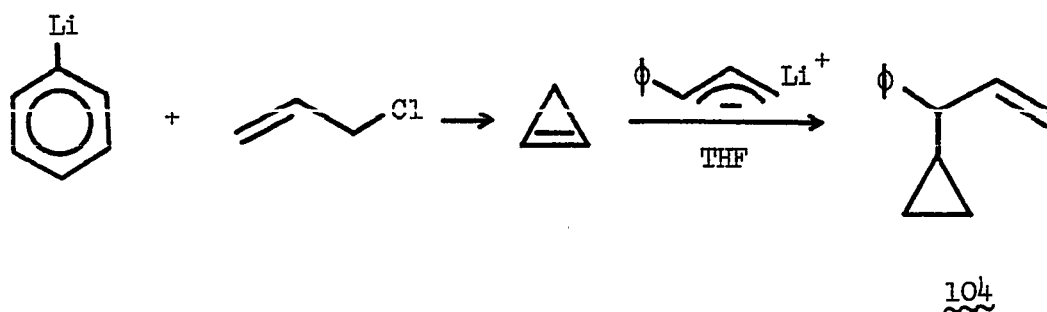
Treatment of 104 with one equivalent of butyllithium in hexane-TMEDA

at slightly elevated temperature produces as the major product 3-methyl-

2-phenylcyclopentene (106) (43% yield) (Table 4) upon water quenching. A

minor product (7% yield) also appears on the chromatogram but was not

isolated and identified.

104   105   106
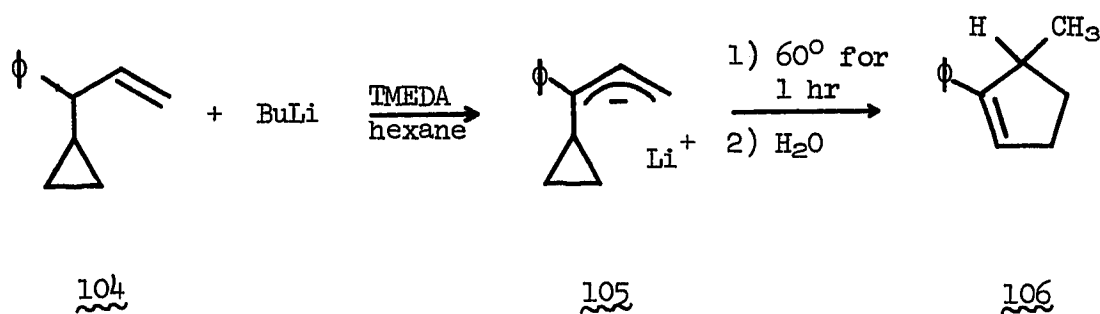
Assuming formation of ion 105, the cyclopentene 106 probably arises from one of two possible mechanisms. The first mechanism proceeds with a familiar cyclopropylcarbanion ring opening[73] followed by addition to the terminal double bond eventually yielding the primary lithium reagent 107. It is worthwhile to note that such a stepwise process could also

107
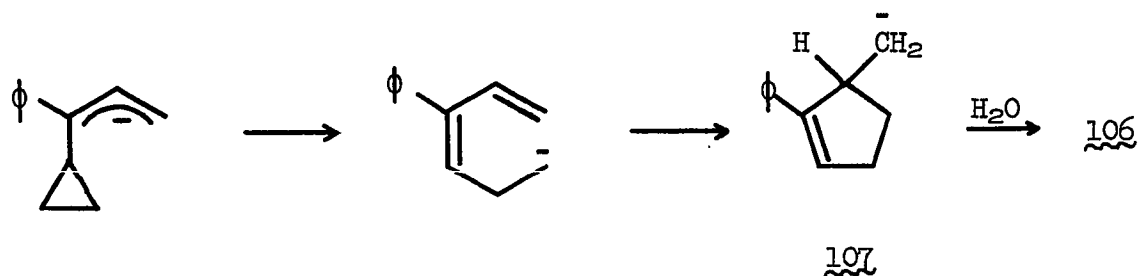
explain adequately any product resulting from the [1,4] shift.

The second possibility is a concerted [1,3] shift proceeding with
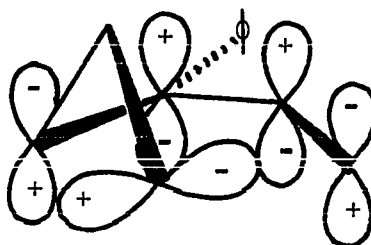
inversion at the migrating center.[37] Although an example of such a mechanism in a neutral system has been demonstrated,[86] it is also believed

that the vinylcyclopropane-cyclopentene rearrangement avoids a concerted

pathway.[87] The present results do not permit distinction between the

concerted shift and the two-step process.

Molecular models indicate that a [1,4] shift with retention in an

open chain framework may be too long of a jump to permit adequate continual

overlap among all the orbitals involved; consequently it was decided to

switch to cyclic systems to reduce somewhat the expansion needed to be

traversed by the migrating center.

Figure 10 shows a number of straightforward reactions used to synthe-

size the dideuterated 1,4-cyclohexadiene 108. A small amount of the

Figure 10
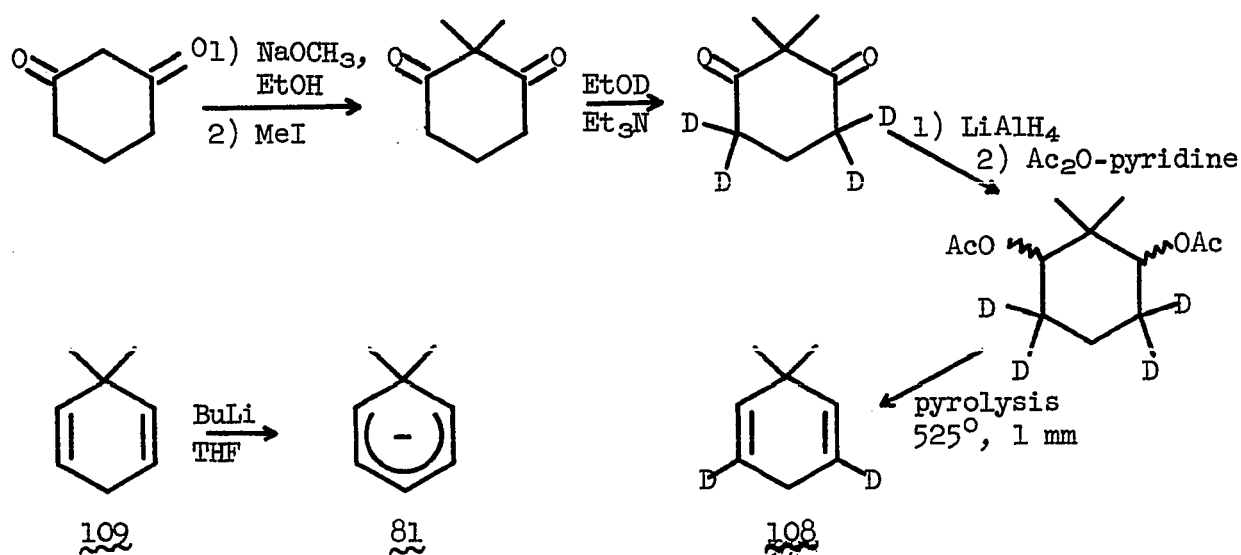
undeuterated compound 109 was also prepared for identification purposes.

Nmr analysis substantiates greater than 98% dideuteration of 108 in the

vinyl positions.

It had already been shown that treatment of 109 with butyllithium in

THF produces 81, an ionic species as determined by nmr.[48] Also an example

of disrotatory electrocyclic ring closure of a pentadienyl anion (110)

appeared in the literature.[75]

110
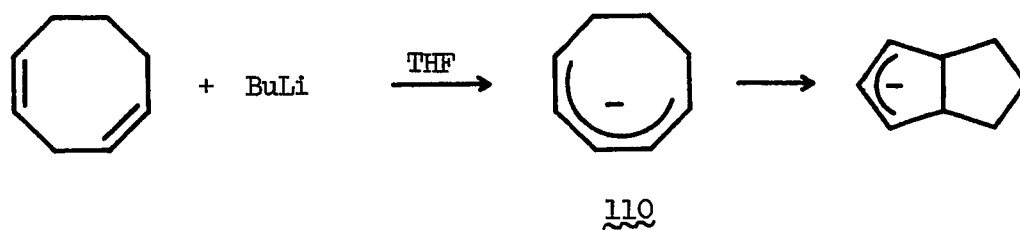
Combining these reactions with the possibility of a [1,4] anionic carbon shift at higher temperatures would lead to scrambling of the deuteriums on 108. Quenching 81 in water produces two dienes as the sole

Figure 11
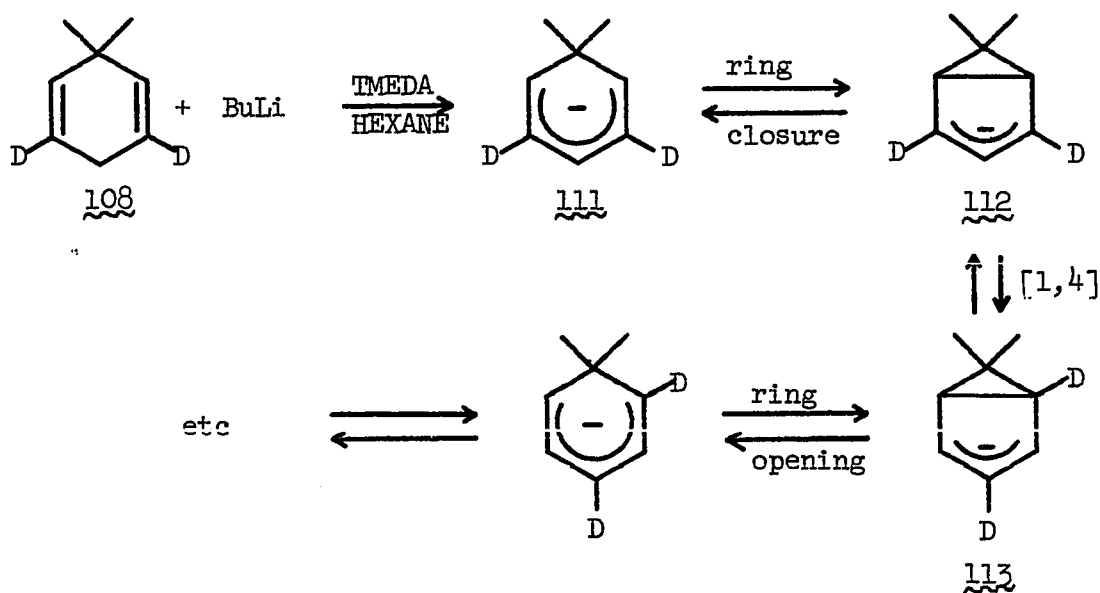
products, 109 and 114. Assuming complete equilibration as outlined in
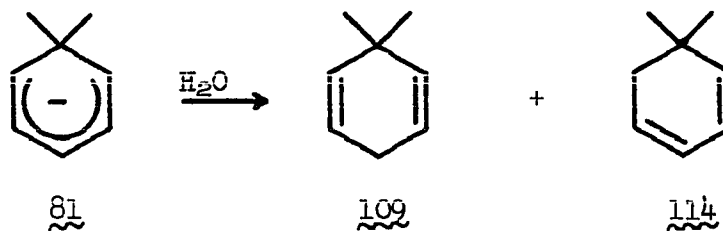
Figure 11, quenching the dideuterated ion in water would give 109 and

114 with 0.4 deuteriums at the methylene positions and 1.6 deuteriums at the vinyl positions. Without scrambling the deuteriums remain the sole possessions of the vinyl carbons.

In an initial experiment, 108 is allowed to react with one equivalent of butyllithium in hexane-TMEDA at $0°$. Quenching in deuterium oxide yields two products which prove to be homogeneous to glpc analysis; however, an nmr investigation shows these compounds to be the trideuterated cyclohexadienes 115 and 116, obtained in a nearly statistical ratio of 31% and 69% respectively. Thus the desired ion is produced quantitatively.
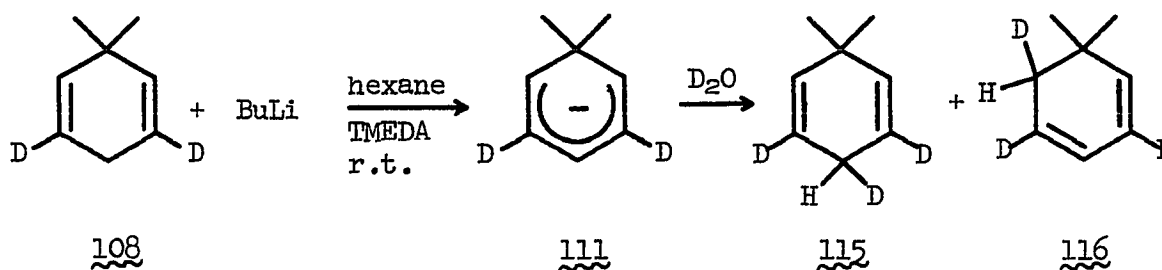
When the dideuterated ion 111 is heated in hexane-TMEDA to $93°$ for one hr and then worked up in water, only 108 and 117 result in a ratio practically identical to the low temperature quench. No deuterium
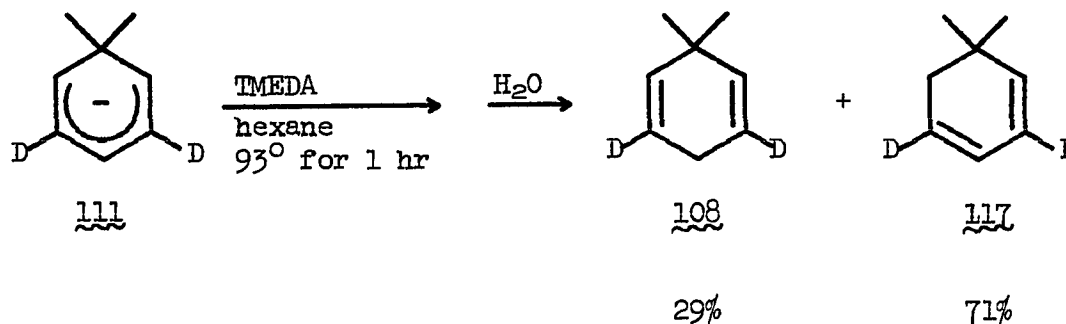
scrambling could be detected. The utility threshold of this system is reached around $93°$ since a small amount of toluene is formed presumably by loss of methyllithium from 111.

It is not known if ring closure of the type $\underset{\sim\sim}{111}$ —— $\underset{\sim\sim}{112}$ is actually available to this system. The anion $\underset{\sim\sim}{111}$ possesses an added stability due to its homoaromaticity.[74]

Although the suprafacial [1,4] shift with retention in this system is allowed by orbital symmetry considerations, a suprafacial shift with inversion is favored by the least motion principle.[83] Atomic repositioning is at a maximum for R_1 and R_2 as a consequence of retention at the
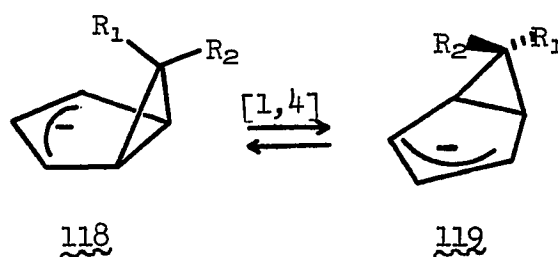
$$\underset{\sim\sim}{118} \qquad \underset{\sim\sim}{119}$$

migrating center ($\underset{\sim\sim}{118} \rightleftharpoons \underset{\sim\sim}{119}$).

The least motion principle may be violated in the ring-walking phenomenon involving the norcaradiene skeleton.[84] However, it has not yet been verified that this transformation proceeds with retention at the migrating center.[37]

While studying these systems it was observed that in hexane-TMEDA two equivalents of butyllithium are readily consumed by $\underset{\sim\sim}{96}$. Quenching in water gives $\underset{\sim\sim}{97}$ in 73% yield while deuterium oxide work-up produces completely dideuterated $\underset{\sim\sim}{97}$. The dilithium salt of type $\underset{\sim\sim}{120}$ is presumably the stable intermediate. It is interesting to note that adjacent unsaturation appears necessary for the second mole of butyllithium to be consumed; i.e., compound $\underset{\sim\sim}{121}$ forms only the monoanion when put in contact with two equivalents of butyllithium.
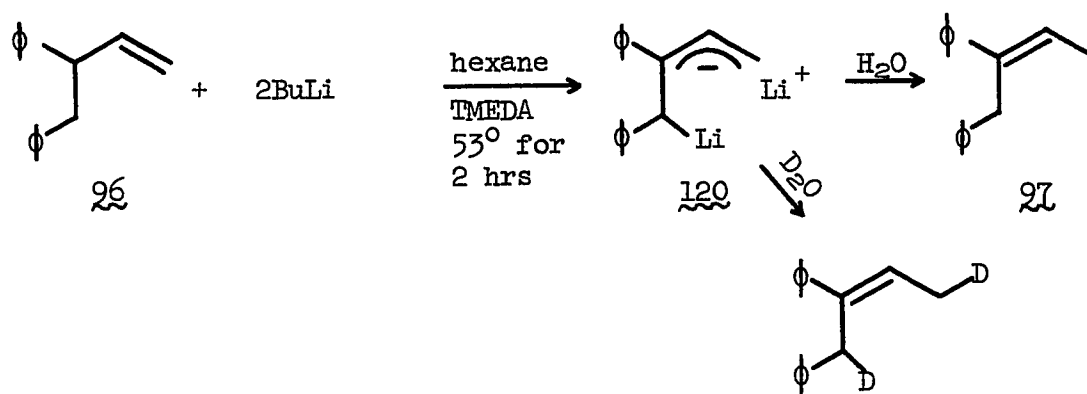
A most remarkable transformation occurs when compound 95 is mixed
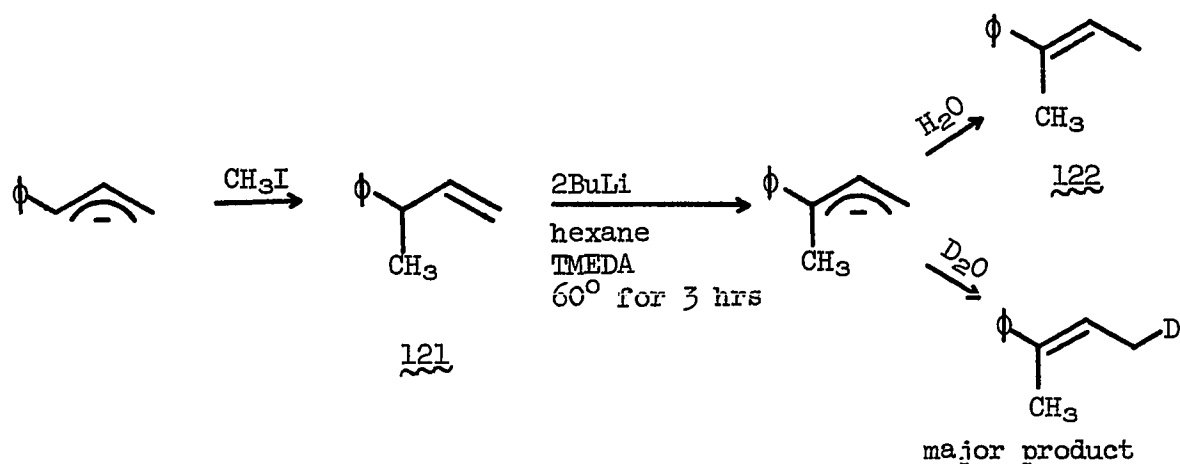
major product

with two equivalents of butyllithium. Under gentle conditions water quenching produces two major products, 123 and 124, the stereochemistries of which have not been determined. The gross structures of 123 and 124 directly follow from analysis of their nmr spectra (Table 4). Precisely two deuterium atoms are incorporated in 123 and 124 upon quenching in deuterium oxide. These materials can be separated and isolated by preparative glpc.
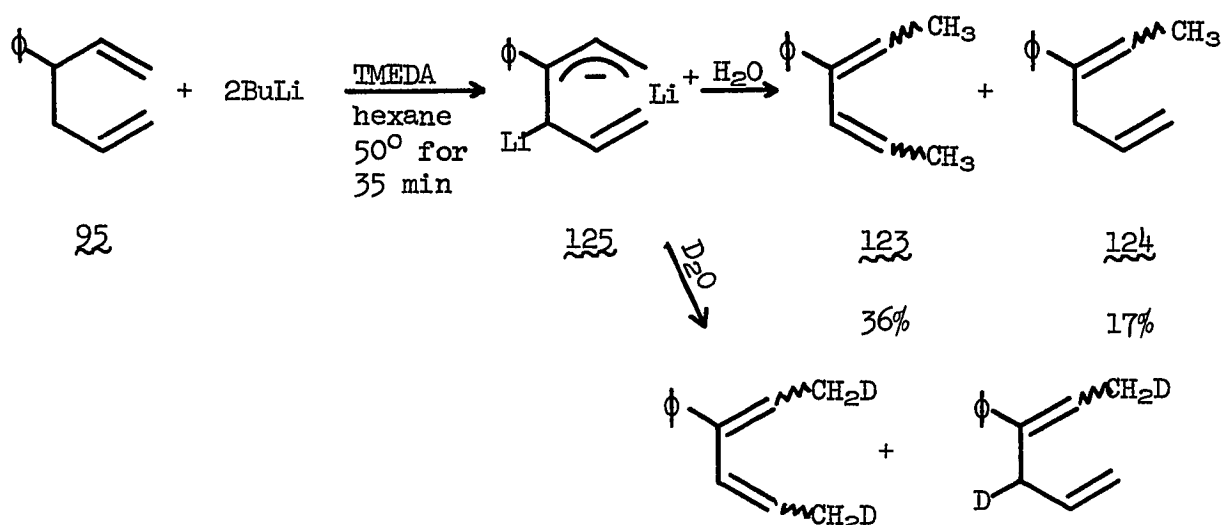
If the same solution is heated to 60° for two hours, only one

product can be isolated in 77% yield. This product is a white solid

whose nmr spectrum coincides perfectly with that of an authentic sample

of biphenyl. A light brown solid collects on the walls of the flask

during this reaction and the water quench is noticed to exhibit much more

vigor than usual. This behavior can be attributed to lithium hydride

formation. If only one equivalent of butyllithium is employed under these

conditions, only a trace of biphenyl is detected by glpc.

Albeit somewhat premature an intriguing mechanism can be proposed for

biphenyl formation. The ground state of 125 could perhaps possess some

dianionic character if viewed as two allyl anions geometrically insulated

from π overlap with one another by virtue of orthogonality (126). As

heat is applied rotation insues about the bond joining carbons 3 and 4.

While at the energy maximum of this rotation the system finds itself

properly oriented for electrocyclic ring closure (127).[37] Such an

electrocyclic reaction should proceed in a conrotatory fashion being
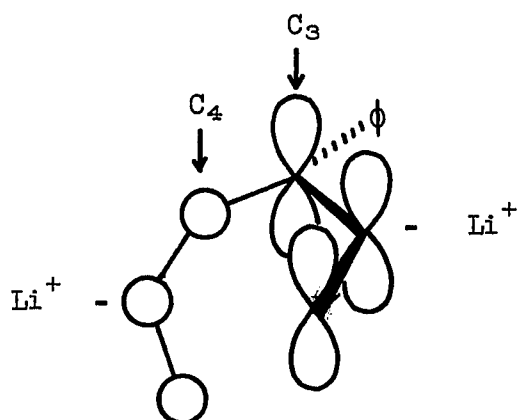
<u>126</u>

controlled by the lowest antibonding orbital (the highest filled molecular orbital in this case). In this respect it resembles the photo-

<u>126</u> →rotation← <u>127</u> →ring closure← <u>128</u> —2LiH→
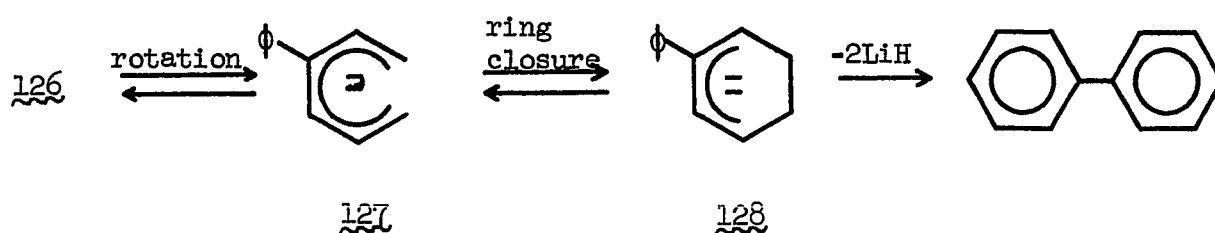
chemical electrocyclic ring closure of hexatriene.[37] The highly reactive species <u>128</u> would have the option of reversing or shedding two moles of lithium hydride to create an aromatic system. Loss of lithium hydride might proceed stepwise or in a concerted double barrelled elimination having simultaneous aromatization as a driving force. It is well established that aromatic systems form from monoanions quite rapidly by loss of lithium hydride even at low temperatures (<u>130</u>).[48]

Although adequate systems can be created to answer the interesting questions posed by this reaction, time has not yet permitted this to be accomplished.

129   130
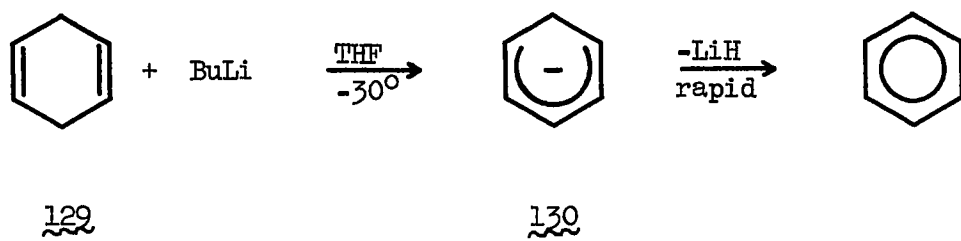
EXPERIMENTAL

General:

A Varian Associates A-56/60A spectrometer was used to record all nmr spectra. The chemical shift values are reported in parts/million downfield from tetramethylsilane which was employed as an internal standard. In most cases the nmr sample contained A.C.S. reagent grade carbon tetrachloride as the solvent.

The quantitative analytical glpc analyses were performed on a Perkin-Elmer Model 800 Gas Chromatograph with a flame ionization detector or on a Varian Aerograph Model 202-1B Gas Chromatograph with a thermal conductivity detector. The principal method of yield determination employed an internal standard.

In cases where the products were hydrocarbons, a hydrocarbon internal standard was added. Equal weight responses were assumed using the flame ionization detector in such instances; equal molar responses were assumed using the thermal conductivity detector.[96] When hetero atoms appeared in the product, the relative responses for product and internal standard were arrived at in separate experiments. Enough examples were checked to ensure analysis within the linear dynamic range of the detector system.

The external standard method of quantitative analysis was used only sparingly. This method required the preparation of a solution of known concentration of product and the injection of a known volume of this solution into the chromatograph. The response was then compared with that observed for an unknown solution. By this procedure the concentration of the product in the unknown solution could be readily acquired.

All peak areas needed to calculate yields were determined by use of a Disc-Integrator. Analytical glpc work was conducted using the following

columns:

Column A: XF 1150 (15%) on Chromosorb P, 1/8 in. x 10 ft;

Column B: SE-30 (20%) on Chromosorb P, 1/4 in. x 10 ft;

Column C: SE-30 (7%) on Chromosorb W,AW,DMCS, 1/8 in. x 10 ft;

Column D: Carbowax 20M (10%) on Chromosorb P, 1/8 in. x 6 ft;

Column E: β,β'-Oxydipropionitrile (15%) on Chromosorb P, 1/8 in. x
10 ft;

Column F: Apiezon L (15%) on Chromosorb P, 1/8 in. x 10 ft;

Column G: SE-30 (15%) on Chromosorb P, 1/8 in. x 3 ft;

Column H: Ucon 50HB260 (20%) on Chromosorb P, 1/8 in. x 10 ft;

Column I: TCEP (10%) on Chromosorb P, 1/8 in. x 10 ft.

The preparative glpc work was performed on the Varian Aerograph
instrument using the following columns:

Column J: SE-30 (30%) on Chromosorb P, 3/8 in. x 20 ft;

Column K: Carbowax 20M (10%) on Chromosorb W, 3/8 in. x 3 ft;

Column L: SE-30 (25%) on Chromosorb P, 3/8 in. x 3 ft;

Column M: Carbowax 20M (10%) on Chromosorb W, 3/8 in. x 2 ft;

Column N: TCEP (15%) on Chromosorb P, 3/8 in. x 9 ft.

All reactions involving alkali metals or organolithium reagents were
performed under an inert atmosphere (nitrogen or argon). No corrections
were made on boiling point data.

Solvents:

Unless otherwise specified, reagent grade solvents were used in this
work.

Ethanol. U. S. I. absolute pure ethyl alcohol (U.S.P.-N.F.) was
distilled from sodium metal directly into the reaction flask.

Diethyl Ether. Anhydrous ether, made by J. T. Baker Chemical Co.,

was distilled from lithium aluminum hydride and stored over sodium ribbon.

Tetrahydrofuran (THF). Sold by Matheson Coleman and Bell, THF (bp 65.5-66.5) was distilled from lithium aluminum hydride and stored over sodium ribbon or molecular sieves.

N,N,N',N'-Tetramethylethylenediamine (TMEDA). This material was obtained from Eastman Organic Chemicals and was dried over molecular sieves before use.

N,N-Dimethylformamide (DMF). Bearing the Matheson Coleman and Bell label, DMF was dried over molecular sieves before use.

Carbon Tetrachloride. A.C.S. reagent carbon tetrachloride, supplied by Allied Chemical, was used directly from the bottle.

Benzene. Thiophene-free benzene, product of J. T. Baker Chemical Co., was dried over sodium ribbon before use.

Petroleum Ether. This solvent (br 20-40°), obtained from Allied Chemical, was not treated in any way.

Acetone. Originating from Allied Chemical, A.C.S. reagent acetone was not subjected to any purification before use.

Reagents:

All reagents were C.P. grade reagents, A.C.S. reagents, or analyzed reagents unless otherwise stated. Table 5 provides a list of reagents, as well as their sources, which were not purified or analyzed in any way.

Table 5

Reagent	Source
Lithium Aluminum Deuteride	Metal Hydrides Incorporated
Styrene	Eastman Organic Chemicals (white label)

Table 5 (contd.)

Reagent	Source
2,3-Dimethyl-2-butene	Aldrich Chemical Co., Inc.
Triphenylmethane	Matheson Coleman and Bell
Lithium Metal Wire	A. D. Mackay, Inc.
Lithium Metal Wire (1% Na)	Alfa Inorganics, Inc.
Dimethylmercury	Alfa Inorganics, Inc.
Methyl Iodide	Matheson Coleman and Bell
2,5-Norbornadiene	Eastman Organic Chemicals (yellow label)
tert-Butanol	Matheson Coleman and Bell
Sodium Metal Lumps	J. T. Baker Chemical Co.
Allylbenzene	Aldrich Chemical Co., Inc.
Allyl Chloride	Eastman Organic Chemicals (white label)
Benzyl Chloride	Allied Chemical
Ethyl Benzoate	Matheson Coleman and Bell
Pyridine	Fisher Scientific Company
Phosphorus Trichloride	J. T. Baker Chemical Co.
1,3-cyclohexanedione	Aldrich Chemical Co., Inc.
Sodium Methoxide	Matheson Coleman and Bell
Triethylamine	Matheson Coleman and Bell
Lithium Aluminum Hydride	Alfa Inorganics, Inc.
Acetic Anhydride	Matheson Coleman and Bell
Deuterium Oxide	Stohler Isotope Chemicals
Trichloroacetic Acid	Fisher Scientific Co.
Methylene Iodide	Matheson Coleman and Bell

n-Butyllithium. The n-butyllithium solution in hexane was analyzed by the triphenylmethane method (see experimental) and found to be 1.45 N in n-butyllithium. The hexane solution was obtained from the Foote Mineral Co.

Methyllithium (LiCl). Foote Mineral Co. produced ether solutions of methyllithium which were labelled as ca. 5% by weight methyllithium and ca. 0.4% lithium chloride.[90] Analysis (both by acid titration and the triphenylmethane method) gave varying results from bottle to bottle.

Methyllithium (LiBr). This reagent (ca. 2.3 N) was sold in ether solution by Alfa Inorganics, Inc. and contained one equivalent of lithium bromide.

Methylene Chloride. This material was provided by Matheson Coleman and Bell and was dried over molecular sieves before use.

Table 6 lists a number of compounds used as internal standards or as authentic samples needed for retention time or nmr spectrum comparisons. The sources of these materials are also provided.

Table 6

Compound	Source
cis- and trans-1-methyl-2-phenylcyclopropane	Dr. James G. Welch, Rice University
Phenylcyclohexane	Eastman Organic Chemicals (white label)
Cyclooctane	Eastman Organic Chemicals (white label)
endo-Tricyclo[3.2.1.0^{2,4}]oct-6-ene	Dr. James G. Welch, Rice University
cis-Propenylbenzene	Chemical Samples Co.

Table 6

Compound	Source
trans-Propenylbenzene	Aldrich Chemical Co., Inc.
Diphenylmethane	Aldrich Chemical Co., Inc.
Toluene	Allied Chemical
Biphenyl	Matheson Coleman and Bell
Methallylbenzene	Aldrich Chemical Co., Inc.
Dodecane	Eastman Organic Chemicals (yellow label)
Naphthalene	Fisher Scientific Co.

Prepared Materials:

Cyclopentadiene. This material was collected by distillation[91] from dicyclopentadiene which was obtained from Aldrich Chemical Co., Inc.

Phenyllithium. This reagent was prepared in diethyl ether solution from bromobenzene and excess lithium wire.[93] The phenyllithium was standardized using the triphenylmethane procedure.

Methyllithium (LiI). The slow addition of methyl iodide to excess lithium wire in diethyl ether produced a solution which was standardized (1.40 $\underline{N}$) by acid titration or the triphenylmethane procedure. The lithium iodide concentration (1.87 $\underline{N}$) was determined by the Volhard method.[94]

Halide-free Methyllithium. As in the procedure of Seitz and Brown,[92] dimethylmercury was permitted to react with excess lithium wire in anhydrous diethyl ether. The resulting solution was analyzed by standard acid titration and found to be 1.03 $\underline{N}$ in base.

Chloroiodomethane. Chloroiodomethane was prepared from the reaction of sodium iodide and methylene chloride in acetone.[88] The yield was 60% (bp 107-109°).

Lithium Shot. Easily prepared by agitation of a hot mixture of lithium (1% sodium) wire and mineral oil, lithium shot was stored floating on light petroleum ether.[95]

Tri-n-butyltin Hydride. This substance was prepared by the reduction of tri-n-butyltin chloride (Aldrich Chemical Co., Inc.) with lithium aluminum hydride in diethyl ether as described by Van Der Kerk.[51] A high yield of product was obtained, bp 81°/0.9 mm. This material was stored under argon.

Pentachlorocyclopropane. Trichloroethylene (J. T. Baker Chemical Co.) and sodium trichloroacetate (prepared from trichloroacetic acid and sodium methoxide in methanol followed by removal of solvent under vacuum) were heated in 1,2-dimethoxyethane following the literature procedure.[49a] The product distilled at 56° under 7 mm pressure.

Tetrachlorocyclopropene. Elimination of hydrogen chloride by treatment of pentachlorocyclopropane with potassium hydroxide in water led to formation of tetrachlorocyclopropene.[49b] This material boiled at 130-131° under atmospheric pressure and was stored in a refrigerator.

3-Chlorocyclopropene, 3,3-Dichlorocyclopropene, and 1,3-Dichloro-cyclopropene. These materials proved to be the volatile products when tetrachlorocyclopropene was treated with tri-n-butyltin hydride in paraffin oil as described by Breslow, et al.[50] These compounds were not separated or purified in any way before use.

Cyclopropene. According to the procedure of Magid and Welch,[31a] cyclopropene was prepared by the slow addition of phenyllithium to excess allyl chloride. This was followed by the dropwise addition of

water releasing even more cyclopropene.

Ethanol-O-d. Gaseous sulfur trioxide (generated by heating
fuming sulfuric acid) was bubbled into a mixture of triethylorthoformate
(Matheson Coleman and Bell) (5.0 moles) and deuterium oxide (2.5 moles).
After the mixture became homogeneous, it was distilled through a
1 in. x 15 in. glass helices column and the material boiling at
78-80° was collected. Nmr analysis showed this material to be greater
than 99% monodeuterated.

Reactions:

Triphenylmethane Standardization Procedure for Organolithium
Reagents. As measured by a syringe, a 10-ml portion of methyllithium
in diethyl ether was added rapidly to 6.0g (ca. 0.025 mole) of
triphenylmethane dissolved in 25 ml of dry tetrahydrofuran. A red
color developed immediately and slow evolution of gas ensued. The
reaction solution was stirred for 3 hr past the addition point. The
solution was then titrated with a 0.86 N solution of absolute ethanol
in benzene. The standard solution was prepared by pipetting 25.0 ml
of absolute ethanol into a 500-ml volumetric flask and diluting to
the mark with anhydrous benzene. The end point was reached when the
deep red hue turned to a light yellow.

This procedure measures only the methyllithium concentration and
is oblivious to the presence of lithium alkoxides. Standard acid
titration always gave slightly higher results, presumably due to the
presence of non-organolithium base.

The concentrations of butyllithium and phenyllithium were also
determined in this manner and agreed with established methods of

analysis.[98]

Anhydrous Lithium Iodide. A 100-ml, three-necked flask was flamed out with nitrogen flowing through it. In the flask was placed 10g (0.039 mole) of iodine and 8 ml of anhydrous ether. A methyllithium solution (28 ml), which was 1.4 $\underline{N}$ in total base (acid titration) and 1.9 $\underline{N}$ in lithium iodide (Volhard method),[94] was added at a rate that caused gentle reflux until the solution turned clear. The methyl iodide and diethyl ether were driven off under reduced pressure and nitrogen was permitted to reenter the system. A white solid ($\underline{ca}$. 0.092 mole of lithium iodide) remained which was soluble in diethyl ether.

General Procedure for the Reaction of Olefin, Methylene Chloride, and Methyllithium. The apparatus consisted of a dry 50-ml, three-necked flask, equipped with magnetic stirrer, addition funnel, and inert gas inlet. The flask was immersed in an ice bath after being partially filled with 0.080 mole of olefin and 3.4g (0.040 mole) of methylene chloride. Methyllithium (0.020 mole), dissolved in diethyl ether, was slowly added to the flask contents over a period of 25-35 min. A gas evolved during the addition and lithium chloride precipitated. The mixture was stirred for 1 hr while warming to room temperature. The reaction was hydrolyzed with 20 ml of water, washed twice with 10-ml portions of saturated sodium chloride solution, dried over Drierite, and filtered.

Reaction of Styrene, Methylene Chloride, and Halide-free Methyllithium. The general procedure outlined above was followed. Analysis of the product solution by glpc (Column $\underline{B}$) revealed the presence of cis- ($\underline{19a}$) and trans-1-chloro-2-phenylcyclopropane ($\underline{19b}$) in a ratio

of 2.3:1.0. The yield of both isomers was 23.4% as calculated by the external standard method of glpc quantitative analysis. Authentic samples of these compounds were available for retention time comparison.[97] No other cyclopropanes were detected as products of this reaction.

Reaction of Styrene, Methylene Chloride, Lithium Iodide, and Methyllithium. Anhydrous lithium iodide (0.092 mole) was combined with 46 ml of freshly prepared halide-free 1.03 N methyllithium (0.047 mole). The resulting solution yielded a total base concentration of 0.78 N (acid titration) and a lithium iodide concentration of 1.52 N (Volhard method).[94] By removing portions of this standard solution and diluting with halide-free 1.03 N methyllithium, four methyllithium-lithium iodide solutions were prepared: 0.78 N CH$_3$Li, 1.52 N LiI; 0.87 N CH$_3$Li, 0.96 N LiI; 0.93 N CH$_3$Li, 0.61 N LiI; 0.97 N CH$_3$Li; 0.39 N LiI. In a separate operation a fifth solution was prepared having 1.2 N CH$_3$Li and 0.12 N LiI. The general procedure was followed with styrene as the olefin. The final solutions were analyzed by glpc (Column B) using the external standard technique for determination of the yields. The results are given in Table 1.

Reaction of Styrene, Methylene Chloride, Methyllithium, and Methylene Iodide or Chloroiodomethane. The general procedure was adhered to except for the presence of 0.020 mole of methylene iodide. Quantitative glpc analysis (Column G) disclosed the presence of 6.3% yield of phenylcyclopropane (17) using phenylcyclohexane as an internal standard. No products of higher molecular weight than 17 could be detected on the chromatogram. The same result held when chloroiodomethane was substituted for methylene iodide in the reaction.

Column E was used to determine the yield of methyl iodide in the reaction involving methylene iodide. With dodecane as an internal standard the yield of methyl iodide was placed at 76%.

Reaction of cis- (19a) or trans-1-Chloro-2-phenylcyclopropane (19b) with Lithium Shot. A solution of 1 ml of trans-1-chloro-2-phenyl-cyclopropane (19b) in 5 ml of anhydrous ether was added over a period of 30 min to a stirred mixture of 1.0g of lithium (1% sodium) shot in 20 ml of anhydrous ether at 0°. The flask contents were stirred for 2 hr at 0° and overnight at room temperature. A small aliquot was quenched in iodine/ether and the resulting solution was analyzed by glpc (Column C). The chromatogram revealed three products: 19% phenylcyclopropane (17), 14% cis-1-iodo-2-phenylcyclopropane (20a), and 67% trans-1-iodo-2-phenyl-cyclopropane (20b). The ratio 20b/20a was 4.8/1.0.

When the same reaction was conducted using cis-1-chloro-2-phenyl-cyclopropane (19a), the following product distribution was obtained: 23% 17, 58% 20a, and 19% 20b. The ratio 20a/20b was 3.1/1.0.

cis- (20a) and trans-1-Iodo-2-phenylcyclopropane (20b). A solution of cis- (50a) and trans-2-phenylcyclopropyllithium (50b) was prepared by the reaction of 20g (0.13 mole) of 1-chloro-2-phenylcyclopropane (19) (cis/trans = 6.9/1.0) with excess lithium shot in 150 ml of anhydrous ether. In a concerted process the flask contents were filtered through glass wool and quenched in an excess iodine/ether solution under an inert atmosphere. Several washings with aqueous sodium thiosulfate yielded a light yellow solution. After a drying procedure the ether was stripped off and the remaining oil subjected to vacuum distillation. Material distilling at 68-73° under 0.45 mm pressure was collected. Glpc analysis (Column D) disclosed the formation of 20b (18%) and 20a

(82%). The nmr spectrum of this mixture corresponded to those of authentic samples of 20a and 20b.[97] The yield based on 19a and 19b was 35%.

Reaction of cis- (20a) and trans-1-Iodo-2-phenylcyclopropane (20b), Methylene Chloride, and Methyllithium. To a combination of 1.1g (0.0045 mole) of 20a and 20b, 3.4 ml (0.040 mole) of methylene chloride, and 9.1 ml of hexane was added slowly 13 ml (0.01 mole) of 0.77 N methyllithium (LiI). The reaction was conducted at 0°. Five aliquots were removed during various stages of the addition and analyzed by glpc (Column C). Compounds 20a and 20b suffered gradual reaction under these conditions. The only substance to appear on the final chromatogram along with 20% of unreacted 20a and 20b was phenylcyclopropane (17). The retention time of the product was found to be identical with that of an authentic sample of 17.[97] No 1-methyl-2-phenylcyclopropanes were observed. With phenylcyclohexane as an internal standard, the conversion was found to be quantitative.

When this reaction was repeated in the presence of 0.01 mole of methyl iodide, the results were not altered in any way.

Reaction of cis- (20a) and trans-1-Iodo-2-phenylcyclopropane (20b), Methyl Iodide (large excess), and Methyllithium. The reaction was conducted by adding 10 ml (0.0077 mole) of 0.77 N methyllithium (LiI) solution over a 20-min period to 0.50g (0.0025 mole) of 1-iodo-2-phenylcyclopropane (20) (mostly cis isomer) and 62 ml (1.0 mole) of methyl iodide in 200 ml of anhydrous ether. An internal standard (naphthalene) was placed in the reaction solution before the addition of methyllithium. A water bath surrounded the reaction flask and gas evolved during the addition. Glpc analysis (Column C) before and 10 min after the addition revealed only a slight conversion (ca. 5%) of 20 into 1-methyl-2-phenylcyclopropane (18).

Reaction of 2-Phenylcyclopropyllithium (50) and Methyl Iodide

(large excess). The 2-phenylcyclopropyllithium used in this experiment
was demonstrated by iodine/ether quenching to contain 16% phenylcyclo-
propane, 23% trans-2-phenylcyclopropyllithium (50b), and 61% cis-2-
phenylcyclopropyllithium (50a). The glpc analysis was performed using
Column C.

About 10 ml of methyllithium solution was syringed into a solution
of 62 ml (1.0 mole) of methyl iodide in 200 ml of anhydrous ether to
rid the system of any last traces of water. The flask was immersed in
a water bath at room temperature. Over a 5-min period 3.5 ml (0.0028
mole) of 0.80 N 50 in diethyl ether was added to the flask contents.
Stirring was continued for 10 min and then an aliquot was removed and
examined by glpc (Column C). Two products appeared on the chromatogram.
Their retention times corresponded to those of authentic samples of
1-methyl-2-phenylcyclopropane (18) and 1-iodo-2-phenylcyclopropane
(20).[97] The ratio 18/20 was 1.45/1.0.

1,1,2,2-Tetramethyl-3-chlorocyclopropane (37). Treatment of 24g
(0.28 mole) of 2,3-dimethyl-2-butene and 63.5g (0.75 mole) of methylene
chloride with 312 ml (0.50 mole) of 1.6 N methyllithium (LiCl) eventually
gave, after hydrolysis, work up, solvent removal, and distillation, 20g
of a clear oil (bp 40-43.5° at 30 mm).

The nmr spectrum was characterized by a 1-proton singlet at 2.68_δ
and two closely spaced singlets at 1.17_δ and 1.21_δ (12 protons). A
chromatogram (Column C) of this material confirmed its purity.

2,2,3,3-Tetramethylcyclopropyllithium (49). A solution of 6.6g
(0.050 mole) of 37 in 5 ml of diethyl ether was added over a period of
1 hr to a stirred mixture of 3.0g (large excess) of lithium (1% sodium)

shot in 40 ml of anhydrous ether. The reaction was run at ice-bath temperature and was stirred for 6 hr at that temperature. It was then stirred at room temperature overnight. The solution developed a light butterscotch hue while a grey precipitate settled to the bottom.

The nmr spectrum of this solution displayed a singlet at -2.38δ due to the cyclopropyl proton bonded to the same carbon as the lithium atom. Much of the remainder of the spectrum was blocked out by diethyl ether absorption.

Quenching an aliquot of the solution in cold methyl iodide yielded the following relative distribution of compounds as determined by glpc analysis (Column C) and comparison with authentic samples: 10% 1,1,2,2-tetramethylcyclopropane (48), 3% pentametnylcyclopropane (38), and 85% 1,1,2,2-tetramethyl-3-iodocyclopropane (47).

1,1,2,2-Tetramethylcyclopropane (48). An ethereal solution of 49 was prepared from 6.6g (0.05 mole) of 37 and excess lithium shot. All of the lithium reagent solution was syringed into ice water. The water layer was washed with a wholesome volume of ether. The ether layer plus washing was treated with a saturated sodium chloride solution and dried over Drierite. A chromatogram (Column C) of this solution indicated the presence of only one product in high yield. Distillation was conducted at atmospheric pressure through a 1 cm x 10 cm Vigreux column. The material distilling at $72-72.4°$ was collected and glpc analysis revealed that it harbored a small amount of ether (ca. 2%) as a contaminant.

The nmr spectrum (CCl_4) of this substance gave a 12-proton singlet at 1.09δ and a 2-proton singlet at 0.09δ.

1,1,2,2-Tetramethyl-3-iodocyclopropane (47). An ethereal solution

of 49 (made from 0.050 mole of 37) was syringed into excess methyl

iodide. The resultant liquid was washed with water and worked up in

the usual way. The solvent was removed under reduced pressure and most

of the remaining low boiling compounds were stripped off at a pressure

of 10 mm for 1 hr at room temperature.

A dark red liquid remained which, when subjected to glpc analysis

(Column C), proved to be 95% pure. The nmr spectrum (CCl$_4$) of this

material exhibited a 1-proton singlet at 2.57δ, a 6-proton singlet at

1.28δ, and a 6-proton singlet at 1.17δ.

Pentamethylcyclopropane (38). Cyclooctane (0.54g) was added as an

internal standard to a flask containing 1.77g (0.0079 mole) of iodo

compound 47 in 5 ml of anhydrous ether. A small portion of this solution

was analyzed by glpc (Column C) for yield purposes. By means of a syringe

25 ml (0.029 mole) of 1.15 N methyllithium (LiI) was rapidly added to

the flask. The solution was stirred for 1 hr at 0°. Glpc analysis

(Column C) of an aliquot indicated no reaction had occurred. The reaction

was allowed to proceed for 12 hr at room temperature. Examination of

a small sample by glpc showed that 41% of 47 had reacted. One major

product appeared along with a small amount of a minor product. The

solution was refluxed for 11 hr and glpc analysis indicated that 85% of

47 had reacted. After 11 additional hours of reflux all of 47 had

disappeared. The major product was produced in 60% yield and the minor

product in 6% yield. The minor product possessed the same retention

time as 1,1,2,2-tetramethylcyclopropane.

The reaction was hydrolyzed and worked up. The ether was distilled

off through a short Vigreux column and the residue was subjected to

preparative glpc (Column J). Only the major component was collected.

The nmr spectrum (CCl_4) of this material showed a 1-proton quartet centered at 0.13δ, a 6-proton singlet at 0.92δ, and a 6-proton singlet at 1.08δ. What appeared to be a doublet centered around 0.89δ was somewhat camouflaged by the huge singlet at 0.92δ. However, the coupling constant of 6.5 cps for this doublet was the same as that for the quartet.

Reaction of 2,3-Dimethyl-2-butene, Methylene Chloride, and Methyllithium (LiI). The general procedure was adhered to except the addition of methyllithium (LiI) was extended over 135 min.

Cyclooctane was used as an internal standard for glpc analysis. The quantitative determination of yields was obtained from Columns C, E, and F. Retention times were compared with those of authentic samples synthesized by independent routes. The following yields were obtained by glpc analysis: 6.0% 37, 0.96% 47, 9.8% 38 (based on 2 equivalents of methyllithium), and a maximum yield of 0.07% for 48.

endo, anti-3-Chlorotricyclo[$3.2.1.0^{2,4}$]oct-6-ene (86) and endo, anti-2,3-Dichlorotricyclo[$3.2.1.0^{2,4}$]oct-6-ene (89), the Diels-Alder Adducts of 3-Chlorocyclopropene (84) and 1,3-Dichlorocyclopropene (88) with Cyclopentadiene. About 0.6g of a mixture of 84 (59%) and the dichlorocyclopropenes 87 and 88 (41%) was dissolved in 5 ml of carbon tetrachloride. To this solution was added quickly 2 ml of freshly distilled cyclopentadiene. A rapid exothermic reaction ensued. Most of the solvent and cyclopentadiene were removed by means of a rotary evaporator. The remaining liquid was subjected to preparative gas chromatography (Column K) and the two major components were isolated. The nmr spectrum (Table 2) of the compound which eluted first was consistent with that expected for endo, anti-3-chlorotricyclo[$3.2.1.0^{2,4}$]oct-6-ene (86). The structure of the second component

as determined by nmr analysis (Table 2) was assigned endo, anti-2,3-dichlorotricyclo[3.2.1.0^{2,4}]oct-6-ene (89).

exo, anti-3-Chlorotricyclo[3.2.1.0^{2,4}]oct-6-ene (85) and endo, anti-3-Chlorotricyclo[3.2.1.0^{2,4}]oct-6-ene (86), the Addition Products of Chlorocarbenoid and Norbornadiene. To a combination of 32 ml (0.50 mole) of methylene chloride, 92g (1.0 mole) of norbornadiene, and 100 ml of dry ether was added dropwise 0.25 mole of methyllithium (LiBr) in diethyl ether over a period of 3 hr. The flask contents were held at 0° during the addition and then were permitted to stir at room temperature for an additional hour. After being quenched with 100 ml of water, the ethereal solution was separated from the water layer and dried over anhydrous magnesium sulfate. A rotary evaporator removed most of the volatile components and the resulting liquid was subjected to simple vacuum distillation. A substance distilling at 75-80° (10 mm) was collected.

This material was treated with excess aqueous silver nitrate solution at 60° for 15 min to remove any allylic halides. The aqueous silver nitrate solution was washed several times with ether. The ether washings were dried and the solvent was removed by means of a rotary evaporator. The liquid which remained was purified by preparative glpc using Column K. The nmr spectrum (Table 2) of the major constituent revealed the presence of two compounds: 74% of 85 and 26% of 86.

endo-Tricyclo[3.2.1.0^{2,4}]oct-6-ene (90), the Reduction Product of 86 with Sodium and Tert-Butanol. A mixture of 12 ml of tetrahydrofuran, 2 ml of tert-butanol, 0.5g of 86, and 1.0g of sodium was heated to reflux for 8 hr under an argon atmosphere. After the solid material had settled to the bottom of the flask, the clear solution was removed with a syringe and added to 10 ml of water. The organic layer was dried

over anhydrous magnesium sulfate and the solvent was removed by simple

distillation. The major product was isolated by glpc preparative

procedure (Column $\underline{J}$).

The nmr spectrum (CCl_4) of the product corresponded to the spectrum

obtained from the Diels-Alder adduct of cyclopropene and cyclopentadiene.

The structure of the reduction product was therefore assigned as <u>endo</u>-

tricyclo[3.2.1.0^{2,4}]oct-6-ene (90).

<u>The Effect of Solvent on the Reaction of Tetrachlorocyclopropene</u>

(59) <u>and Cyclopentadiene</u>. <u>General Procedure</u>. A flask containing

0.710 ml (8.60 mmoles) of freshly distilled cyclopentadiene, 0.015 ml

of phenylcyclohexane as an internal standard, and 3.0 ml of solvent

was immersed in a water bath maintained at 25°. Into this solution was

quickly syringed 0.050 ml (0.43 mmole) of 59. The flask was stoppered

with a septum cap to make possible easy withdrawal of small samples by

means of a syringe. Aliquots were removed at given time intervals and

analyzed by quantitative glpc (Column $\underline{G}$).

The ratios of the peak area of the reaction product, 2,3,4,4-tetra-

chlorobicyclo[3.2.1]octa-2,6-diene (63a), to that of the internal

standard, phenylcyclohexane (131), were determined at various times from

the chromatograms. The value of this ratio at the end of the reaction,

$\left[\dfrac{(63a)\ area}{(131)\ area}\right]_f$, was easily obtained by permitting the solution to sit for

several days followed by glpc analysis. Since the glpc response is

proportional to concentration, eq 5 and eq 6 can readily be derived. The

slope of the straight line obtained in plotting log $\dfrac{[63a]_f}{[63a]_f - [63a]_t}$ vs.

time was divided by the calculated concentration

of cyclopentadiene (2.28 $\underline{M}$) to give k_{obs}. The k_{obs} values for four

solvents at 25° are listed in <u>Table 3</u>. In all cases except carbon tetra-

chloride the reaction was followed for at least one half-life. During

$$\log \frac{\left[\dfrac{(63a)_{area}}{(131)_{area}}\right]_f}{\left[\dfrac{(63a)_{area}}{(131)_{area}}\right]_f - \left[\dfrac{(63a)_{area}}{(131)_{area}}\right]_t} = \log \frac{[63a]_f}{[63a]_f - [63a]_t} \qquad (5)$$

$$\log \frac{[63a]_f}{[63a]_f - [63a]_t} = k_{obs}\left[\ \right]t \qquad (6)$$

this time the maximum amount of depletion of cyclopentadiene due to

dimerization was calculated to be ca. 7%. No consideration was taken

of any change in volume with mixing.

The first-order dependence of the rate on cyclopentadiene concentra-

tion was confirmed in acetone and benzene in more dilute solutions at a

higher temperature. A combination of 0.71 ml (8.6 mmoles) of cyclo-

pentadiene, 0.015 ml of phenylcyclohexane, and 10 ml of solvent was

allowed to equilibrate in a flask immersed in an oil bath maintained

at 47°. Into this solution was syringed 0.050 ml (0.43 mmole) of 59.

The solutions were handled and the data analyzed in the same manner

as described earlier. With twice as much cyclopentadiene present

(1.420 ml of cyclopentadiene and 9.290 ml of solvent) the value for

k_{obs} was twice as great within experimental error.

Reactions of 1-Phenylallyllithium (78). a. With Water. To 7.0 ml

(0.010 mole) of 1.45 N butyllithium in hexane was added 7.0 ml of

anhydrous THF. After this solution had cooled in an ice bath, 1.18g

(0.010 mole) of allylbenzene was rapidly added. A red hue developed

which intensified as the solution was permitted to warm to room temperature for one hour. Upon being syringed into swirling ice water, the red solution turned clear. The organic layer was analyzed by glpc (Column F) which revealed the presence of three compounds. The three compounds were identified as allylbenzene (92) (39%), cis-propenyl-benzene (93) (9%), and trans-propenylbenzene (94) (52%) by retention time comparison with authentic, commercially available samples.

b. With Allyl Chloride. A solution containing 0.1 mole of 1-phenylallyllithium (78) in hexane-THF (50:50) was cooled to -30°. Addition of a slight molar excess of allyl chloride in THF was carried out over 30 min with the temperature of the flask contents never rising above -30°. After warming to 0°, the solution was quenched in water and the organic layer was worked up as usual. The solvent was removed under reduced pressure. Glpc analysis (Columns D and G) showed the formation of two compounds in practically quantitative yield: 3-phenyl-1,5-hexadiene (95) (81%) and 1-phenyl-1,5-hexadiene (132) (19%). The two compounds were separated by preparative glpc (Column K). The nmr spectrum of 132 exhibited a 4-proton multiplet at 2.21δ, a 2-proton multiplet at ca. 5.05δ, a 3-proton multiplet at ca. 6.17δ, and a 5-proton multiplet at 7.19δ. As indicated in Table 4 the nmr spectrum (CCl₄) of 95 was consistent with the structure shown. The ratio of 95 to 132 as determined by the nmr spectrum of the reaction mixture proved to be identical to the glpc result. The stereochemistry of the internal double bond in 132 was not determined. Pure 95 was isolated in good yield by spinning-band distillation of the reaction mixture. This clear liquid distilled at 49° under 1 mm pressure.

<u>c</u>. With <u>Benzyl</u> <u>Chloride</u>. Slightly more than 12.7g (0.10 mole)
of benzyl chloride in THF was added dropwise over a period of 15 min
to a solution of 1-phenylallyllithium (0.10 mole) in hexane-THF
(50:50) at -30°. After water quench, work up, and removal of solvent,
the reaction mixture was subjected to simple vacuum distillation. The
clear liquid which distilled at 85-87.5° under a pressure of 0.075 mm
produced an nmr spectrum (CCl$_4$) consistent with the structure of
3,4-diphenyl-1-butene (96) (<u>Table</u> <u>4</u>). The distilled yield of 96 was
<u>ca</u>. 80%.

<u>d</u>. With <u>Methyl</u> <u>Iodide</u>. A hexane-THF (50:50) solution containing
0.1 mole of 78 was prepared. The solution was cooled to -30° and then
20g (0.14 mole) of methyl iodide was added dropwise over a 20-min
period. The reaction mixture was subjected to normal work up with the
solvent being removed by means of a rotary evaporator. Spinning-band
distillation at reduced pressure (15 mm) yielded a clear oil (bp 65-67°).
The nmr spectrum (CCl$_4$) of this material substantiated 3-phenyl-1-butene
(121) as the structure (Table 4). A 55% distilled yield of the product
was obtained.

<u>e</u>. With <u>Cyclopropene</u>. Cyclopropene, generated from 1.0 mole of
phenyllithium and 1.5 mole of allyl chloride, was bubbled through a
hexane-THF (50:50) solution containing 0.1 mole of 78 at 0°. The
reaction solution, which remained dark red, was quenched in water and
worked up in the normal manner incorporating solvent removal. Spinning-
band distillation at 1.0 mm yielded a clear liquid with a boiling point
of 45-66°. In order to remove all the impurities the liquid was
subjected to preparative glpc (Column <u>L</u>). Two grams (13% yield based
on 78) of 3-phenyl-3-cyclopropylpropene (104) was isolated in this
manner giving a nmr spectrum (CCl$_4$) consistent with the proposed

structure (Table 4).

Reaction of 3,4-Diphenyl-1-butene (96) with One Equivalent of
Butyllithium. While at 0°, 19 ml (0.030 mole) of 1.6 N butyllithium
in hexane received 19 ml of anhydrous THF. To this solution was added
6.2g (0.030 mole) of 96 by means of a syringe. A deep red color became
prominent as the solution was permitted to warm to room temperature.
Half of this solution was removed by syringe and quenched in water to
give two clear immiscible liquids. The organic layer was worked up in
the normal manner. After removal of solvent under reduced pressure,
the major product was isolated as a clear liquid by preparative glpc
(Column M). The nmr spectrum (CCl$_4$) of this compound (Table 4)
corresponded to that expected for 1,2-diphenyl-cis-2-butene (97).
Quantitative glpc analysis (Column G) of the original reaction mixture
disclosed a 78% yield of 97, 17% return of starting material, and 5%
of uncharacterized material.

The remainder of the solution was quenched in deuterium oxide.
Compound 97 was isolated as described above and its nmr spectrum (CCl$_4$)
revealed the presence of at least 0.8 deuterium atom on the methyl
group.

Benzyl-α,α-d$_2$ Alcohol. To a stirred mixture of 5.0g (0.12 mole)
of lithium aluminum deuteride in 100 ml of anhydrous ether was added 33g
(0.22 mole) of ethyl benzoate in 50 ml of anhydrous ether. The ethyl
benzoate solution was added at such a rate to cause gentle reflux
(75 min). The mixture was refluxed for an additional 3 hr. The
following were then added in a dropwise fashion: 4.5 ml of water,
4.5 ml of 15% sodium hydroxide solution, and 14 ml of water. A white
solid formed which was filtered off and was washed several times with
copious amounts of ether. The original solution plus washings were

dried over anhydrous magnesium sulfate. The magnesium sulfate was filtered off and most of the ether was removed by means of a rotary evaporator. Simple distillation at reduced pressure afforded only one material (bp 59.5° at 1.3 mm). The nmr spectrum (CCl$_4$) showed a 1-proton singlet at 4.38δ and a 5-proton singlet at 7.13δ. Thus the material was virtually completely dideuterated benzyl-α,α-d$_2$ alcohol.

Benzyl-α,α-d$_2$ Chloride. Under a dry atmosphere a solution of 1.1 ml (0.013 mole) of pyridine in 14.3g (0.13 mole) of benzyl-α,α-d$_2$ alcohol was added over 30 min to 11.3g (0.13 mole) of phosphorus tri-chloride maintained at -20°. After stirring at room temperature over-night, the reaction mixture was dumped into 100 ml of an ice-water mixture. The resulting water layer was extracted 4 times with 25-ml portions of light petroleum ether. After drying and filtration, the solvent was removed under reduced pressure. Simple distillation at 8 mm pressure gave a clear oil as the only volatile product (bp 55°). The distillate weighed 11.1g (66% yield) and its nmr spectrum (CCl$_4$) exhibited only a singlet at 7.18δ. No nonaromatic hydrogens could be detected in the nmr spectrum of this sample of benzyl-α,α-d$_2$ chloride.

Reaction of 1-Phenylallyllithium (78) with Benzyl-α,α-d$_2$ Chloride. The procedure employed was the same as already described for the coupling of 78 and benzyl chloride.

Using benzyl-α,α-d$_2$ chloride the coupling product was again obtained in ca. 80% distilled yield. Although the starting material was completely dideuterated, the nmr spectrum (CCl$_4$) of the coupling product, 3,4-diphenyl-1-butene-4,4-d$_2$ (101), showed it to be only 90% dideuterated on carbon 4.

Reaction of 3,4-Diphenyl-1-butene-4,4-d$_2$ (101) with One Equivalent
of Butyllithium. Compound 101 (1.0g, 0.0050 mole) was rapidly syringed
into a solution of 0.005 mole of butyllithium in 7.0 ml of hexane-THF
(50:50) at -30°. The solution was allowed to come to 0° and was
stirred at this temperature for 5 hr. After being heated to reflux
overnight, the dark red liquid was quenched in water and was worked up
in the normal fashion. The major product, 1,2-diphenyl-cis-2-butene-
1,1-d$_2$, was isolated by preparative glpc (Column M) and contributed an
nmr spectrum showing no noticeable migration of deuterium to the
terminal methyl position.

Reaction of 3-Phenyl-3-cyclopropylpropene (104) with One Equivalent
of Butyllithium. A solution consisting of 4.0 ml (0.0063 mole) of
1.6 N butyllithium in hexane and 4.0 ml of TMEDA was cooled to 0° in an
ice bath. Compound 104 (1.0g, 0.0063 mole) was rapidly added to the
butyllithium solution. The solution was stirred for 1 hr at room
temperature and was then heated to 60° for 1 hr. The reaction mixture
was quenched in 20 ml of water, and then 20 ml of light petroleum ether
was added to the two immiscible layers. The petroleum ether layer was
washed with 25 ml of 10% aqueous acetic acid, 25 ml of 10% aqueous
sodium hydroxide, and saturated sodium chloride solution. This procedure
was employed to rid the petroleum ether solution of any remaining TMEDA.
After the pentane was removed under reduced pressure, the resulting
light yellow oil was exposed to preparative glpc (Column K) and
yielded a liquid whose nmr spectrum (CCl$_4$) was consistent with the
structure 3-methyl-2-phenylcyclopentene (106) (Table 4). A 43% yield
of 106 and a 7% yield of an uncharacterized material were determined
by quantitative glpc analysis (Column H) of the crude reaction mixture.

<u>2,2-Dimethyl-1,3-cyclohexanedione</u>. A combination of 100g (0.89

mole) of 1,3-cyclohexanedione, 48g (0.89 mole) of sodium methoxide,

and 1000 ml of absolute ethyl alcohol was heated to $50°$, resulting in

the formation of a dark red solution. Over a period of 20 min, 126g

(0.89 mole) of methyl iodide was added dropwise to the stirring

solution. Sodium methoxide (48g, 0.89 mole) was again added to the

reaction mixture followed by dropwise addition of 126g (0.89 mole) of

methyl iodide. After being refluxed overnight the reaction mixture

was poured into <u>ca</u>. 1000 ml of water. The water was saturated with

sodium chloride and then extracted repeatedly with copious volumes

of ether. The ether washings were dried over Drierite and filtered.

A dark oil remained after the removal of ether under reduced pressure.

The oil was dissolved in hot THF and, upon cooling, this solution

yielded light tan crystals. After two crops had been collected, the

solvent was stripped off by means of a rotary evaporator and the

remaining oil was subjected to simple vacuum distillation. A clear

liquid boiling at $75-85°$ under 2 mm pressure was collected. The

distillate was redistilled through a spinning band column at 1.5 mm.

The material boiling at $73-75°$ weighed 29.6g (21% yield). Although

this material was not pure, as determined from the nmr spectrum, the

major component was assigned the structure of 2,2-dimethyl-1,3-cyclo-

hexanedione as judged from the sharp singlet at 1.22δ, the multiplet

at 1.94δ, and the multiplet at <u>ca</u>. 2.60δ. The impurity was probably

the result of O-alkylation.

<u>2,2-Dimethyl-1,3-cyclohexanedione-4,4,6,6-d$_4$</u>. A 20-g (0.14 mole)

sample of 2,2-dimethyl-1,3-cyclohexanedione was dissolved in 94g (2.0

mole) of ethanol-O-<u>d</u> along with 5 ml of triethylamine. This solution

was heated to 50° for 6 hr and then the solvent and triethylamine were removed under reduced pressure. This procedure was repeated 4 times and terminated in the distillation of a clear liquid (bp 73-75° at 1.5 mm). The nmr spectrum (CCl$_4$) indicated considerable deuterium incorporation, but due to the presence of an impurity no accurate number for the amount of deuteration could be assigned. Assuming complete equilibration with the solvent, the diketone was estimated to be greater than 99% tetradeuterated.

3,3-Dimethyl-1,4-cyclohexanedione-1,5-d$_2$ (108). A solution of 14g (0.10 mole) of 2,2-dimethyl-1,3-cyclohexanedione-4,4,6,6-d$_4$ in 10 ml of dry ether was added to a mixture of 4.0g (0.105 mole) of lithium aluminum hydride and 100 ml of ether at such a rate as to cause gentle reflux. After the addition was complete, the reaction mixture was allowed to stir at room temperature for 1 hr. A saturated ammonium chloride solution was added cautiously until a lumpy precipitate formed. The ether solution was decanted and the precipitate was washed several times with generous amounts of ether. After the original solution plus washings were dried over Drierite and filtered, the solvent was removed under vacuum leaving an extremely viscous oil.

This oil was dissolved in 100 ml of acetic anhydride along with 2.0 ml of pyridine. The solution was heated to reflux for 2 hr. The acetic acid and anhydride were distilled off under 25 mm pressure and the remaining dark oil was subjected to simple vacuum distillation. A sweet smelling clear oil (13.2g) boiling at 106-107° under 3 mm pressure was collected. A portion of this diacetate crystallized upon sitting undisturbed at room temperature.

A 5.0-g sample (0.022 mole) of the diacetate was pyrolyzed by passing it through a horizontal tube (1 in. x 16 in.) packed with glass

helices at a pressure of 1.0 mm and a temperature of 525°. All material

passing through the tube was collected in a Dry Ice/acetone trap. The

substance trapped was distilled at 100 mm pressure; only distillate

boiling as high as 65° was collected. The oil remaining in the

distilling pot was again subjected to pyrolysis followed by distillation.

This procedure was repeated five times in order to consume most of the

diacetate. This type of procedure was found necessary to avoid high

levels of toluene formation. The distilled product was purified by

preparative glpc (Column $\underline{N}$) giving a hydrocarbon weighing 0.45g

(19% yield based on the diacetate). The nmr spectrum (CCl_4) revealed

a sharp singlet at 1.02δ (6 protons), a multiplet at 2.57δ (2 protons),

and a multiplet at 5.48δ (2 protons). The nmr analysis substantiates

greater than 98% dideuteration in the vinyl positions. This material

was therefore assigned the structure of 3,3-dimethyl-1,4-cyclohexa-

diene-1,5-$\underline{d}_2$ (108).

A small sample of 3,3-dimethyl-1,4-cyclohexadiene (109) was also pre-

pared by the above series of reactions using undeuterated starting

material. The nmr spectrum (CCl_4) of 109 (Table 4) was in agreement

with what was anticipated.

Reaction of 3,3-Dimethyl-1,4-cyclohexadiene-1,5-$\underline{d}_2$ (108) with One

Equivalent of Butyllithium. To 2.0 ml of TMEDA was added 1.3 ml

(0.0018 mole) of 1.45 $\underline{N}$ butyllithium in hexane at 0°. A 0.2-g sample

(0.0018 mole) of 108 was rapidly syringed into this solution. Stirring

continued for 1 hr at 0° followed by quenching in 2 ml of deuterium

oxide. About 5 ml of light petroleum ether was added and the organic

layer was washed successively with 10 ml of 10% acetic acid, 10 ml of

10% sodium hydroxide solution, and 10 ml of saturated sodium chloride

solution. Most of the solvent was removed by distillation. The remaining substance was subjected to preparative glpc (Column $\underline{N}$). Only one product could be detected by glpc having the same retention time as 108. The nmr spectrum (CCl$_4$) of this substance disclosed the presence of two compounds. One compound corresponded to 3,3-dimethyl-1,4-cyclohexadiene-1,5,6-$\underline{d}_3$ (115) (31%) since the chemical shifts of all the protons in 115 were the same as those in 108. Integration showed the presence of only one methylene proton in 115 however, compared to two in 108. The major product (69%) of the deuterium oxide quench gave an nmr spectrum exhibiting a 6-proton singlet at 1.99δ, a 1-proton multiplet at 2.05δ, a 1-proton multiplet at 5.37δ, and a 1-proton multiplet at 5.71δ. This second component was assigned the structure of 5,5-dimethyl-1,3-cyclohexadiene-1,3,6-$\underline{d}_3$ (116).

The reaction was repeated with the exceptions that the reaction mixture was heated to 93° for 1 hr and the quench was performed with water rather the deuterium oxide. The same work-up and isolation procedure was followed. The nmr spectrum (CCl$_4$) of the two components showed the presence of 29% of starting material 108 and 71% of 5,5-dimethyl-1,3-cyclohexadiene-1,3-$\underline{d}_2$ (117). This was essentially the same ratio found in the deuterium oxide quench. In neither 108 nor 117 had any deuterium scrambling (within the limits of nmr integration) taken place. Glpc analysis (Column $\underline{I}$) uncovered the presence of a small amount of toluene in the reaction mixture.

Reaction of 3,4-Diphenyl-1-butene (96) with Two Equivalents of Butyllithium. Treatment of 1.0g (0.0050 mole) of 96 with 0.01 mole of butyllithium in a solvent mixture containing 7.0 ml of hexane and 10 ml of TMEDA at 0° gave a dark red solution. The reaction mixture

was heated to 53° for 2 hr. The solution was then syringed into water
and worked up in the normal manner designed to remove TMEDA. Quanti-
tative glpc analysis (Column G) showed the major product to be formed
in 73% yield. Preparative glpc (Column M) resulted in the isolation
of the major product. The nmr spectrum (CCl4) of this compound (Table 4)
corresponded to that expected for 1,2-diphenyl-cis-2-butene (97).

Repetition of this experiment employing deuterium oxide quenching
resulted in the isolation of the major product, 1,2-diphenyl-cis-2-
butene-1,4-d2. This structural conclusion was based on both fine
splitting and proton integration determined by nmr technique.

Reaction of 3-Phenyl-1-butene (121) with Two Equivalents of
Butyllithium. A 0.66-g sample (0.0050 mole) of 121 was added rapidly
to 0.01 mole of butyllithium in a solvent mixture containing 7 ml of
hexane and 10 ml of TMEDA. The reaction mixture (orange solid present)
was heated to 60° for 3 hr and then quenched in water and worked up in
the usual fashion. Glpc analysis (Column G) demonstrated the presence
of a sole product along with a minor amount of starting material. The
major product was isolated by preparative glpc (Column L). Its nmr
spectrum (CCl4) (Table 4) was consistent with that expected for 2-phenyl-
cis-2-butene (122). The chemical shift of the vinyl proton was used to
determine the stereochemistry of the double bond in 122.

A deuterium oxide quench eventually yielded a compound whose nmr
spectrum (CCl4) revealed the presence of only one deuterium atom,
2-phenyl-cis-2-butene-4-d1.

Reaction of 3-Phenyl-1,5-hexadiene (95) with Two Equivalents of
Butyllithium. Treatment of 0.86g (0.0055 mole) of 95 with 0.011 mole
of butyllithium in 16 ml of hexane-TMEDA (50:50) at 0° produced an

immediate dark red solution. The flask contents were heated to 50° for 35 min, syringed into water, and worked up in the normal manner to remove TMEDA. Glpc analysis (Column I) showed the presence of a considerable number of products. The two major products, produced in 17% and 36% yields, were isolated by preparative glpc (Column N). The more bountiful component was assigned the structure 3-phenyl-2,4-hexadiene (123) and the minor component was determined to be 4-phenyl-1,4-hexadiene (124) on the basis of their nmr spectra (Table 4). No attempt to decipher the stereochemistries about the various double bonds was made.

Quenching the reaction mixture in deuterium oxide produced these same two compounds with incorporation of exactly two deuterium atoms in each compound. Nmr analysis (CCl_4) pinpointed the positions of deuterium attachment. The major compound was assigned 3-phenyl-2,4-hexadiene-1,6-d_2; the minor component, 4-phenyl-1,4-hexadiene-3,6-d_2.

This experiment was repeated with the exception that the reaction mixture was heated to 60° for 2 hr. The water quench was noticeably more vigorous than previously observed. The major product was collected by preparative glpc (Column K) as a white solid. The nmr spectrum (CCl_4) of this material exactly coincided with that of an authentic sample of biphenyl. The yield of biphenyl was set at 77% as determined by quantitative glpc (Column I).

Repetition of this experiment employing only one equivalent of butyllithium led to formation of only a trace amount of biphenyl (Column I).

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