

AN ABSTRACT OF THE THESIS OF

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Title: PART 1. THE INTRAMOLECULAR CYCLIZATION OF ORGANOALUMINUM
COMPOUNDS. PART 2. REDUCTIONS USING LOW-VALENT TITANIUM
AND ZIRCONIUM COMPLEXES

Abstract Approved: _____

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Stanley E. Wilson

Intramolecular cyclization of organometallic compounds represents a promising tool for synthesis in general. The reaction involves exothermic consumption of intramolecular double bonds via insertion into a carbon metal σ -bond. This represents an intramolecular example of the reaction type responsible for metal catalyzed polymerization of olefins.

A simple cyclization involving one double bond may occur to form possibly two rings. Generation of the smaller ring is called exocyclization and larger ring formation, endocyclization. In the case of organoaluminum compounds, exocyclization leading to the formations of five- and six-membered rings was found to proceed efficiently.

The organoaluminum intermediates were generated by the addition reaction of dialkylaluminum hydride to a carbon-carbon multiple bond. Dialkylaluminum hydride was used as a catalyst for the high temperature cyclization process. With the assistance of aluminum trichloride, the intramolecular cyclization reaction was found to proceed smoothly

at low temperature. Polycyclic compounds containing five- and six-membered rings were generated by these processes in one step.

A great variety of functional groups in organic molecules are known to undergo reduction in reaction with low-valent titanium and zirconium complexes. With the combination of titanium tetrachloride and lithium aluminum hydride, carbon-carbon multiple bonds were found to undergo selective reduction reactions, and in some cases, products were produced reasonably stereoselectively. The possible synthetic applications of this reaction were explored.

Part 1. The Intramolecular Cyclization
of Organoaluminum Compounds
Part 2. Reductions Using Low-Valent Titanium
and Zirconium Complexes

by

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To My Parents

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PART 1. THE INTRAMOLECULAR CYCLIZATION OF ORGANOALUMINUM COMPOUNDS

I. Introduction

One of the major criteria for measuring endurance in organic synthetic methodology focuses on the efficiency of a certain process, i.e., how efficiently the readily available starting materials are converted into the eventual product. Two approaches are available to enhance efficiency: the use of only high-yield transformations in a multistep synthesis; and reduction of the total number of steps by accomplishing several bond formations in a single step. A combination of the best features of both approaches would represent a perfect synthesis.

Two distinct directions of research in the science of organic synthesis can also be discerned. A particular target molecule can act as the paramount driving force, with its preparation usually being accomplished through reactions known to proceed in reasonable yields. Occasionally, reactions are invented to consummate a certain transformation more efficiently. A rich variety of organic reactions has been discovered using this type of specific, target molecule approach.

A second method concentrates on a process which by its very nature embodies the concept of efficiency. The study of such a process need not be conducted with the intent of preparing any definite compound, but it does hold the promise of permitting access to the simple manufacture of many different molecules. The process should proceed in high yield, accomplish the construction of a major portion

of the desired molecule, and lend itself to alteration for the purpose of generating multifarious structural types. The notion is to allow the process to reveal through research what molecules it is capable of generating efficiently.

Since polycyclic substances abound in natural product chemistry, any process that results in the formation of several rings in one step from an acyclic precursor is of potential value. Intramolecular cyclization of organometallic compounds represents a promising tool for accomplishing this objective. The reaction involves exothermic consumption of intramolecular double bonds by means of insertion into carbon-metal σ -bonds. Such a transformation represents an intramolecular example of the reaction type responsible for metal catalyzed polymerization of olefins.

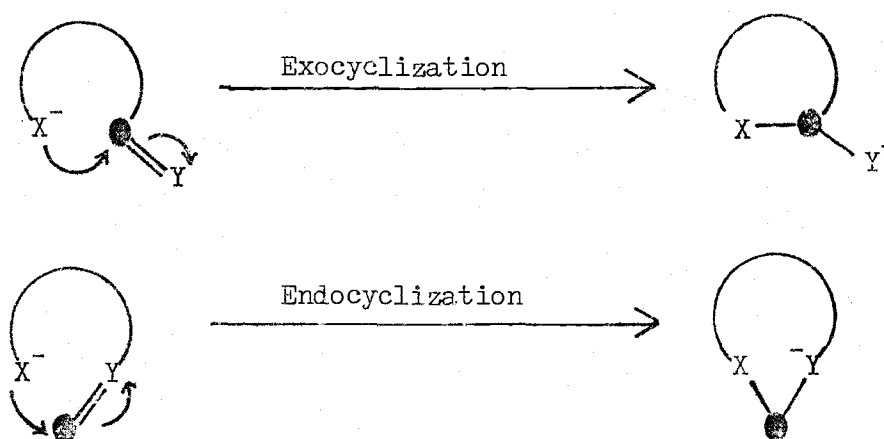
Intramolecular cyclizations have been observed or proposed for organometallic compounds containing lithium (1), magnesium (2), aluminum (3), zirconium (4), titanium (5), gallium (6), indium (6), rhodium (7), nickel (8), iron (9), palladium (10), copper (11), thorium (12), and cobalt (13). Organoaluminum compounds were found to undergo intramolecular cyclization efficiently, resulting in formation of cyclic products in high yields. The organoaluminum intermediates were generated by the addition reaction of dialkylaluminum hydride to carbon-carbon double or triple bonds. Dialkylaluminum hydride was employed both as a catalyst and as a reagent to effect the cyclization process. The scope and possible synthetic application of the process were explored, and the results are presented in the following pages.

II. Historical

Ring formation is an important and common process in organic chemistry. It has been known for a number of years that intramolecular cyclization of polyenes can occur through common organic intermediates : free radicals, carbonium ions, carbanions, and organometallic compounds. Some have been studied to a greater extent than others, but each offers the synthetic potential of accomplishing a great deal of the construction of a molecule in a single step.

In principle, two modes of closure are commonly observed in the ring-forming reactions, i.e., the formation of exocyclic or endocyclic rings as illustrated in Scheme 1. These differ in the regiochemistry of addition to the unsaturated unit, and result in the construction of rings of differing size.

Scheme 1



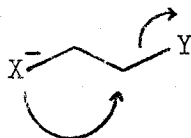
Baldwin (14,15,16) has presented a set of rules which are useful in predicting the relative facility of different modes of ring closure. These rules are based on the stereochemical preferences of the transition

state for the various modes of the ring closure process; each mode of ring closure is most facile in a specific transition state geometry. The rules are summarized below and generalized examples of each type are provided.

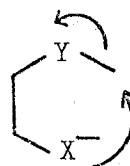
Baldwin's Rules for Ring Closure

Rule 1: Tetrahedral Systems

- (a) 3 to 7-Exo-Tet are all favored.
- (b) 5 to 6-Endo-Tet are disfavored.



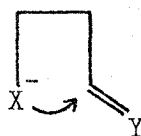
3-Exo-Tet
(favored)



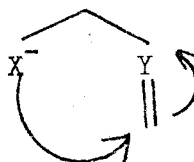
5-Endo-Tet
(disfavored)

Rule 2: Trigonal Systems

- (a) 3 to 7-Exo-Trig are favored.
- (b) 3 to 5-Endo-Trig are disfavored; 6 to 7-Endo-Trig are favored.



4-Exo-Trig
(favored)

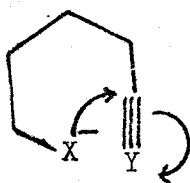


4-Endo-Trig
(disfavored)

Rule 3: Digonal Systems

(a) 3 to 4-Exo-Dig are disfavored; 5 to 7-Exo-Dig are favored.

(b) 3 to 7-Endo-Dig are favored.



6-Exo-Dig
(favored)



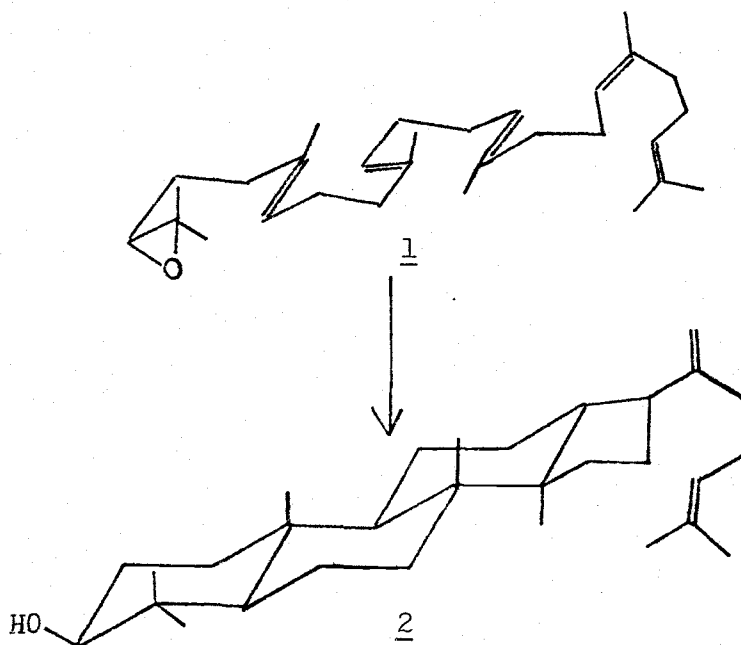
3-Endo-Dig
(favored)

The mode of ring closure is designated by the use of a number, indicating the number of atoms incorporated in the new ring; Exo or Endo; and the suffixes Tet, Trig, or Dig which refer to the hybridization state of the carbon atom undergoing the ring-closure reaction. Reasonable adherence to these rules is expected only when X is a first row element since these display small enough atomic radii and bond lengths to be strongly influenced by the geometric restraints of the suggested transition states.

Baldwin has provided many examples which lend experimental support to these rules, but a few exceptions are also recognized. Although cyclizations involving tetrahedral and digonal systems are of both mechanistic and synthetic interest, the research has concentrated on trigonal systems which offer considerable potential for use in organic synthesis. The effort further focused on the creation of 5- and 6-membered rings since the more highly strained systems would be expected to be reversible and lead to considerable rearrange-

ment.

Some of the most elegant examples of trigonal cyclizations are those proceeding through carbonium ion intermediates. The conversion of squalene 2,3-oxide (1) into dammaradienol (2) represents not only an efficient multiple-bond forming carbocyclization but also a highly stereoselective transformation (17), which results in the production of virtually one diastereomer. The overall process could be

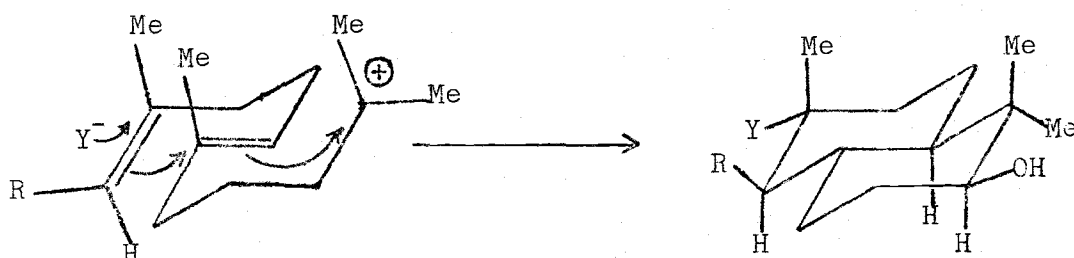


considered as three 6-Endo-Trig cyclizations followed by one 5-Exo-Trig cyclization. All of these are formally favored according to Baldwin's Rules.

The second synthetically significant feature of this cyclization, stereoselectivity, is in no way predicted from Baldwin's rules. The stereoselectivity has been rationalized using the Stork-Eschenmoser hypothesis (18) which envisions simultaneous bond formations while requiring trans addition across the olefinic units. This hypothesis

predicts stereospecificity: the stereochemistry of ring fusion is dependent upon the stereochemistry of the double bond undergoing cyclization (Scheme 2).

Scheme 2

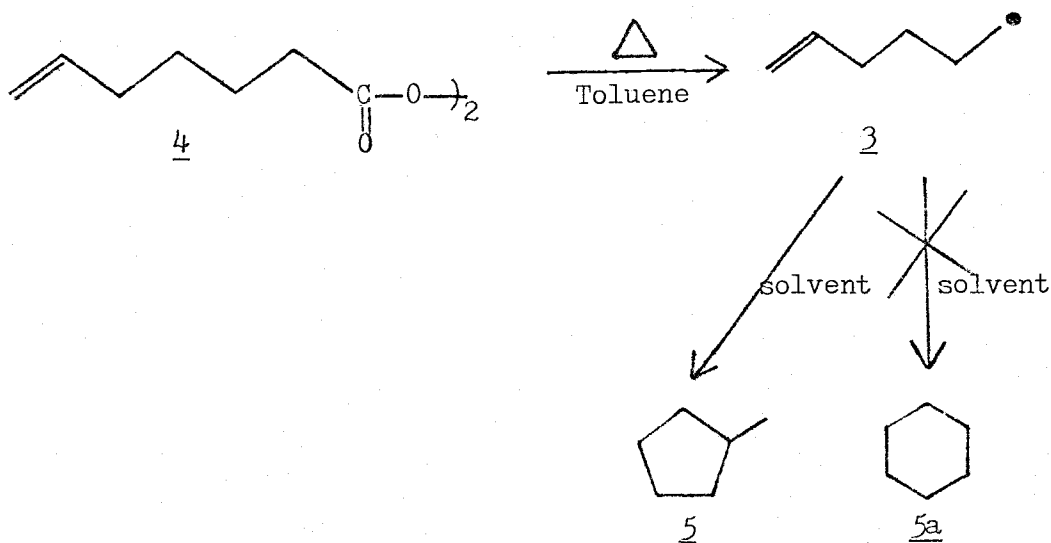


Caution is dictated in the use of the Stork-Eschenmoser hypothesis since exceptions do exist.

Many additional examples of carbonium ion cyclizations have appeared in the literature (19). These were initiated from allyl alcohols, epoxides, sulfonate esters, or acetals. Many proved to be highly stereospecific reactions which proceeded in good yields.

The 5-hexenyl radical 3 generated by pyrolysis of 6-heptenoyl peroxide (4) is known to cyclize to give methylcyclopentane (5) after hydrogen abstraction from solvent (20) (Scheme 3). This apparently is

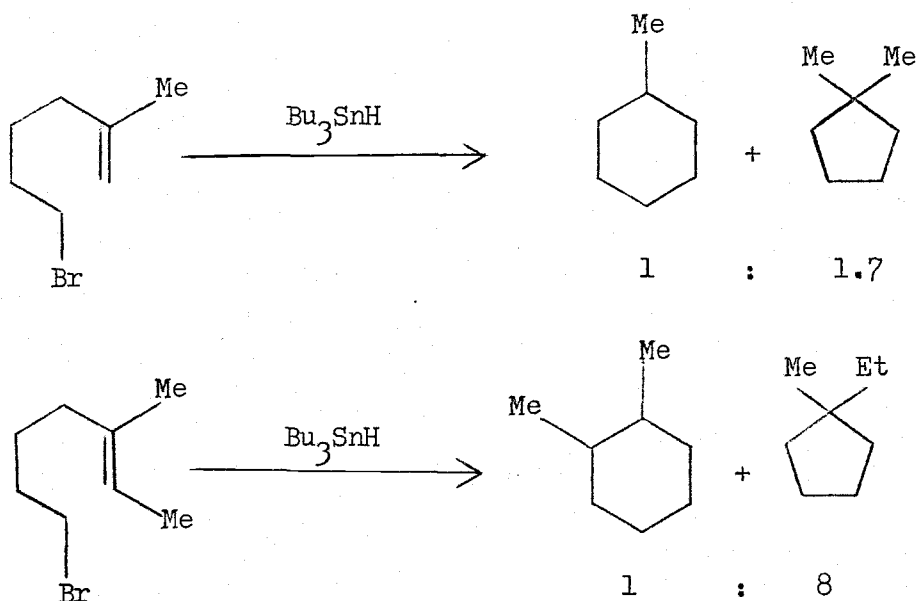
Scheme 3



a kinetic result rather than a thermodynamic one since cyclohexane is more stable than methylcyclopentane by 742 cal/mole (20). Both modes of cyclization are favored according to Baldwin's Rules.

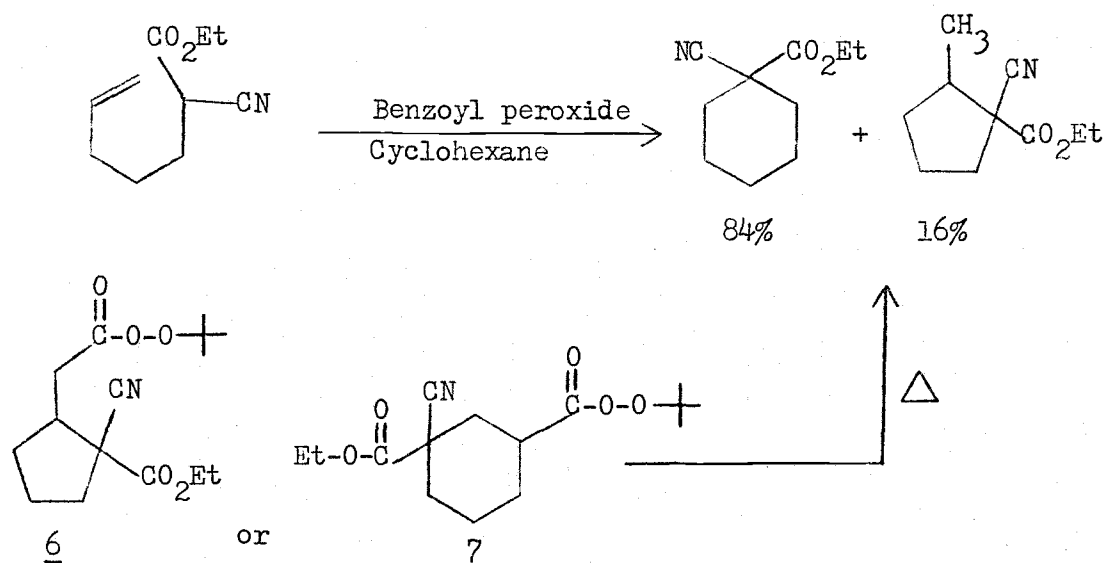
In radical cyclizations the regiochemistry is heavily dependent upon the substitution pattern about the double bond (21) (Scheme 4).

Scheme 4

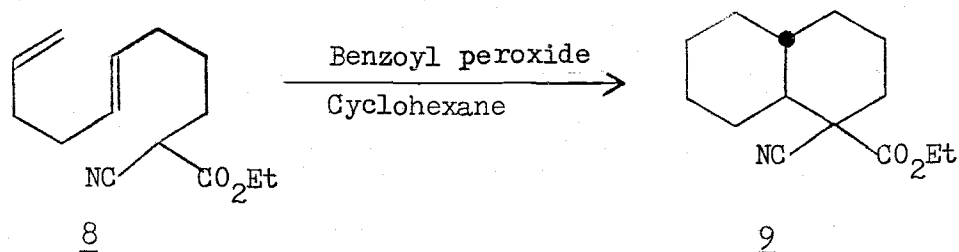


When the radical center in the acyclic intermediate is stabilized by resonance, the cyclization easily reverses which eventually permits the attainment of an equilibrium product distribution. Such a rationale was confirmed by the fact that decomposition of 6 or 7 led to the same product distribution (22) (Scheme 5).

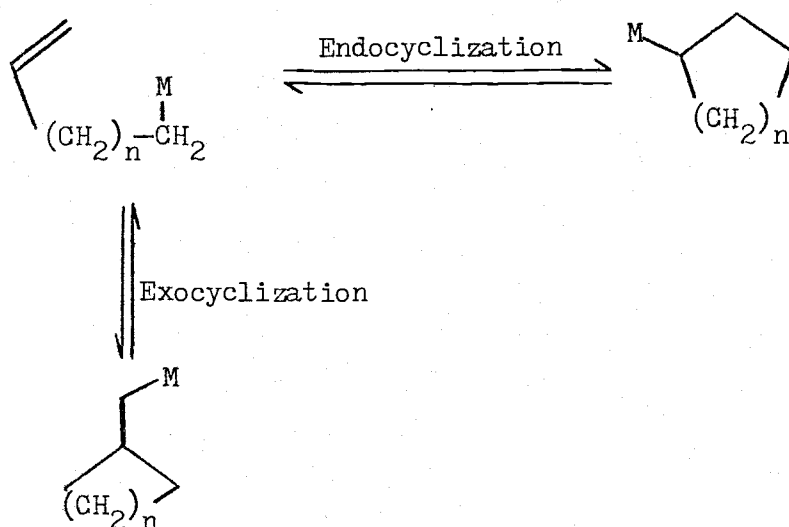
Scheme 5



Multiple cyclizations have also been accomplished using free radical intermediates (22). Although in most cases a mixture of isomers is produced, occasionally a single diastereomer (9) is formed preferentially (22).



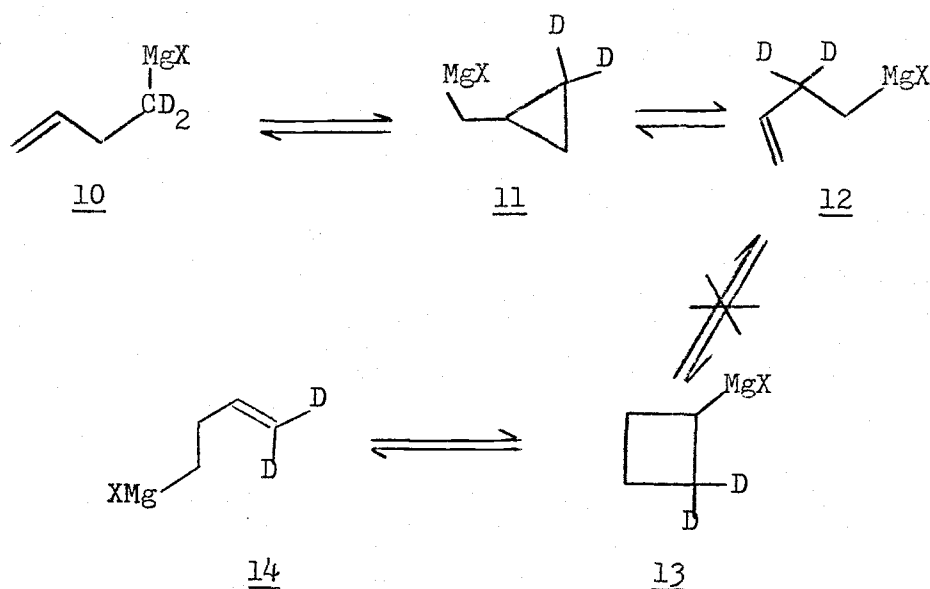
Intramolecular additions of organometallic reagents across a carbon-carbon double bond resulting in the formation of 3- to 6-membered rings has been observed or proposed for organometallic compounds containing lithium (1), magnesium (2), aluminum (3), zirconium (4), titanium (5), gallium (6), indium (6), rhodium (7), nickel (8), iron (9), palladium (10), copper (11), thorium (12), and cobalt (13). number of literature examples are available, mostly involving organolithium, -magnesium and -aluminum reagents, and indicate that $n = 1, 2$, and 3 , the exocyclic route is preferred (1,2,3).



In the $n = 1$ process, sufficient proof for the exocyclization mechanism has been provided by the deuterium-labelled magnesium reagent

The ready interconversion of 10 and 12 was observed but no deuterium appeared in the vinyl position. Clearly this negates the intermediate creation of the 4-membered ring 13 (23) (Scheme 6).

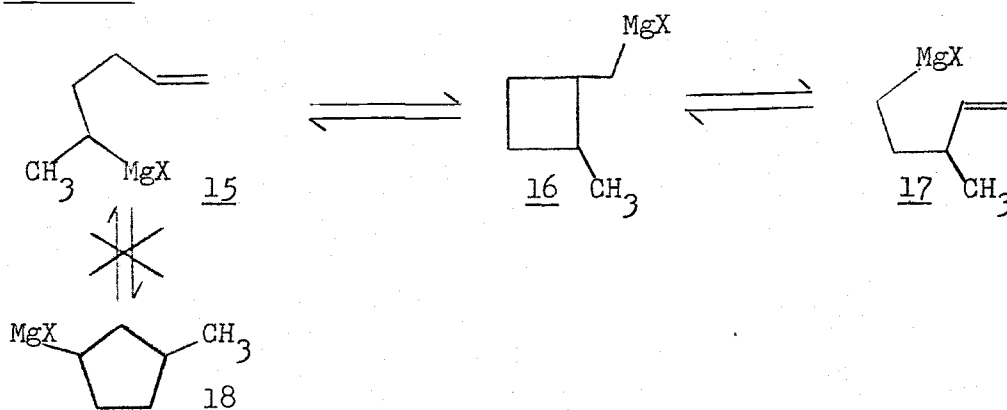
Scheme 6



Substantial ring strain inherent in the cyclopropyl (28 Kcal/mole) and the cyclobutyl (26 Kcal/mole) rings usually commands the equilibrium to be displaced toward the open chain structure, but exceptions involving special polycyclic structures and highly stabilized carbanions do exist (24)

The normal $n = 2$ process kinetically resists the endocyclic reaction in favor of the presumable less thermodynamically stable exocyclic intermediate (25). The less stable secondary magnesium reagent 15 has become primary (17), defining the reorganizational rationale (Scheme 7). On strain arguments one would predict 18 to be

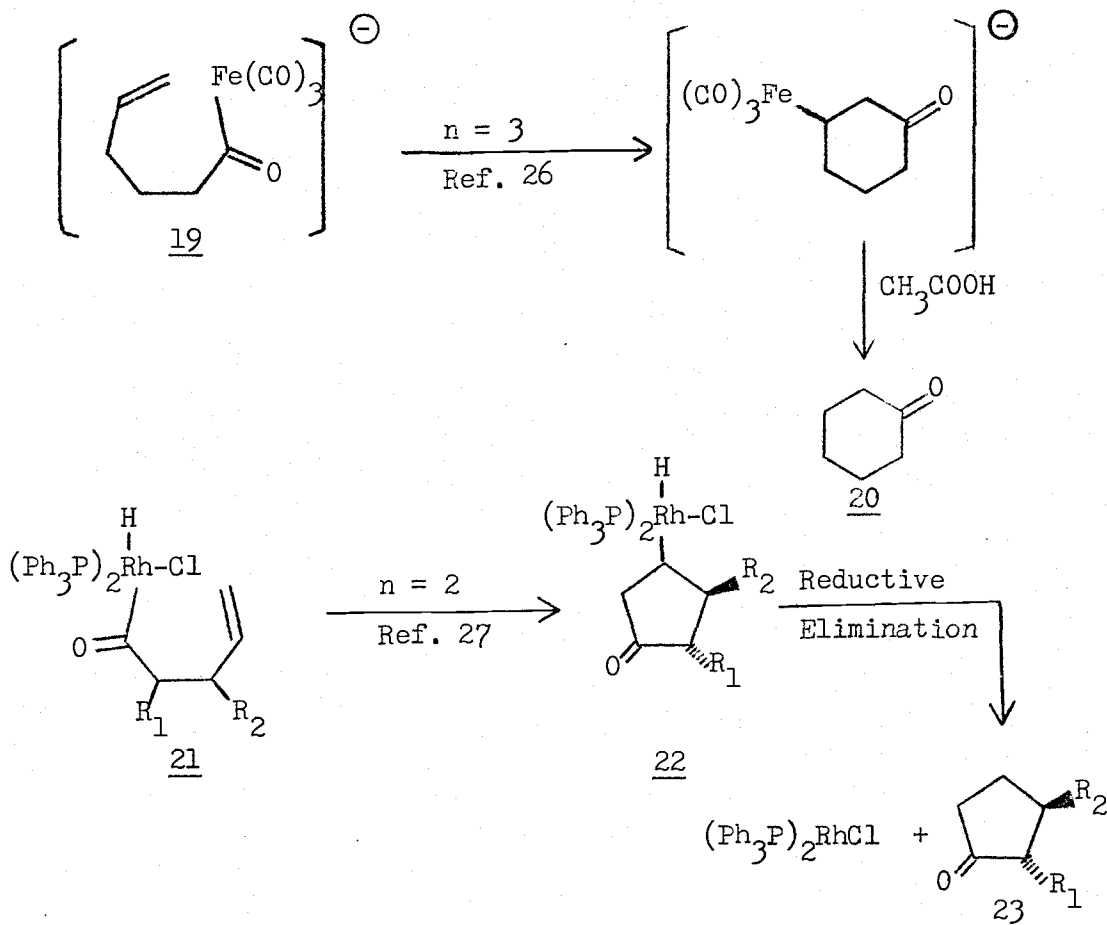
Scheme 7



more stable than 16, even though 18 possesses a secondary carban-ionic center.

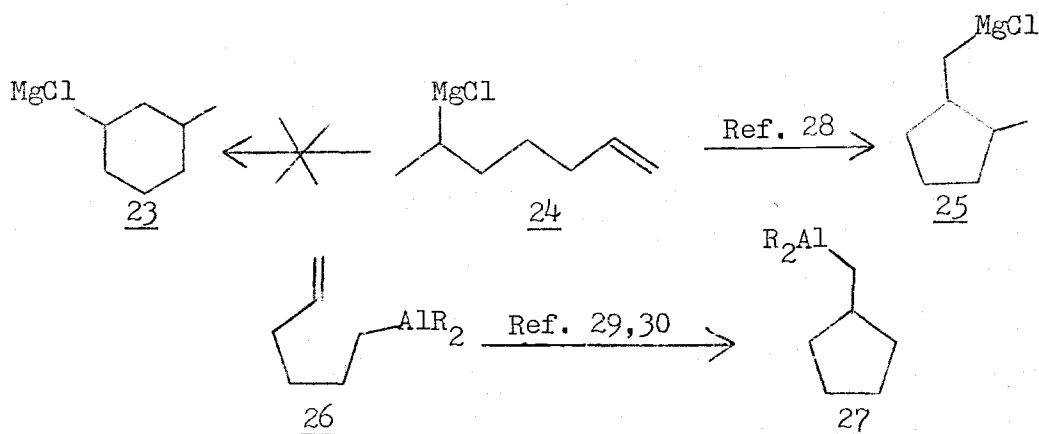
Insertion of an olefinic unit into an acyl-transition metal σ -bond often proceeds in an endocyclic fashion (Scheme 8). This tendency can be pronounced enough to violate Baldwin's Rules ($n = 2$).

Scheme 8



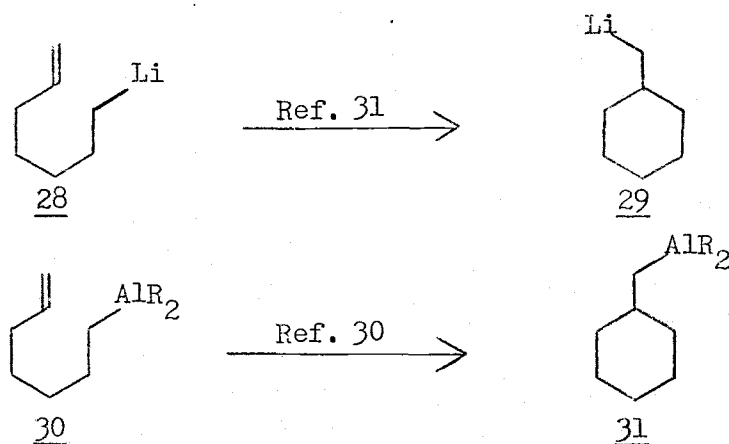
The $n = 3$ case assumes a significant synthetic role due to the stability of the cyclic isomer. These systems have been investigated to some extent and most available evidence supports closure to form a 5-membered ring from the exocyclic organometallic species (Scheme 9). A couple of examples are readily provided by the literature (28,29,30).

Scheme 9



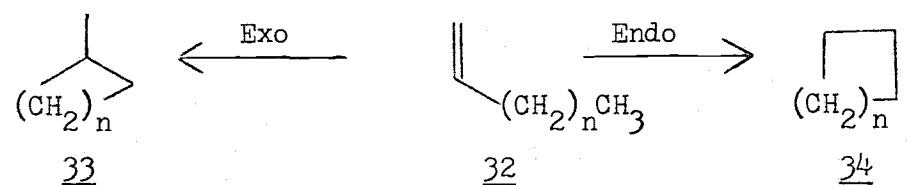
The $n = 4$ cyclization appears to provide the larger ring obtainable through the insertion process (Scheme 10).

Scheme 10



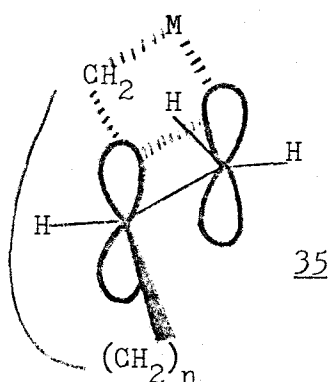
Analysis of a significant portion of the thermodynamics associated with these ring closures can be achieved by calculation of the standard Gibbs free energy differences between the opened and closed forms of a given hydrocarbon using the method outlined by Benson (32). The results are shown in Table 1.

Table 1. ΔG for Exocyclization and Endocyclization Processes

		
<u>n</u>	<u>ΔG (Exocyclization)</u>	<u>ΔG (Endocyclization)</u>
1	+ 7.6 Kcal/mole	+ 9.5 Kcal/mole
2	+ 6.9 "	- 9.5 "
3	-12.2 "	- 13.6 "
4	-16.0 "	- 7.5 "
5	- 8.7 "	- 2.6 "

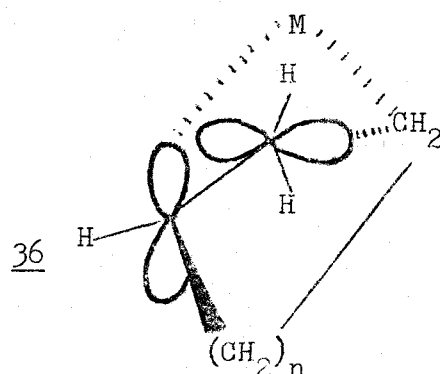
As indicated from the examples given previously, the cyclization preferred thermodynamically need not be kinetically accessible. Both $n = 2$ and $n = 3$ cyclizations exemplify this fact. In the $n = 2$ case, the cyclopentyl system is much more stable than the cyclobutylcarbinyl system. However, the energy of activation required to form the endocyclic organometallic is substantially greater than that needed for exocyclic organometallic formation. Because of this, reversible closure prevails, generating the cyclobutylcarbinyl organometallic as an intermediate. The $n = 3$ system behaves similarly, but the cyclopentylcarbinyl moiety enjoys a considerable free energy advantage over its open-chain isomer, making the closed form the reaction product with the open form a possible intermediate.

A consistent rationale behind the kinetic bias toward cycloalkylcarbinylmetallic formation suggests that the transition state for cyclization maintains partial double bond character reminiscent of the open-chain isomer (33). Formation of the exocyclic organometallic readily permits continuous overlap of the double bond p orbitals, whereas the endocyclic reaction requires the p orbitals of the double bond to twist out of overlap in generating 4- through 6-membered rings, as depicted by models 35 and 36.



Continuous overlap:
Exocyclic reaction

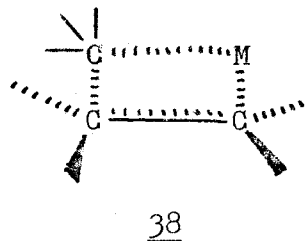
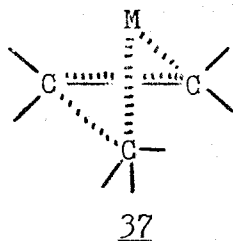
$n = 1 \text{ to } 5$



p Orbital twist:
Endocyclic reaction

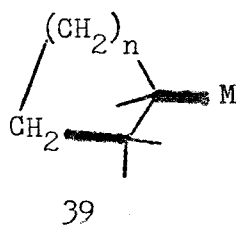
The veracity of the above discussion depends upon the stereochemical restrictions associated with the addition to an unsaturated bond. The stereochemical outcome of intermolecular nonreversible addition to both double and triple bonds has been shown to favor mostly cis-addition for the meager number of systems studied (34). This does not mean trans-addition is impossible. Certain endocyclizations apparently do proceed in a trans-manner (35). Most pictorial views of the transition state for the addition of organometallic reagents to double bond involve a 4-centered molecular array, "perpen-

dicular" (37), or "coplanar rectangular" (38) leading only to cis-addition. Depending on the orbitals and number of electrons involved,



the 4-centered transition state need not impart any special stabilization. The occurrence of trans-addition would tend to negate the theoretical arguments rationalizing preferential exocyclization.

A trans coplanar arrangement of both leaving groups could be more readily achieved by most of the ring systems under consideration than the alternative cis coplanar geometry. A concerted trans-addition

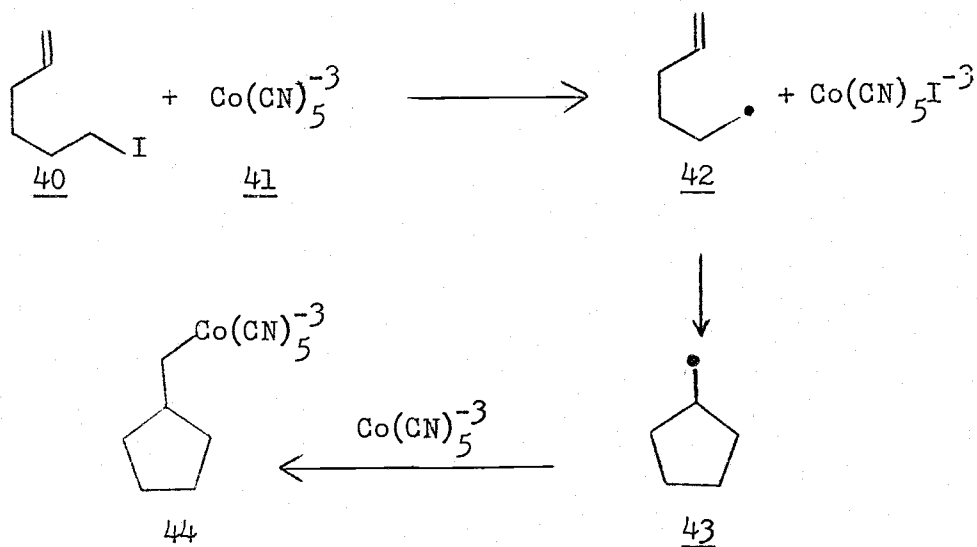


Heavy lines define
 σ -bonds to be broken
in retrocyclization.

is a difficult process to imagine. Either free radicals or the intervention of two metal atoms could be involved in a plausible trans-addition mechanism (36).

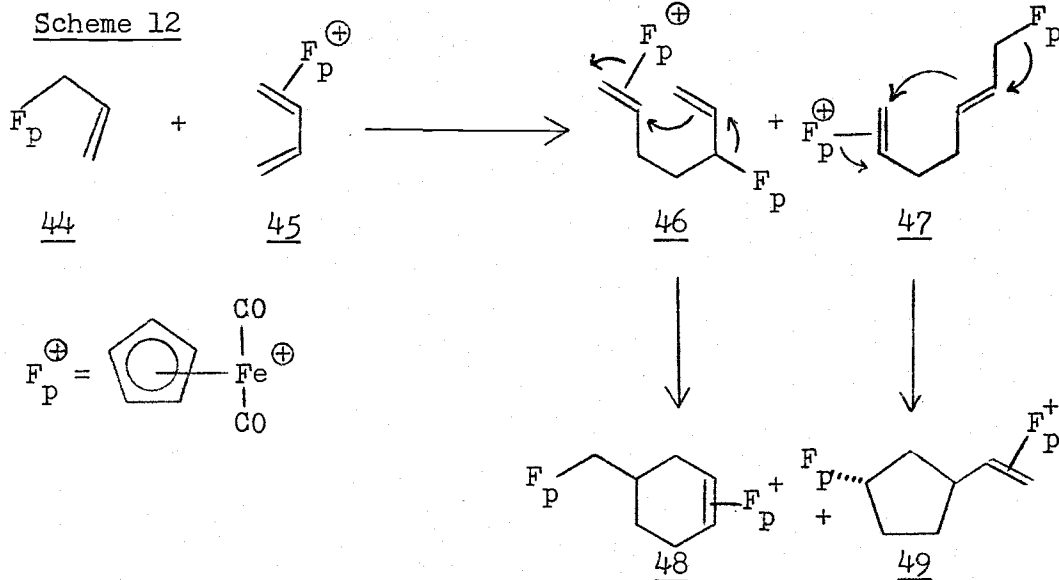
Not many organometallic cyclizations known to involve free radical intermediates have been investigated. The one electron oxidative addition reaction of $\text{Co}(\text{CN})_5^{-3}$ and R-I proceeds through the intermediacy of an alkyl free radical (37,38) (Scheme 11). These cyclizations would be expected to be controlled by the kinetic bias of free radicals toward exocyclization. Furthermore, stereochemical and reactivity pattern

Scheme 11



findings limit the free radical contribution to cyclization of most organometallic systems to a minor percentage.

Cyclizations requiring the presence of two metal atoms are likewise quite rare. Rosenblum has explored the synthetic potential of certain olefinic iron complexes (39), a few of which experience intramolecular cyclization (Scheme 12). These preliminary results do

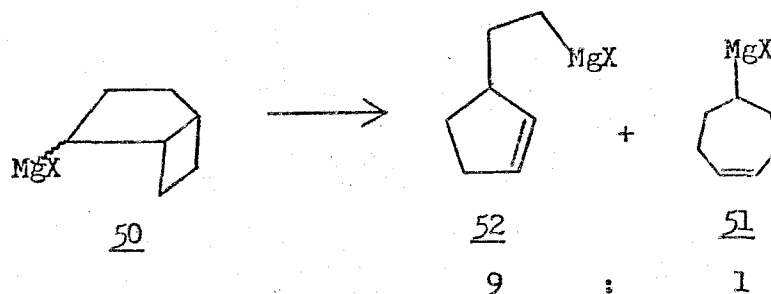


indicate that trans-addition across the double bond can relinquish a substantial quantity of endocyclization.

E. Alexander Hill (25,40,41) has reported kinetics performed on the retrocyclization of certain Grignard reagents which provides useful information concerning the structure of the transition state leading to cyclization (or retrocyclization by application of the Principle of Microscopic Reversibility). These experiments lend credence to the preferential formation of the "perpendicular" rather than the "coplanar rectangular" transition state mentioned earlier.

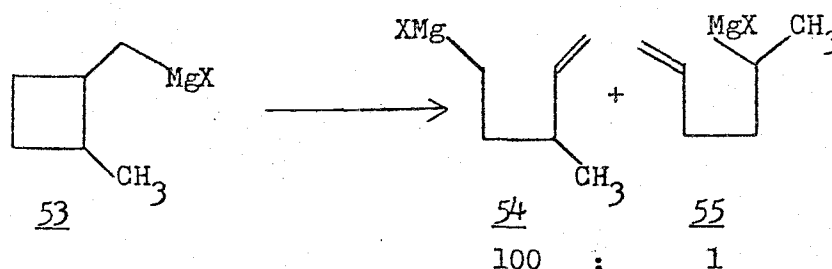
Bicyclic Grignard reagent 50 will experience retrocyclization due to considerable loss of strain energy to relinquish a secondary (51) and a primary Grignard reagent (52) (40,41) (Scheme 13).

Scheme 13



The ratio of primary product 52 to secondary product 51 was shown to be 9 : 1. Surprisingly, a similar ring opening of the monocyclic Grignard 53 also provided two products but in a primary (54) to secondary (55) ratio of 100 : 1 (Scheme 14) (25). Kinetic studies

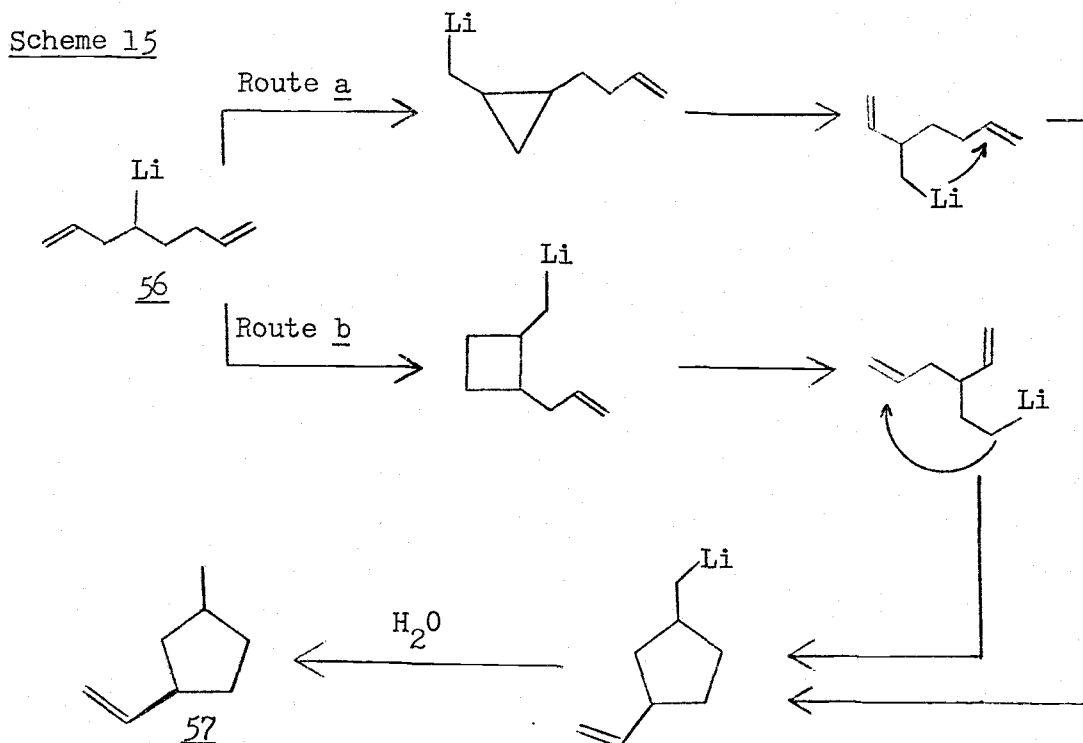
Scheme 14



confirmed that the two secondary Grignard reagents 51 and 55 were generated with very similar rate constants. The latter system possesses considerable conformational freedom and would presumably assume the optional transition state geometry. The former system is much more restricted and would require the transition state leading to the secondary Grignard product 51 to approximate the "perpendicular" arrangement. This result lends support to the preferential formation of the "perpendicular" transition state. Generation of 54 is much faster than that of 52, which leads to the conclusion that the rearrangement of bicyclic Grignard 50 to give 52 is slow because the system cannot attain the "perpendicular" transition state.

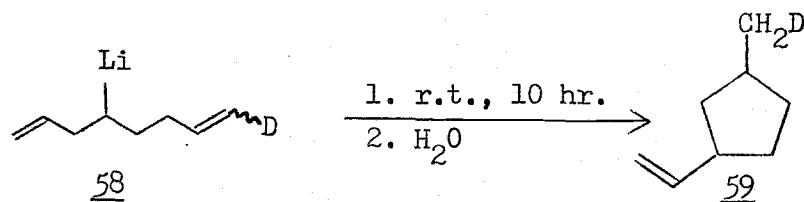
The relative rates for formation of various sized rings is of particular importance in synthetic planning. The following order has been established in the instance of lithium: 5-membered > 3-membered > 4-membered ring (42). Simple kinetics has also revealed 5-membered > 6-membered ring (31), but the relationship between 3- and 6-membered processes has yet to be examined.

Much information was gleaned by intramolecularly pitting one ring formation against another. Lithium reagent 56 was found to undergo thermal rearrangement giving 1-methyl-3-vinylcyclopentane (57) as the final product (42). Alkene 57 could be formed by two distinct pathways involving insertion of a double bond into a carbonlithium bond as delineated in Scheme 15. Route a and route b were differentiated by deuterium labelling. Subjection of the lithium reagent 58 to reaction conditions liberated compound 59 with



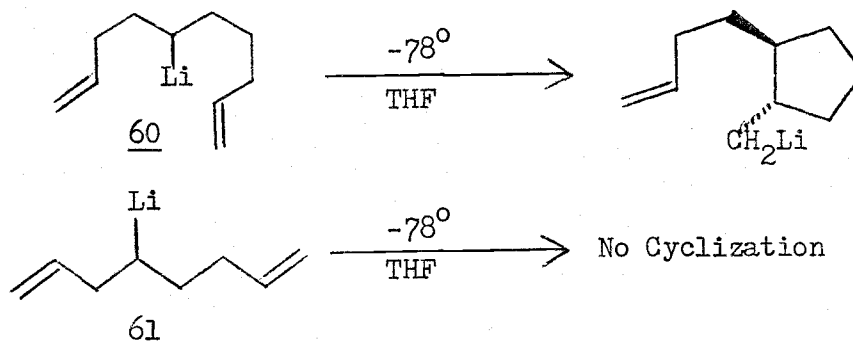
deuterium residing exclusively at the methyl position (route a) and not at the vinyl position (route b) as readily determined from its NMR spectrum (Scheme 16). This evidence strongly lends support to route a and a more facile formation of the 3-membered ring.

Scheme 16



A number of pieces of evidence suggests that the 5-membered ring is formed most easily of all ring sizes in organometallic cyclization. Lithium reagent 60 underwent cyclization even at -78° , whereas lithium reagent 61 experienced no rearrangement at all (31) (Scheme 17).

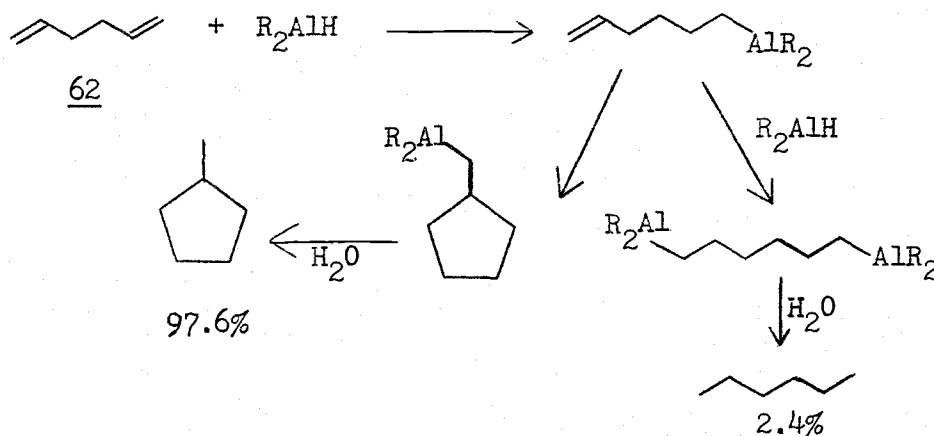
Scheme 17



5-Hexenyllithium cyclized readily at 0° , whereas 6-hexenyllithium underwent intramolecular cyclization sluggishly even at room temperature (43).

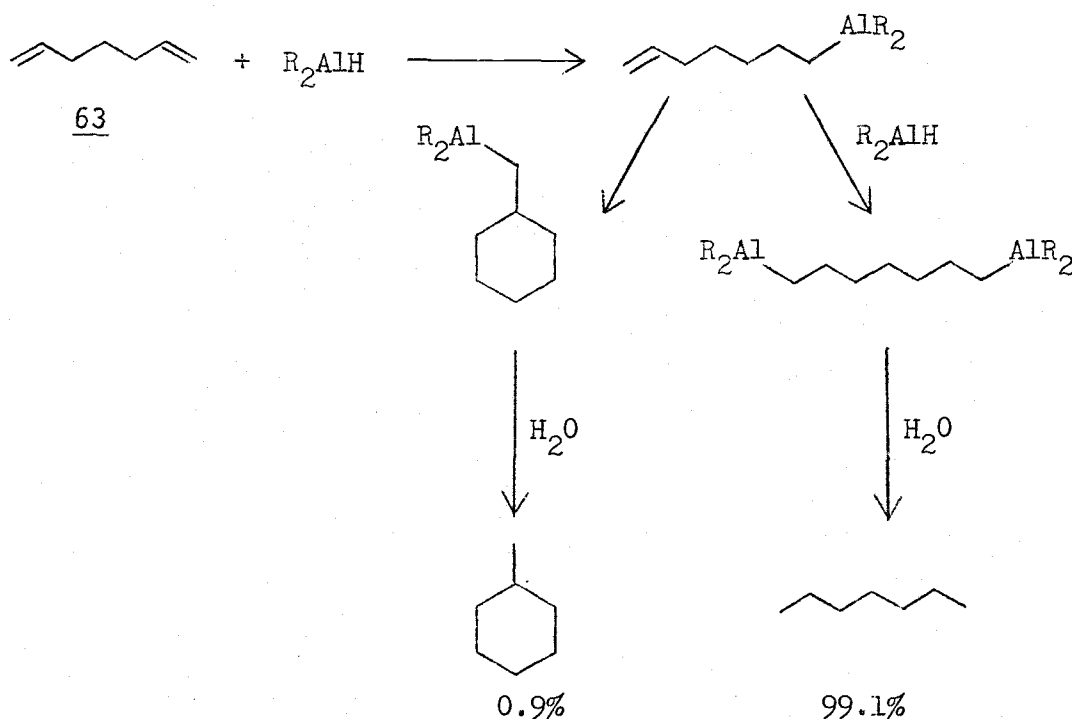
An example of intramolecular cyclization of an organoaluminum compound reported by G. Hata et.al. (30) once again demonstrated the kinetic advantage of 5-membered ring formation. When 1,5-hexadiene (62) was permitted to react with two moles of diisobutylaluminum hydride, the product composition was 97.6% methylcyclopentane and 2.4% n-hexane after hydrolysis (Scheme 18). While under the same conditions, 1,6-hepta-

Scheme 18



diene (63) gave 0.9% cyclic product and 99.1% n-heptane (Scheme 19).

Scheme 19

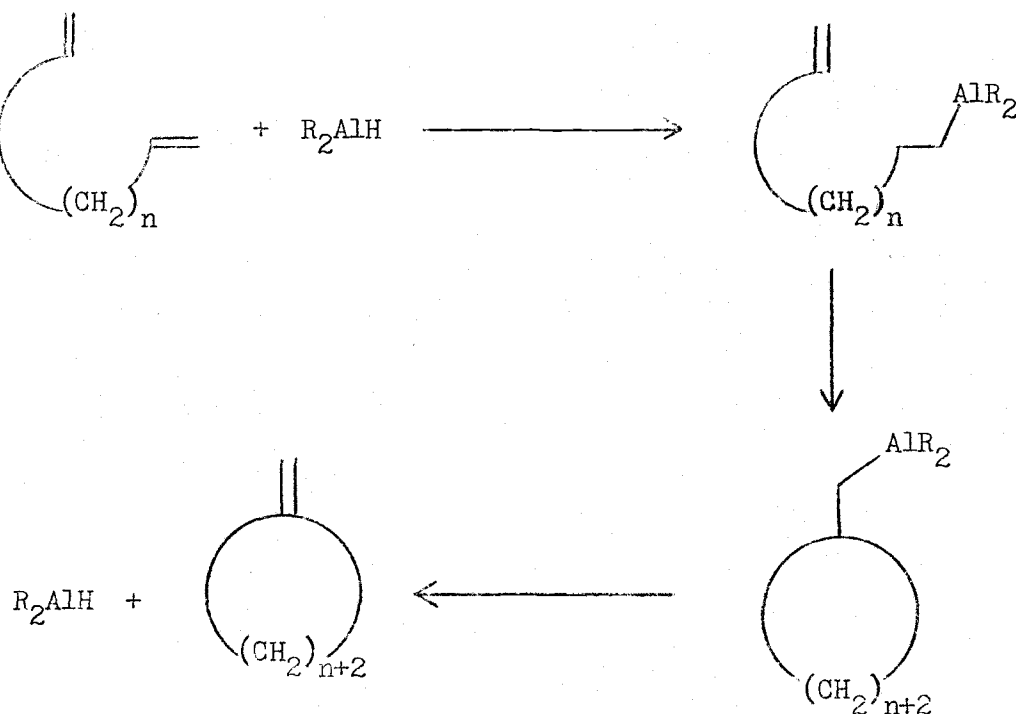


Of all the cyclizations reported in the literature, those proceeding through organoaluminum compounds appeared the most promising for synthetic application. The desirable ingredients of facile σ -bond generation via hydralumination (44), efficient intramolecular insertion (31), potential extension into combinations with transition metals such as titanium and zirconium (45), and a potent arsenal of structural and mechanistic studies (46) sufficiently tempted the synthetic palate to test the scope of organoaluminum cyclizations.

III. Results and Discussion



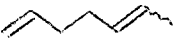

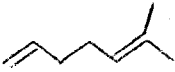

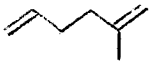
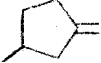

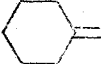
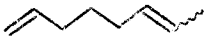

It has been recognized for some time that a carbon-aluminum σ -bond can be generated quite easily by means of hydroalumination: the insertion of carbon-carbon multiple bond into an aluminum-hydrogen bond (44). In the case of a terminal olefin, the hydroalumination reaction proceeds regioselectively to provide a terminal carbon-aluminum bond. Since hydroalumination is known to be reversible at elevated temperatures, it seemed possible that carbocyclization could be accomplished using a catalytic quantity of dialkylaluminum hydride as shown in Scheme 20.

Scheme 20



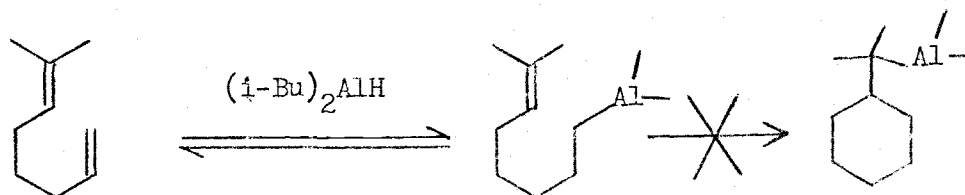
Treatment of 1,5-hexadiene with a catalytic amount of commercially available diisobutylaluminum hydride in mineral oil resulted in the generation of methylenecyclopentane in good yield. Shown in Table 2 are the results of monocyclization for the formation of 5- and 6-membered rings using a catalytic quantity of diisobutylaluminum hydride.

Table 2. Monocyclization of Dienes using Diisobutylaluminum Hydride as Catalyst

Reaction No.	Starting Material	Temp. (°C)	Reaction Time (hr)	Product	% Yield
1		115°	56		81
2		170°	12		77
3		160°	16		80
4		120°	72		35
5		105°	48		56
6		160°	18		40

Because the study merely concerned model systems, more emphasis was placed on ease of preparation rather than efficiency in the synthesis of starting materials. The starting dienes for reactions 1-5 were purchased from commercial sources. The simple starting material used in reaction 6, 1,6-octadiene (103), was easily prepared by coupling 3-butenylmagnesium bromide and 1-bromo-2-butene (47).

It is readily apparent, from the first three reactions, that cyclization to provide the 5-membered ring is a very facile process. Although higher temperatures are required for complete reaction, the presence of one or even two terminal methyl groups did not alter the efficiency of the cyclization process. Lower yields were obtained in the case of 6-membered rings, with no cyclization at all being observed for 7-methyl-1,6-octadiene under a variety of conditions.

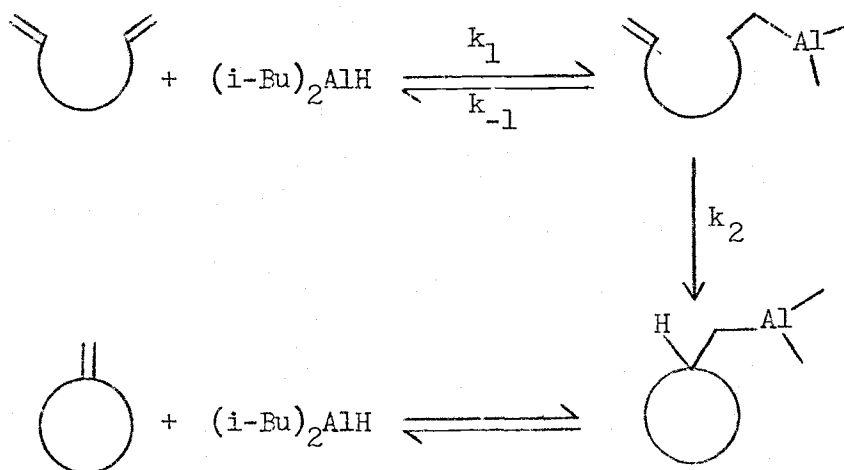


It is well established that cyclizations of alkenylaluminum compounds occur more readily to provide the 5-membered ring than the 6-membered ring (30). The lower overall yields to produce the 6-membered ring probably reflect an increased amount of the competitive intermolecular insertion taking place which resulted in the formation of polymers.

Ziegler (48) has shown that the rate of hydroalumination of simple olefins follows the order: $\text{CH}_2=\text{CH}_2 > \text{R-CH}=\text{CH}_2 > \text{R}_2\text{C}=\text{CH}_2 > \text{R-CH}=\text{CH-R} > \text{R}_2\text{C}=\text{CHR}$. All of these monocyclizations could be interpreted as proceeding from the site of initial hydroalumination.

In the simplest mechanism conceivable, the rate-determining step could be either the initial hydroalumination or subsequent intramolecular cyclization (Scheme 21). If $k_{-1} > k_2$, insertion of the double bond would play an important kinetic role. On the other hand if $k_{-1} < k_2$, the rate of reaction, as well as the product structure,

Scheme 21

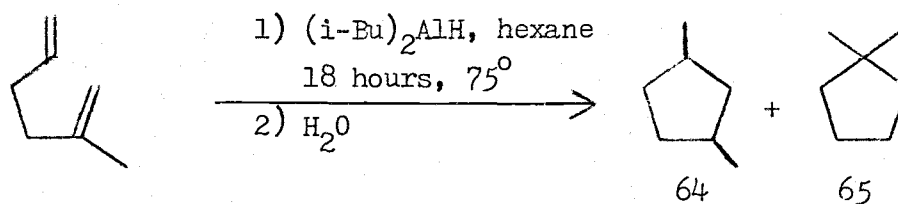


would depend exclusively upon which double bond underwent hydroalumination more rapidly. The prevalent situation could depend heavily upon ring size and substitution patterns about the double bonds.

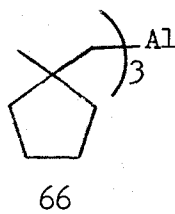
From the systems studied to date (including the bicyclic systems presented later on), it is apparent that neither kinetic scenario can satisfactorily account for all the results. All of the cyclizations did proceed, however, from initial hydroalumination of either $\text{RCH}=\text{CH}_2$ or $\text{R}_2\text{C}=\text{CH}_2$ which provided a primary organoaluminum compound. Intramolecular insertion of $\text{R}_2\text{C}=\text{CHR}$ or $\text{RCH}=\text{CHR}$ into a carbon-aluminum bond is a far faster process than intermolecular insertion of such units into a hydrogen-aluminum bond as revealed from the simple monocyclizations.

Although only one product was isolated from reaction 4, undoubtedly two separate cyclizations had taken place in this reaction. A noncatalytic reaction was conducted using equal molar

quantities of diisobutylaluminum hydride and 2-methyl-1,5-hexadiene at 75° in hexane. Under these conditions cyclization took place but the products did not result from a final dehydroalumination as required by the catalytic process (49). The two possible constitutional isomers resulting from exocyclization were isolated after hydrolysis in a ratio $\underline{64} : \underline{65} = 2 : 3$. It should be noted that no hydro-

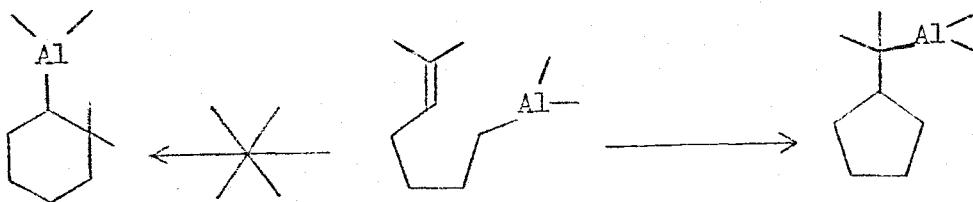


lysis was employed in the work-up procedure for the catalytic reactions, and consequently no 1,1-dimethylcyclopentane would have been detected. The volatile components were simply vacuum transferred from the mineral oil which acted as a solvent. Although only 0.1 equivalents of diisobutylaluminum hydride was employed, the loss of isobutylene at higher temperatures actually provided a total of 0.3 equivalents of hydride. The low yield of product in the catalytic cyclization of 2-methyl-1,5-hexadiene, combined with the fact that a considerable quantity of starting material remained, lends support to the notion that the aluminum catalyst was converted into unreactive 66.



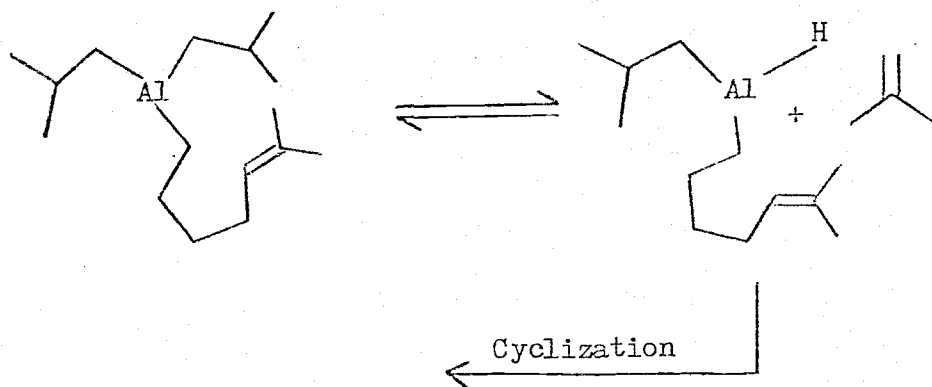
Reactions 1-6 clearly demonstrated that factors other than simple alkyl substitution about the double bond dominate the regiochemistry characteristic of the cycloinsertion. Intermolecular carbalumination

and hydroalumination both generally prefer to place aluminum on the less substituted carbon (50). In the case of reaction 3, a 6-membered ring would have been generated via endocyclization. The reaction avoided this regiochemical course in favor of the exocyclization even though the aluminum atom presumably became bound to a tertiary carbon. As



discussed in the introduction, simple organometallic cyclizations display a marked tendency toward exocyclization under normal circumstances.

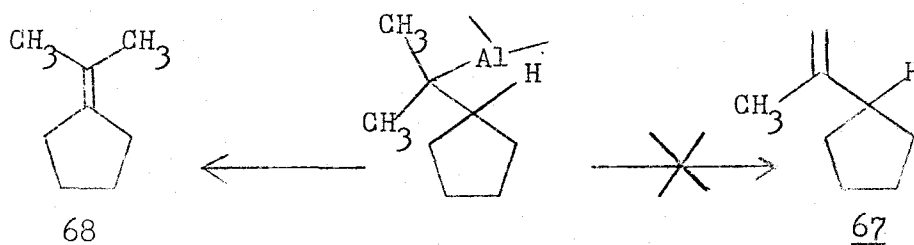
The successful cyclization of highly substituted alkenes, as in reactions 2 and 3, attest to the facility of 5-membered ring formation. Although such cyclizations would at first appear unlikely on steric grounds, alkylaluminums can accommodate steric demands by expelling bulky ligands through dehydroalumination (51). Concern about steric



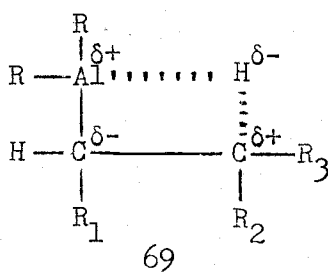
factors may not be warranted in the case of aluminum anyway, since tri-*t*-butylaluminum is a stable compound and known to insert into ethylene

even at 20° (52). It has also been experimentally demonstrated that in the transition state for insertion into a carbon-aluminum bond, the carbon which becomes attached to aluminum in the product accumulates positive character (53). Electron donating methyl substituents should stabilize this electrophilic center and help to counteract adverse steric interactions.

The monocyclizations displayed a strong preference for regio-specific dehydroalumination in the final step and the generation of the thermodynamically most stable olefin. Even in reaction 3 where a six to one statistical advantage existed for the formation of 67, no product other than compound 68 was observed. Egger and Cocks (53)



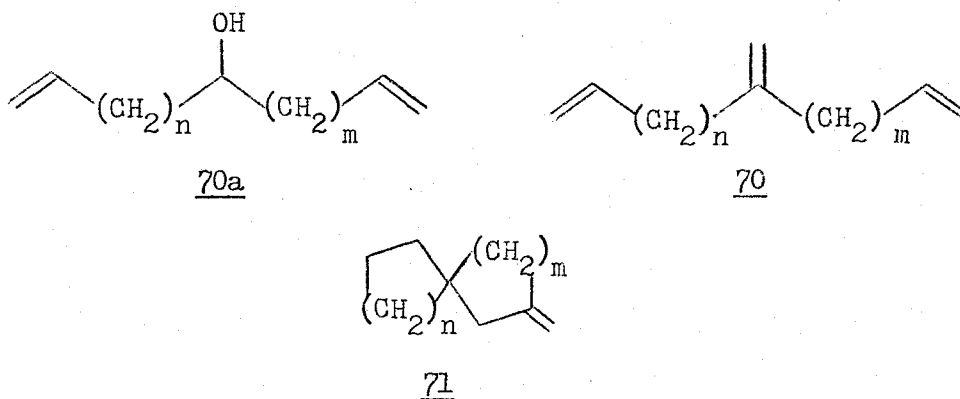
have proposed a tight four-centered transition state (69) as a satisfactory explanation of the observed gas phase kinetics measured for the thermal decomposition of R_3Al . Isotope effect studies have lent support to this proposed structure (54). Such a transition state places partial positive character on the β carbon from which



hydrogen is removed and would be expected to lead to the generation of the most highly substituted olefin possible.

Table 3 gives results of cyclizations which were designed to provide bicyclic units. Represented in this series are 1-1, 1-2, and 1-3 ring-fused molecules.

The 3-allylcyclohexene was prepared from the coupling reaction of allylmagnesium bromide and 3-bromocyclohexene. The straightforward preparation of 1-allyl-2-methylenecyclohexane and 1-(3-butenyl)-2-methylenecyclohexane was accomplished from the corresponding ketones and methyltriphenylphosphonium bromide under normal Wittig conditions. Two of the trienes were prepared by coupling of a Grignard reagent and allyl bromide (47): 4-allyl-1,6-heptadiene from diallylmethylmagnesium chloride and 1,5,9-decatriene from 1-(2,6-heptadienyl)magnesium chloride. Trienes of the type 70 which were designed to produce spiro compounds 71 were obtained from the corresponding alcohols 70a by Jones oxidation



to the ketones followed by the Wittig reaction using methyltriphenylphosphonium bromide.

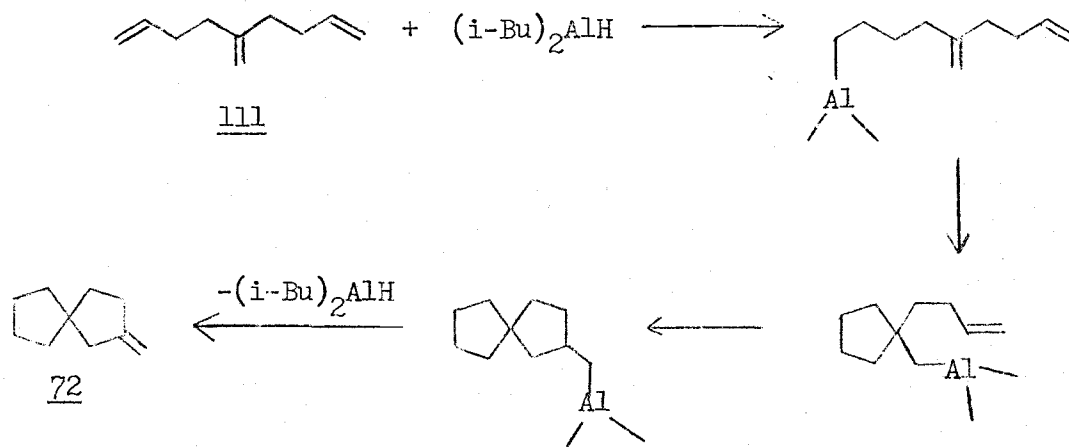
The spiro systems (reactions 7, 8, and 9) reveal a striking difference in behavior between 5- and 6-membered ring formation. Reaction 7 apparently proceeded via hydroalumination of a terminal double bond

Table 3. Cyclization of Polyenes Using Diisobutylaluminum Hydride as Catalyst

Reaction No	Starting Material	Temp. (°C)	Reaction Time(hr)	Product(s) (% Yield)
7		110°	48	(78)
8		150°	72	(37)
9		150°	96	(11) (41)
10		200°	48	(61)
11a		120°	24	
11b	"same as 11a"	120°	48	(40)
12		150°	18	(55) (16)
13		120°	67	(40) (23)
14		120°	72	(15) (45)
15a		160°	6	
15b	" same as 15a "	160°	1.7	(54) (36)

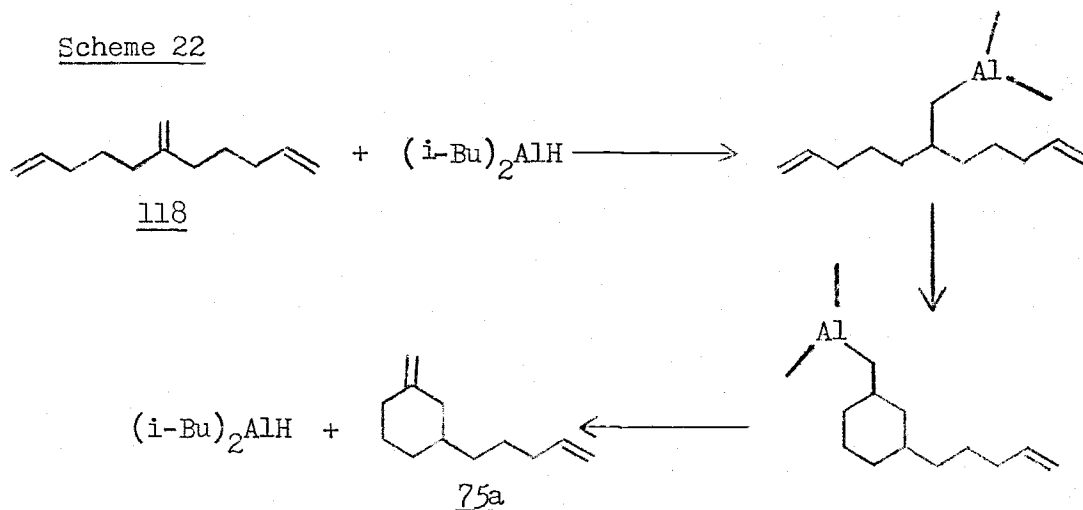
followed by two cycloinsertions as described in Scheme 21. In contrast,

Scheme 21



the major product of reaction 9 resulted from initial hydroalumination at the more highly substituted double bond followed by a single cycloinsertion (Scheme 22).

Scheme 22



Since hydroalumination is known to occur approximately twice as fast with monosubstituted olefins than with 1,1-disubstituted olefins (48), the site of initial hydroalumination cannot explain the degree of constitutional selectivity exhibited in reaction 9. In this reaction a hydroalumination-dehydroalumination preequilibrium needs to be in-

voked with the insertion process itself being rate-determining. This behavior would also appear to explain the formation of compound 73 to the exclusion of structure 74 in reaction 8.

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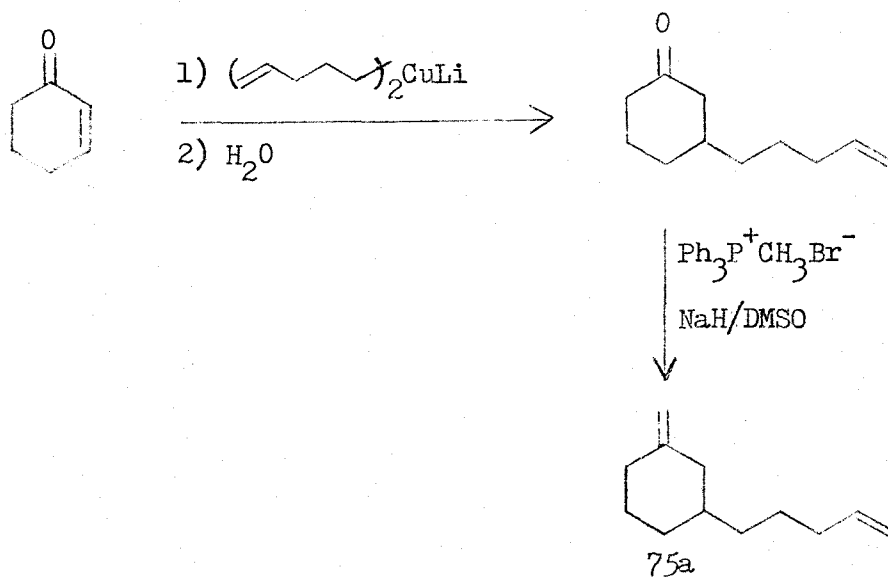
The structures of spiro compounds 72, 73, and 75 were assigned

75

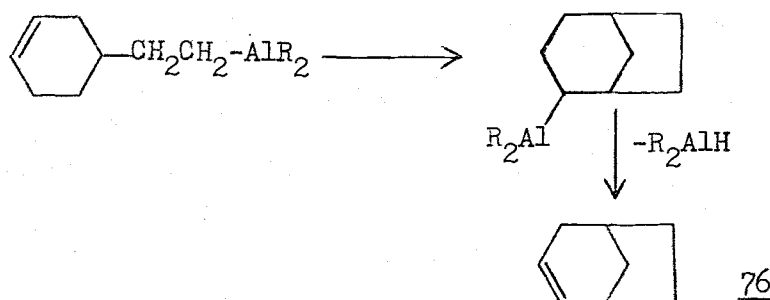
on the basis of elemental analysis, NMR spectral analysis, and the limitations placed on the number of different possibilities due to the known tendencies of the cyclization itself. Considerable structural information was gleaned by comparing the chemical shifts and splitting patterns of the vinyl protons in these spiral molecules to those of simple model systems: methylenecyclopentane, methylenecyclohexane, and methylenecycloheptane. The vinyl protons in compound 72 possessed a chemical shift ($\delta=4.72-4.86$) and splitting pattern identical to those of methylenecyclopentane but different from those of either methylenecyclohexane or methylenecycloheptane. The vinylic and allylic regions were essentially identical in the NMR spectra of compounds 73 and 75.

Confirmation of the structural assignment of compound 75a was achieved by independent synthesis as outlined in Scheme 23.

Scheme 23



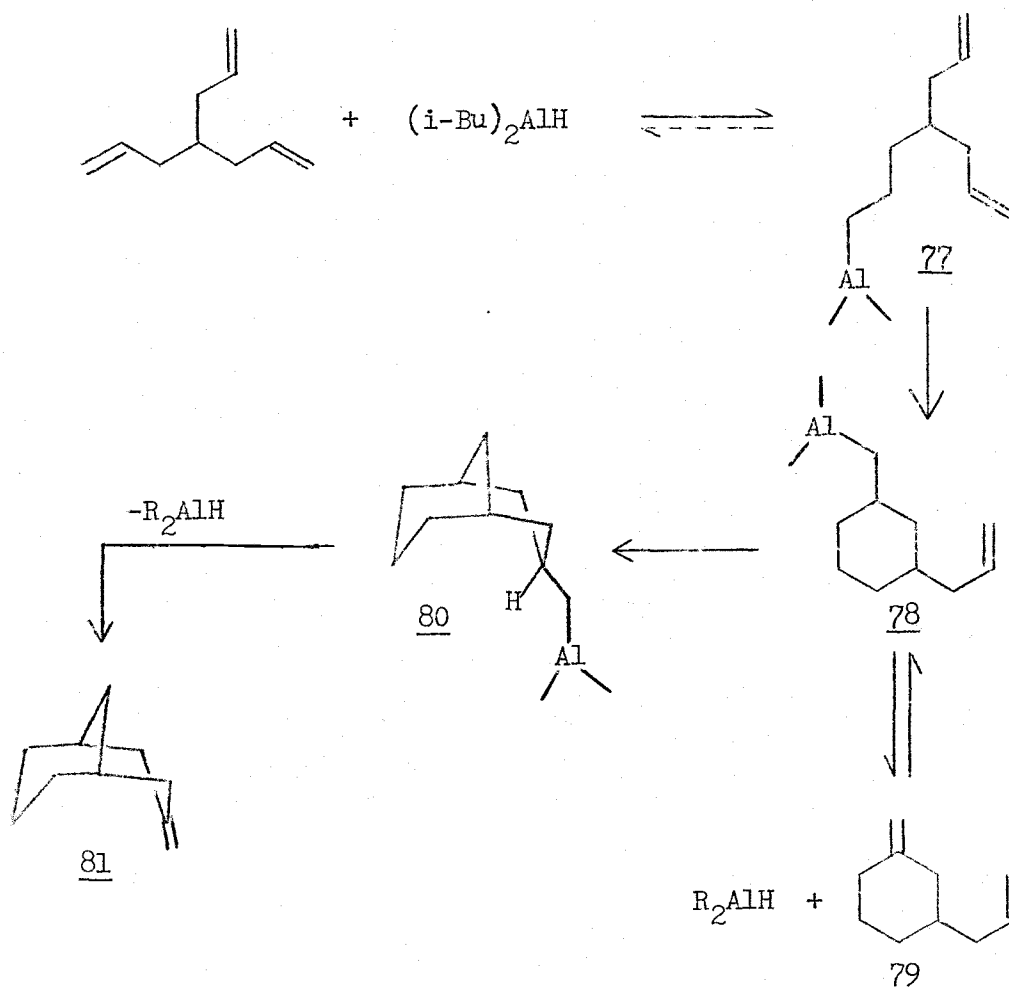
Only two cyclizations were conducted which resulted in 1,3-ring-fused molecules (reactions 10 and 11). The catalytic cyclization of 4-vinylcyclohexene to give bicyclo[3.2.1]oct-1-ene (76) required elevated temperature. This undoubtedly reflects some difficulty the system has in experiencing the insertion process. Intramolecular cyclizations involving the consumption of an olefinic unit which is either endocyclic or exocyclic to a ring appears to be a somewhat sluggish



reaction. Basically the same type of cyclization was reported to occur during the thermal decomposition of tri(cyclohexenylethyl)aluminum (55).

Reaction 11 provided an entry into the bicyclo[3.3.1]nonane system. The highly symmetrical triene, 4-allyl-1,6-heptadiene, can experience hydroalumination at any one of its double bonds to give the same intermediate (77 in Scheme 24). Likewise an intermediate of unique constitution (78) would be expected from an $n = 4$ cyclization involving either unsaturated species. When the reaction was performed over a short

Scheme 24



time span both a monocyclic (79) and a bicyclic compound (81) were produced. Over a longer period of reaction time the bicyclic material was formed in greater quantity at the expense of the monocyclic substance which disappeared entirely. A plausible mechanistic rationale is

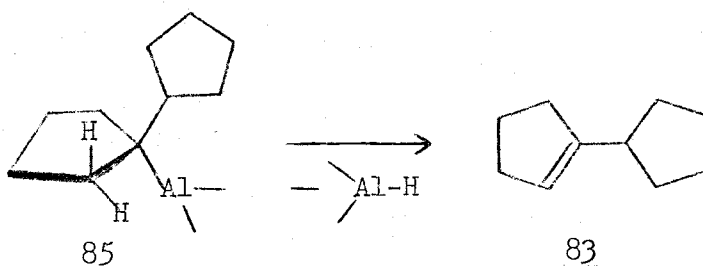
delineated in Scheme 24. The conversion of 77 into 78 can eventuate in the production of two stereoisomers: the trans and cis forms. Because of geometrical constraints, the trans stereoisomer would be incapable of continued cyclization without prior isomerization to the cis form. The interconversion of 78 and 79 provides a ready pathway for trans-78 \rightleftharpoons cis-78 .

The structures of 79 and 80 were assigned principally by comparison of NMR spectra to those of compounds of known similar constitution. Compound 79 displayed an NMR spectrum with vinylic proton resonance identical to that of 75a which had been prepared by independent synthesis. Methylene cyclohexane possessed a chemical shift ($\delta = 4.55-4.67$) and splitting pattern in the vinylic region identical to those of compound 81 .

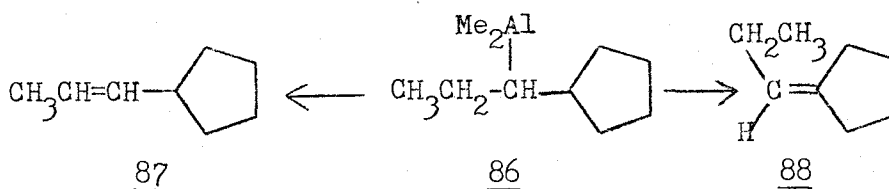
Reaction 12 resulted in the formation of two substances 82 and 83 in 55% and 16% yield respectively. Scheme 25 shows a likely mechanism for generation of the products. The monocyclic intermediate initially formed (84) had the option of undergoing either dehydroalumination in the manner of reaction 2 or further cyclization to give a 4-membered ring. The molecule choose to do the former due to the sluggishness of the latter.

It was shown that products 83 and 82 did not interconvert under reaction or work-up procedures. Consequently, a kinetic regiochemical preference associated with the final dehydroalumination must be invoked. In other systems studied the dehydroalumination process strongly favored the formation of the more highly substituted double bond. This was also the case above but not to the exclusion of the

less highly substituted olefin (83). The hydroalumination reaction across a carbon-carbon double bond has been shown conclusively by Eisch to take place in a synperiplanar fashion (56). By microscopic reversibility, dehydroalumination would require a synperiplanar orientation of departing groups as well. In intermediate 85, loss of a β -hydrogen to form the less highly substituted olefin was enhanced because the 5-membered ring conformationally locked the aluminium and β -hydrogen in the preferred synperiplanar orientation (85)



Egger has calculated a difference of 1.9 kcal/mole at 180° for the gas phase dehydroalumination of the acyclic system 86 leading to formation of 87 and 88 (57). The cyclic system above provided slightly more elimination of the secondary hydrogen but not in a

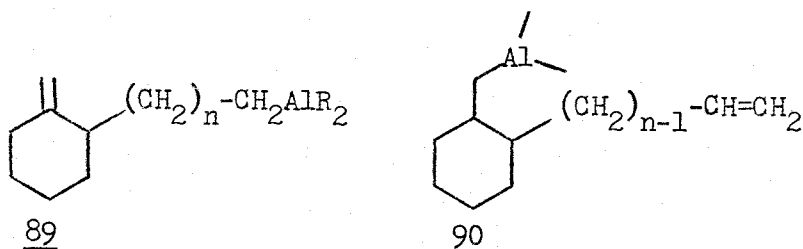


percentage sufficient to overcome the electronic factors which favor the removal of the tertiary hydrogen.

Structural identification of 82 and 83 was effected through both NMR spectral analysis and elemental analysis. The NMR spectrum of 82 displayed no vinylic protons while that of 83 showed a

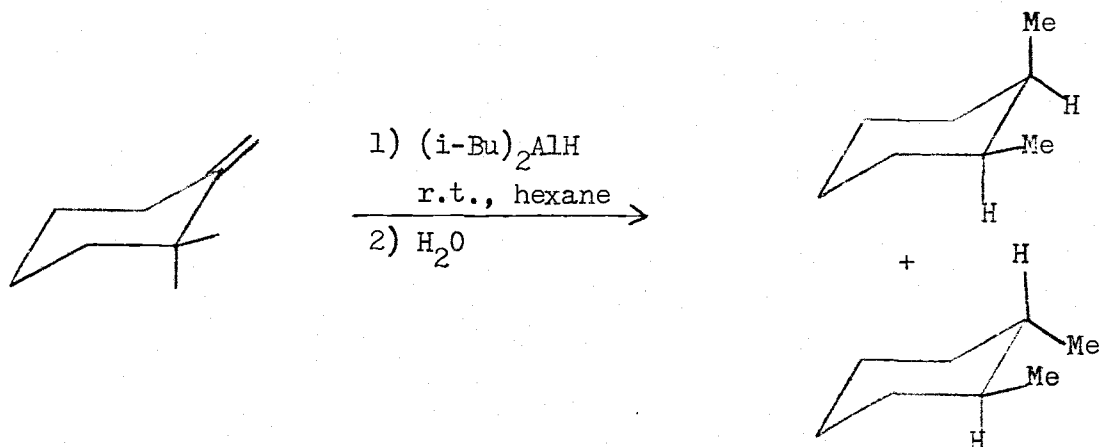
vinyllic proton resonance which integrated to one hydrogen.

Reaction 13 resembles reaction 4 and reaction 14 resembles reaction 9 in their constitutional selectivities. The higher yields for reactions 13 and 14 undoubtedly were a result of an increased retardation toward insertion exhibited by the disubstituted double bond which is exocyclic to a ring (89). Dehydroalumination of 89 would have eventually resulted in increased generation of 90 and



the products derived therefrom.

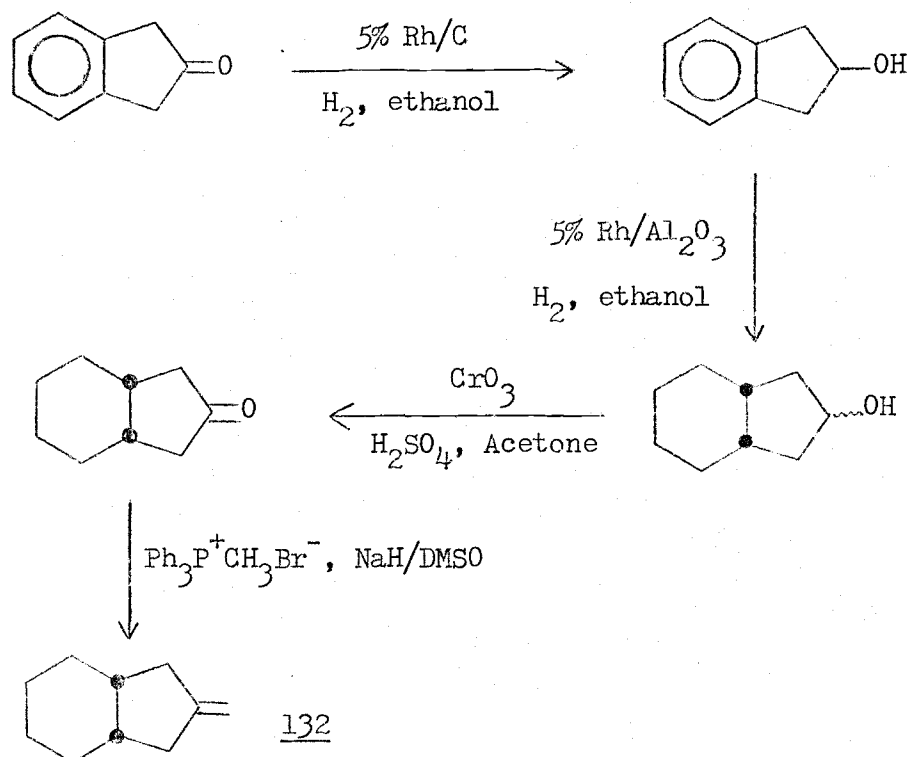
The stereoselectivities associated with reactions 13 and 14 differ markedly. Reaction 13 provided methylenecyclohexane bearing predominantly the cis- fused ring juncture. In contrast, the methylenedecalin obtained in reaction 14 possessed the trans-fused ring juncture in major quantity. In a control experiment 1-methylene-2-methylcyclohexane



was hydroaluminated with diisobutylaluminum hydride under kinetically controlled conditions to relinquish a 1 : 1 mixture of cis- and trans-1,2-dimethylcyclohexane. The hydroalumination did not distinguish equatorial from axial approach. Such a result does not permit one to state that the stereochemical dichotomy observed in reactions 13 and 14 cannot be explained in terms of a preferential and rate-determining hydroalumination followed by a rapid cyclization since no stereoisomer was produced in excess of 50% yield. Although the stereochemical results parallel the thermodynamic stabilities of the products (58), the overall kinetic rationale is not immediately apparent.

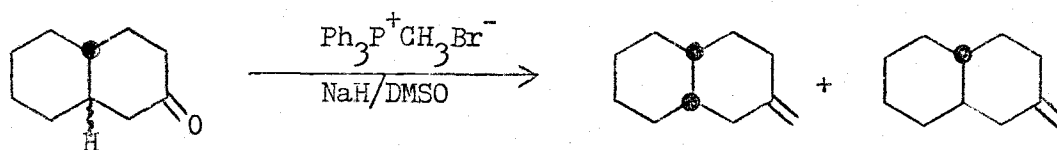
Substantiation of the structure of the major component in reaction 13 was achieved by independent synthesis as outlined in Scheme 26.

Scheme 26

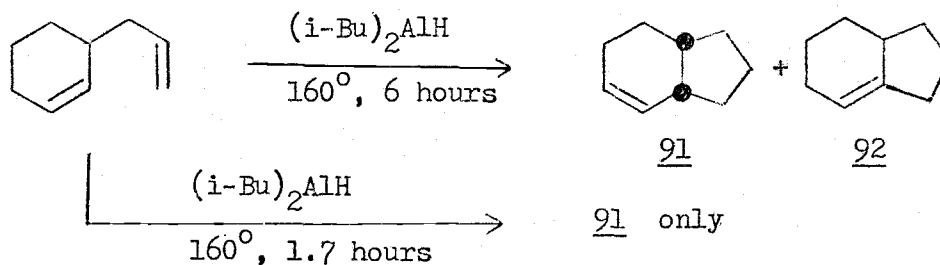


The minor product from reaction 13, trans-2-methylenedrindane, was identified by NMR spectral analysis only.

The products from reaction 14, cis- and trans-2-methylenedecalin, were assigned on the basis of NMR spectral analysis, elemental analysis and independent synthesis from a mixture of 2-decalones which was rich in the cis isomer. The isomers obtained from the Wittig reaction were separated by preparative scale GLC.

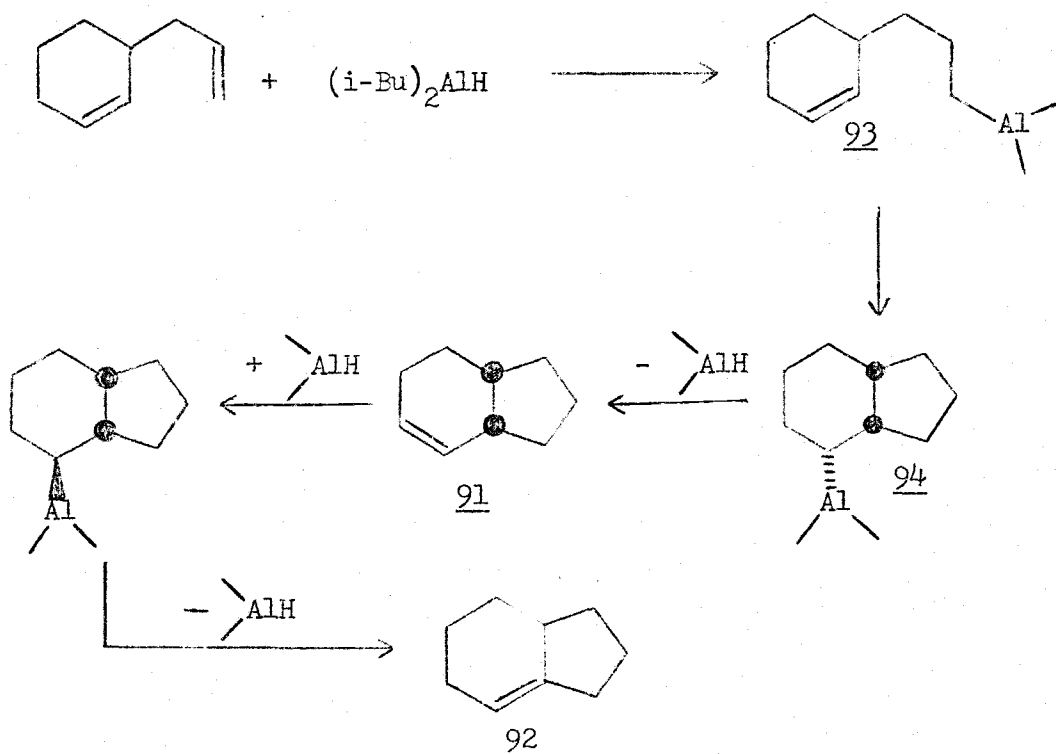


Over a relatively long reaction time, reaction 15 relinquished two major products, 91 and 92 in a ratio of 1 : 3 respectively, plus an unidentified trace component. However, when the reaction was

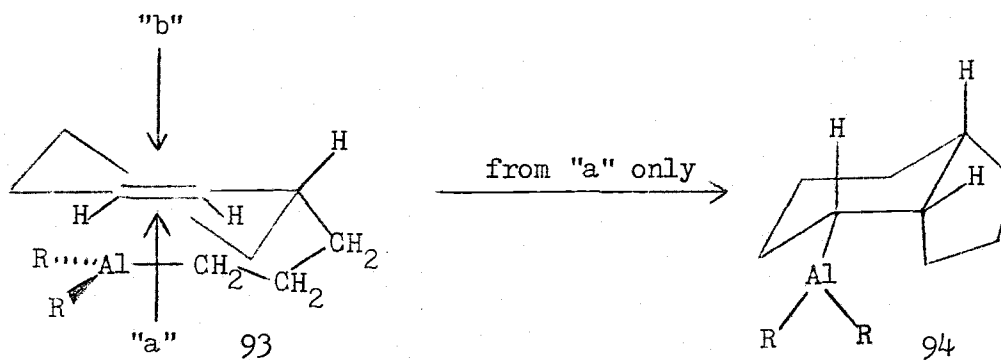


conducted over only 1.7 hour, the product consisted of solely 91 with considerable starting material remaining. It seems safe to surmise that olefin 91 was isomerized to 92 under the reaction conditions as shown in Scheme 26.

Scheme 26

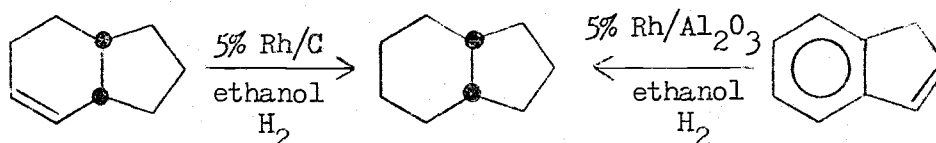


Since evidence is available which gives credence to the syn nature of the carbalumination reaction (56), the early formation of intermediate 94 seems a plausible pathway. In a related study (56), Eisch suggested exclusive carbalumination from direction "a" in initial intermediate 93. Models confirm the greater ease of syn



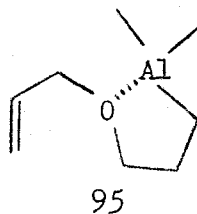
addition from the "a" direction. Normally organoaluminums would be expected to β -eliminate giving the more highly substituted olefin. However, the required synperiplaner arrangement of departing groups was only accessible to intermediate 94 for the formation of the less substituted olefin 91. Apparently, the β -elimination took place faster, to give 91, than the pyramidal inversion reportedly available to a carbon bonded to aluminum (59). As shown in Scheme 26, hydroalumination of the originally formed product 91 provided a route for isomerization to the more stable olefin 92 over longer reaction times.

The structure proposed for 91 was bolstered by catalytic reduction to cis-hydrindane, which was generated independently from indene in a similar fashion.



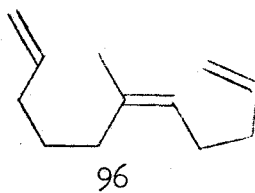
A few attempted cyclizations did not meet with much success. When diallylether was treated with a catalytic quantity of diisobutylaluminum hydride, no cyclic material was observed and only starting material was isolated. This may prove to be the exception rather than the rule since cyclizations are known to proceed in donor solvents, such as diethyl ether, THF, and triethylamine, even though such solvents generally retard the insertion reaction (60). Allyl ethers have been reported to undergo hydroalumination with ease but decompose to cyclopropane and aluminum alkoxides at elevated temperatures (61). In the case of diallyl ether, cyclization was probably dis-

couraged due to intramolecular complexation with the ether functionality (95).



The catalytic cyclization does not appear capable of effecting a simple 7-membered ring cyclization as evidenced from the apparent polymerization of 1,7-octadiene using diisobutylaluminum hydride.

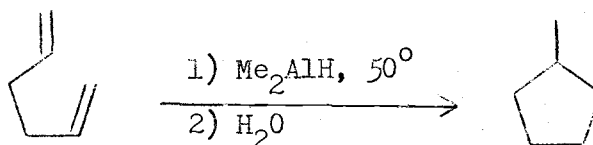
GLC analysis of the product mixture obtained from the reaction of 6-methyl-1,5,10-undecatriene (96) with a catalytic amount of diisobutylaluminum hydride revealed the creation of a multitude of products. None of these products was isolated and characterized, but undoubtedly



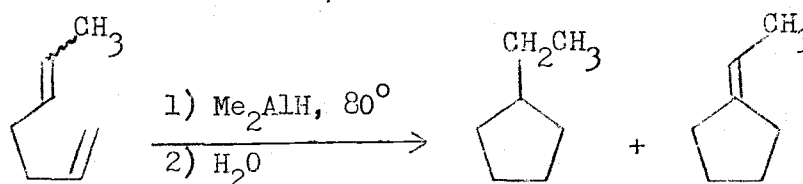
many arose from a dehydroalumination at an early stage prior to complete cyclization (as in reaction 9). It was this capricious mobility of the carbon-aluminum bond, both from which the cyclization ensued and at intermediate stages, that cast doubt on the utility of the catalytic process in organic synthesis. It appeared that conditions would have to be found that promoted the carbocyclizations at temperatures insufficient for dehydroalumination. This meant abandoning the catalytic process altogether at least with aluminum.

Reactivity patterns often change through alteration of steric and electronic factors. Initially, an attempt was made to enhance

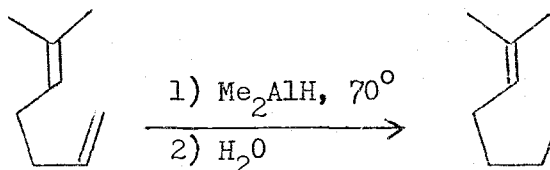
intramolecular insertion by reducing the bulkiness of the alkyl groups on the dialkylaluminum hydride. Dimethylaluminum hydride, prepared by a literature procedure (62), was used in a stoichiometric amount to smoothly cyclize 1,5-hexadiene at 50°C to methylcyclopentane in good yield. However, 1,5-heptadiene refused to experience any cyclization



at 50°C under similar conditions. At 80°C two products were obtained in a ratio of 2 : 1. Although the major component proved to be ethylcyclopentane, some dehydroalumination was evidenced by the production



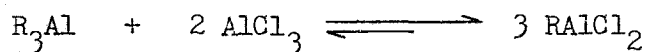
of considerable ethylenecyclopentane. Reaction of 6-methyl-1,5-heptadiene with one equivalent of dimethylaluminum hydride resulted in reduction of the terminal olefin but no cyclization. At this stage



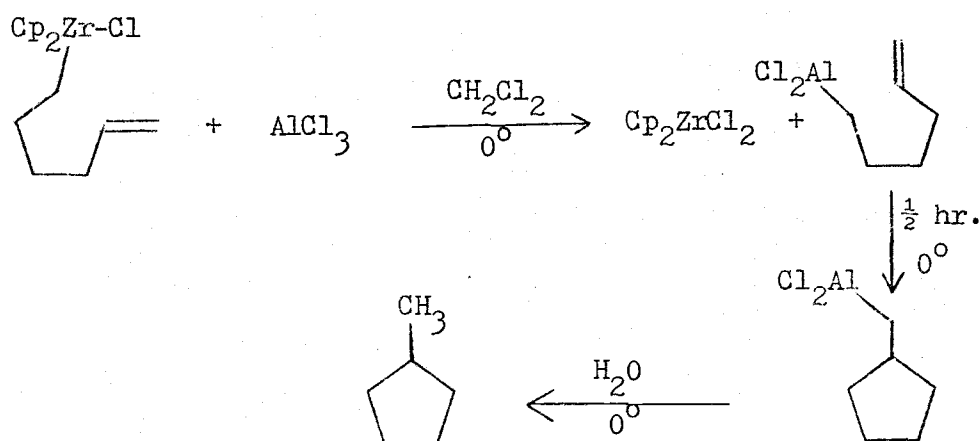
it became obvious that mere diminution of steric demands would not be adequate to achieve the synthetic objective.

The electronic properties of the aluminum atom could be modulated by replacement of the alkyl groups with electron withdrawing halogen atoms. The proportionation reaction between trialkylaluminum and

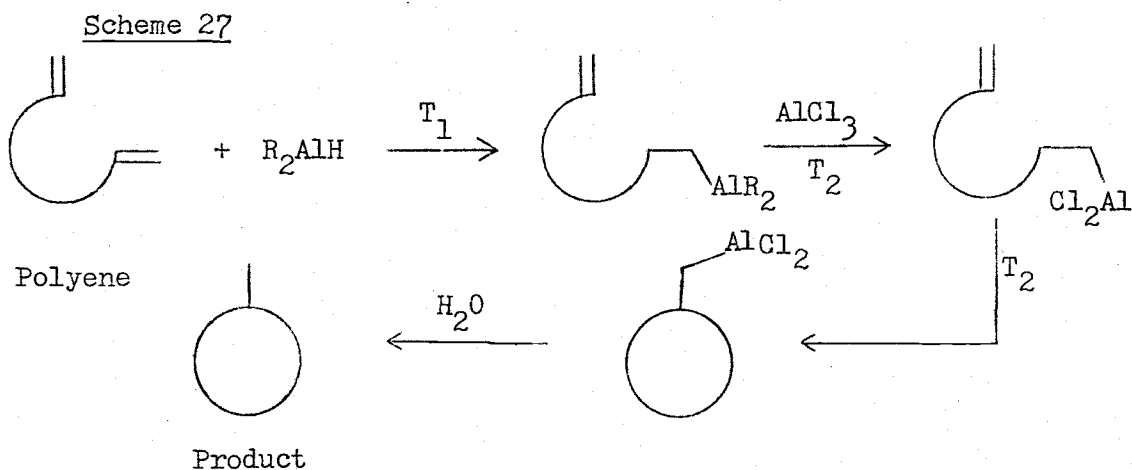
aluminum trichloride is known to reach an equilibrium in which alkylaluminum dichloride commands a concentration advantage (63).



Other methods for generating alkylaluminum dichloride exist. One example extracted from the research of J. Schwartz and coworkers (64) focused on the transmetalation reaction between zirconium and aluminum and also involved an actual carbocyclization at low temperature.

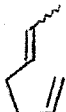
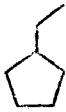

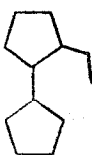

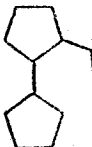
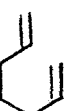



The intramolecular cyclization of alkenylaluminum dichloride reagents was explored by using the proportionation reaction to generate the desired aluminum reagent. The general transformation is outlined in Scheme 27.



Shown in Table 4 are conditions and results of stoichiometric aluminum cyclizations following the basic sequence depicted in Scheme 27.

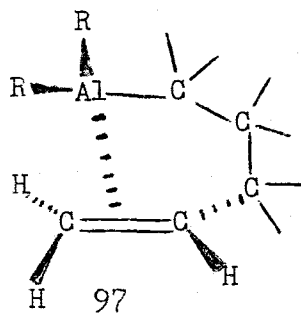
Table 4. Cyclization of Polyenes Using Dialkylaluminum Hydride and Aluminum Trichloride as Reagent

Reaction No	Starting Material	R_2AlH	$T_1(^{\circ}C)$	$T_2(^{\circ}C)$	Product (% Yield)
16		$(i-Bu)_2AlH$	35°	R.T.	 (76)
17		$(i-Bu)_2AlH$	60°	65°	 $(CH_2)_6CH_3$
18		Et_2AlH	60°	65°	 (81)
19		Et_2AlH	35°	60°	 (59)

The presence of chlorine atoms attached to the aluminum enhanced the cycloinsertion under mild enough conditions to avoid dehydroalumination even when a secondary alkylaluminum was the product (reactions 16 and 18). A combination of factors seem to be important in explaining this phenomenon.

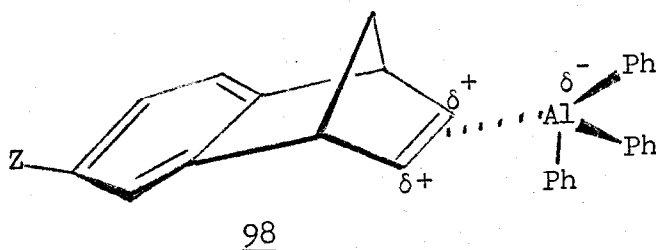
J.P. Oliver and coworkers (65), by NMR data in conjunction with cryoscopic molecular weight data, have proven that a number of trialkenylaluminum derivatives exist in monomeric form with the aluminum atom intramolecularly coordinated to the double bond, as delineated in

the case of tri(4-pentenyl)aluminum (97). Cryoscopic data demonstrated the dimeric nature of the corresponding saturated trialkyl-



aluminum compounds. Such coordination apparently is also important in the intermolecular insertion since these reactions have been reported to proceed only through the monomeric form of the trialkylaluminum reagent employed (66). The dimeric form cannot provide the vacant site on aluminum for coordination to take place.

In the addition reaction of triphenylaluminum to the double bond of 6-substituted benzonorbornadiene, a ρ value of -0.66 was determined from kinetic studies (67). Partial rate factors indicated that the electrophilic attack passed through a rate-determining π -complex transition state 98. Species 98 has partial positive charge residing

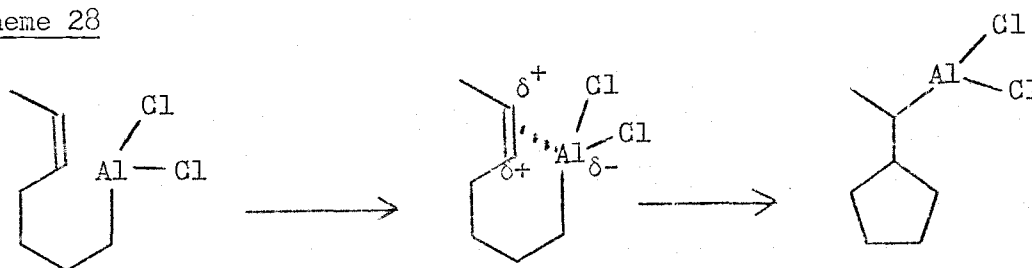


on the carbons of the double bond and partial negative charge on the aluminum.

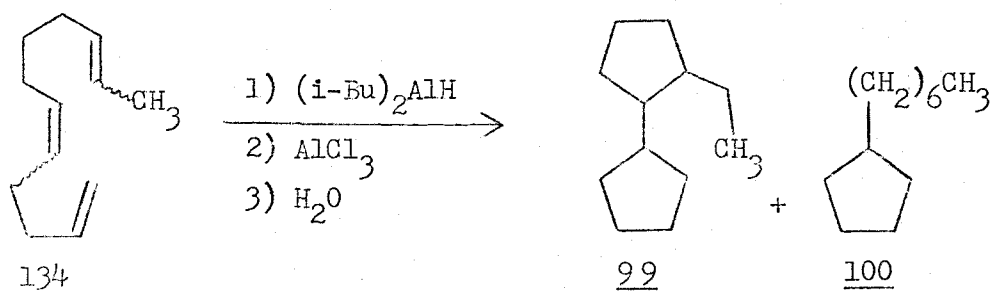
The Lewis-acid strength of aluminum towards external base (ethers

or amines) is enhanced by bonding to chlorine (68). Formation of a π -complex, either as a transition state or an intermediate, in which negative character is placed on aluminum would appear early on the cycloinsertion potential energy surface and would be encouraged by contiguous electron-withdrawing chlorine atoms. The increase in electrophilicity of the aluminum would be expected to result in an increased rate of cyclization (Scheme 28).

Scheme 28

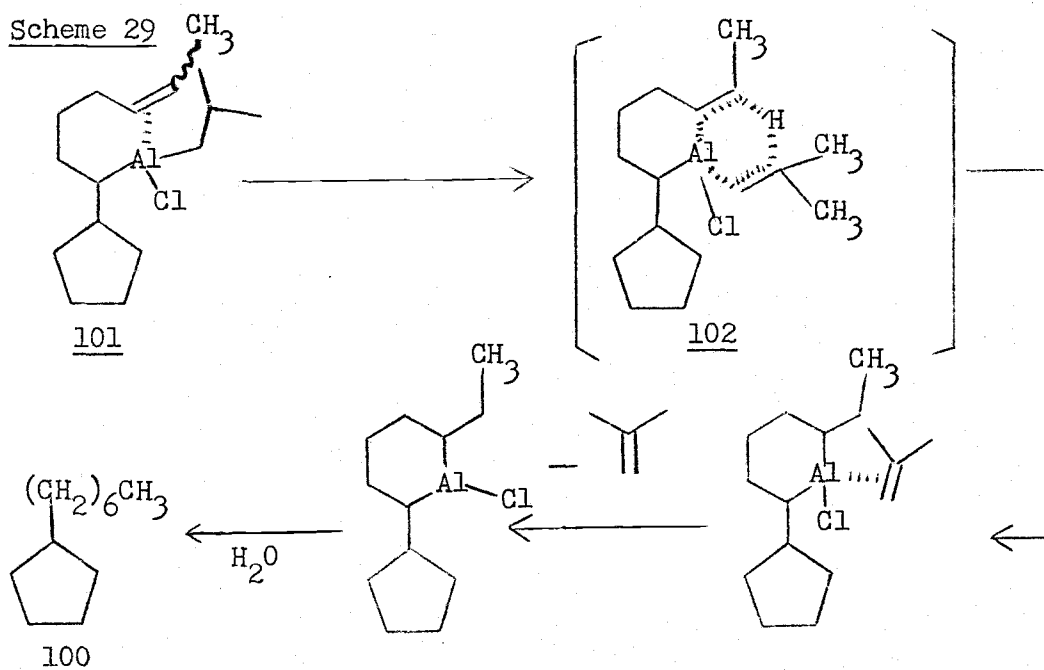


Reaction 16 revealed that the cyclization from a primary to a secondary aluminum reagent could be accomplished without any dehydroalumination by addition of aluminum chloride. Reaction 17 represented an extension of the use of aluminum chloride to accomplish a double intramolecular insertion which incorporated cyclization from a secondary to another secondary aluminum reagent without dehydroalumination. This result is of considerable significance as far as consummating the research objectives is concerned. Two products were produced in



reaction 17. The structures of 99 and 100 were assigned on the basis of NMR, mass spectral, and elemental analyses. The mass spectrum of 99 indicated a molecular weight of 166 and, in conjunction with the elemental analysis, a molecular formula of $C_{12}H_{22}$. The NMR spectrum of this material unveiled no vinylic or allylic hydrogen resonance but rather typical signals expected for a saturated hydrocarbon with a triplet at $\delta=0.9$. Compound 100 produced an NMR spectrum nearly identical to that of an authentic sample of n-pentylcyclopentane. A molecular weight of 168 was indicated from the mass spectrum.

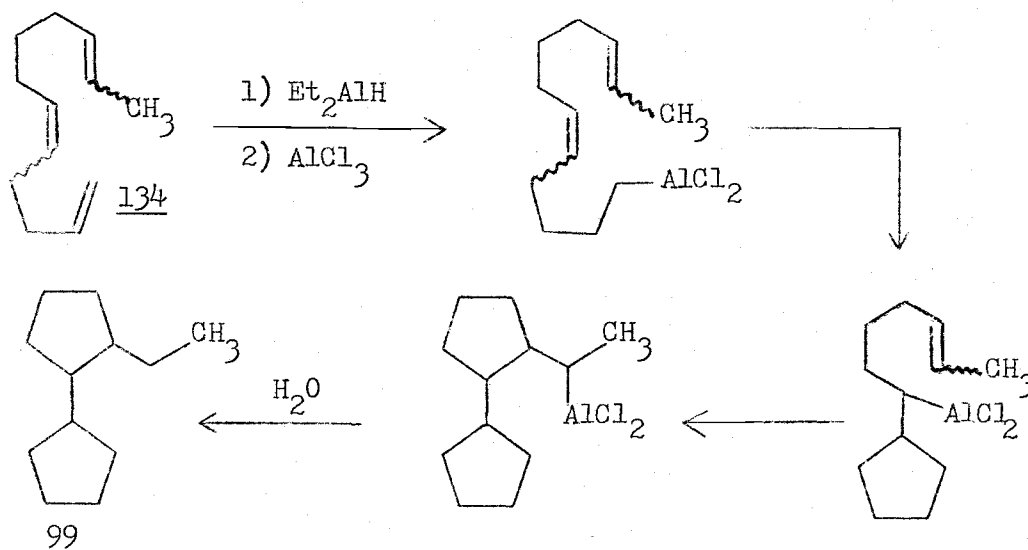
The generation of compound 100 was something of a surprise. The reaction conditions were mild enough that dehydroalumination to provide isobutylene and an additional equivalent of hydride, which could readily have reduced the double bond (44), should not have occurred. The reduction can be rationalized by incorporating the isobutyl group in a hydride transfer process (Scheme 29). The increased electrophilic



tendency of the aluminum, due to the contiguous chlorine might activate the olefinic unit to favor reception of the hydride. A sizable concentration of precursor 101 would be expected to be in equilibrium with other species in solution. The 6-centered transition state 102 is analogous to those proposed to effect very similar reductions of carbonyl compounds using hindered alkylaluminum and magnesium reagents (69).

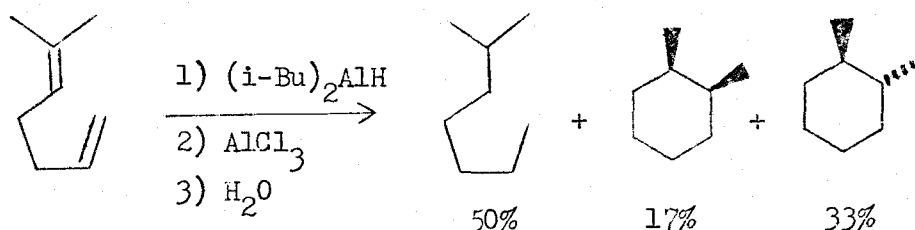
In order to avoid the undesired olefin reduction, it seemed prudent to use a dialkylaluminum hydride in which the alkyl group would not relinquish a β hydrogen as readily as the isobutyl group. Triethylaluminum is known to be more thermally stable to the loss of ethylene than triisobutylaluminum is to the loss of isobutylene (70). As disclosed in reaction 18, the use of diethylaluminum hydride eliminated the troublesome reduction and resulted in the synthesis of 99 in high yield (Scheme 30)

Scheme 30



As shown in reaction 19, 1,6-heptadiene cyclized in reasonably good yield to methylcyclohexane. This transformation was somewhat more efficient than that observed in the catalytic reaction.

Three products were obtained from the reaction of 6-methyl-1,5-heptadiene with diisobutylaluminum hydride, followed by the addition of aluminum chloride, and finally water. The predominant product had



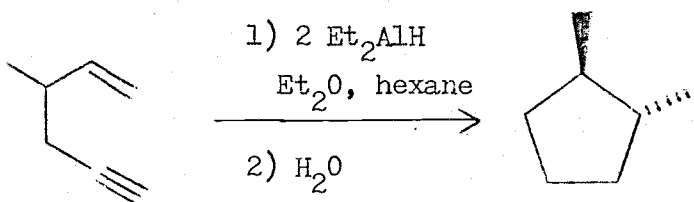
both double bonds reduced without cyclization, presumably by the same hydride shift mechanism outlined earlier in Scheme 29. The mechanism for formation of the minor constituents, cis- and trans-1,2-dimethylcyclohexane, remains elusive. This reaction was not attempted using diethylaluminum hydride.

The use of diethylaluminum hydride in combination with aluminum chloride permitted the easy production of 5- and 6-membered rings without the destruction of constitutional and stereochemical selectivity inherent in the dehydroalumination process. However, no adequate means has been developed for controlling the site of the initial carbon-aluminum bond. Since this is the site from which the multicyclization will ensure, its location will determine the eventual constitution of the product.

It has been reported that hydroalumination of 1-alkynes can be greatly influenced by the choice of solvent; mono-, di- or trihydroalumination products were obtained by carrying out the reaction

Incorporation of the triple bond ensures that cyclization would be initiated from the site which uniquely leads to the desired product. The absence of such control would result in the production of a plethora of constitutional isomers.

Only one reaction has been performed using this concept. The reaction represents a small portion of a much larger stereochemical study. The cyclization of 3-methyl-1-hexen-5-yne with two equivalents of diethylaluminum hydride provided, after quenching with water, trans-1,2-dimethylcyclopentane.



IV. Experimental

General Laboratory Procedures and Conditions

All temperatures are uncorrected. Nuclear magnetic resonance (NMR) spectra were obtained on Varian EM-360 (60 MHz) and Varian HA-100 (100 MHz) spectrometers. Unless otherwise specified, tetramethylsilane was used as an internal reference, and the following abbreviations were used: s = singlet, d = doublet, t = triplet, q = quartet, J = coupling constant in Hertz. Infrared (IR) spectra were obtained on Perkin-Elmer 137 sodium chloride spectrophotometer. Low resolution mass spectra were obtained from an Atlas CH7 instrument using a 70 eV excitation potential. High resolution mass spectra were obtained from a CEC 110B instrument.

Gas-liquid chromatography (GLC) analyses were carried out on a Varian 920 (thermal conductivity detector, using $\frac{1}{4}$ in. columns) and a Hewlett-Packard 5720A (thermal conductivity detector, using $\frac{1}{8}$ in. columns). The chromatograms were recorded by either a Hewlett-Packard 7123A recorder, a Linear Instruments 445 recorder, or a Sargent-Welch XKR recorder.

In cases where the products were hydrocarbons, a hydrocarbon internal standard was added. Equal molar responses were assumed using the thermal conductivity detector. All peak areas needed to calculate yields were determined by use of a Hewlett-Packard integrator model 3373B, or by cutting out and weighing.

Analytical and preparative GLC work was conducted using the following columns:

- Column A: SE-30 (25%) on Chromosorb P, $\frac{1}{4}$ in. x 4 ft.
- Column B: TCEP (5%) on Chromosorb P, $\frac{1}{4}$ in. x 6 ft.
- Column C: SE-30 (3%) on Chromosorb P, $\frac{1}{4}$ in. x 6 ft.
- Column D: SE-30 (20%) on Chromosorb P, $\frac{1}{4}$ in. x 6 ft.
- Column E: SE-30 (10%) on Chromosorb P, $\frac{1}{4}$ in. x 6 ft.
- Column F: UCW-982 (10%) on WAW-DMCS, $\frac{1}{8}$ in. x 1.7 ft.
- Column G: OV-101 (10%) on Chromosorb P, $\frac{1}{4}$ in. x 5 ft.
- Column H: Carbowax (20%) on Chromosorb P, $\frac{1}{2}$ in. x 20 ft.
- Column I: TCEP (5%) on Chromosorb P, $\frac{1}{2}$ in. x 12 ft.
- Column J: OV-17 (5%) on Chromosorb P, $\frac{1}{4}$ in. x 6 ft.
- Column K: OV-101 (3%) on Chromosorb P, $\frac{1}{4}$ in. x 6 ft.
- Column L: SE-30 (20%) on Chromosorb P, $\frac{1}{8}$ in. x 3 ft.
- Column M: SE-30 (20%) on Chromosorb P, $\frac{1}{4}$ in. x 15 ft.
- Column N: OV-101 (10%) on Chromosorb P, $\frac{1}{8}$ in. x 3 ft.
- Column O: Squalane (7%) on WAW-DMCS, $\frac{1}{8}$ in. x 30 ft.

All elemental analyses of analytical samples were performed by Galbraith Laboratories, Inc. (Galbraith Laboratories, Inc., P.O. Box 4187, Knoxville, Tennessee).

General Approach for Preparation of Starting Materials

Because the study merely concerned model systems, more emphasis was placed on ease of preparation rather than efficiency in the synthesis of starting materials. Most of the simple dienes that were not purchased were prepared by coupling of an appropriate allylic bromide and Grignard reagent, for example, 3-allylcyclohexene from allylmagnesium bromide and 3-bromocyclohexene; 1,6-octadiene from 3-butenylmagnesium bromide and 1-bromo-2-butene; 7-methyl-1,6-octadiene from 3-butenylmagnesium bromide and 1-bromo-3-methyl-2-butene. The straightforward preparation of 1-allyl-2-methylenecyclohexane and 1-(3-butenyl)-2-methylenecyclohexane was accomplished from the corresponding ketones and methyltriphenylphosphonium bromide under normal Wittig reaction conditions. The individual syntheses of the starting materials are described in the following pages.

cis- and trans-1,6-Octadiene (103)

A solution of 3-butenylmagnesium bromide was prepared by the dropwise addition of 22.0 g (0.10 mole) of 4-bromo-1-butene in 30 mL of anhydrous diethyl ether to 15 g (0.63 mole) of magnesium turnings in 300 mL of anhydrous ether. The flask contents were maintained at 0° and the reaction was conducted under a nitrogen atmosphere. The flask contents were stirred at 0° for an additional two hours after the addition. The Grignard solution was decanted from the excess magnesium metal into another flask under a nitrogen atmosphere.

A solution consisting of 22.0 g (0.10 mole) of 1-bromo-2-butene

in an equal volume of anhydrous ether was added dropwise to the Grignard solution. The reaction was subjected to refluxing for six hours following the addition. The flask was immersed in an ice bath followed by a cautious dropwise addition of saturated aqueous ammonium chloride solution. The ethereal solution was washed and dried over anhydrous magnesium sulfate. After a filtration process, most of the ether was removed by distillation through a short Vigreux column. The pot residue was vacuum transferred and the liquid collected was analyzed by GLC using column A at 90°. Two products were present in a ratio of 1 : 1.5 . The major product of 2.5 minutes retention time was isolated by preparative scale GLC under the same conditions. The product was assigned as a mixture of cis- and trans-1,6-octadiene; NMR (CCl₄) δ 5.25-5.96 (m, 3H), 4.80-5.10 (m, 2H), 1.80-2.31 (m, 4H), 1.30-1.75 (m, 5H).

The structure of the minor product (retention time in GLC analysis: 1.8 minutes) was assigned as 3-methyl-1,6-heptadiene; NMR (CCl₄) δ 5.50-6.00 (m, 2H), 4.80-5.10 (m, 4 H), 1.95-2.50 (m, 3H), 1.20-1.50 (q, 2H), 0.98-1.10 (d, J=3Hz, 3H).

6-Hepten-2-one (104)

Thirty-eight grams (0.42 mole) of potassium hydride (22% in mineral oil) was put in a 3-necked round bottomed flask equipped with an addition funnel and a condenser. The flask was flushed with nitrogen, kept under a nitrogen atmosphere, and 200 mL of anhydrous THF was introduced. Twenty-five grams (0.223 mole) of 3-methyl-1,6-hexadien-3-ol, which was prepared by the method of H. Fleischaker et.al. (74),

was dissolved in 100 mL of anhydrous THF and added dropwise to the KH-THF mixture at room temperature. The final solution was refluxed for a period of ten hours.

The solution was cooled to room temperature, and 100 mL of saturated aqueous ammonium chloride solution was added cautiously. The organic layer was separated and washed with saturated sodium chloride solution. The aqueous layer was extracted once with 50 mL of THF and the THF solutions were combined. Most of the THF was removed by simple distillation at atmospheric pressure. The residue was subjected to simple vacuum distillation. The pure product, b.p. 45° (20 mm), was obtained in a yield of 72% (0.161 mole); NMR (CCl_4) δ 5.50-5.95 (m, 1H), 4.85-5.10 (m, 2H), 2.30-2.50 (t, $J = \text{Hz}$, 2H), 1.90-2.20 (s on m, 5H), 1.50-1.80 (m, 2H).

(4-Pentenyl)triphenylphosphonium Iodide (105)

In a 500 mL round bottomed flask, 31.4 g (0.12 mole) of triphenylphosphine was dissolved in 250 mL of benzene. About 5 mL of benzene was distilled off under atmospheric pressure. Twenty grams (0.1 mole) of 5-iodo-1-pentene was added to the triphenylphosphine-benzene solution. The reaction was refluxed for 18 hours. A white precipitate was filtered in a Büchner funnel and washed several times with 15-mL portions of anhydrous benzene. It was dried in a high vacuum desiccator and weighed 38 g (0.08 mole); NMR (CDCl_3) δ 7.70-7.95 (m, 15H), 5.55-5.95 (m, 1H), 4.95-4.20 (m, 2H), 3.50-3.85 (m, 2H), 2.35-2.60 (m, 2H), 1.60-2.00 (m, 2H).

cis- and trans-6-Methyl-1,5,10-
undecatriene (96)

Sodium hydride (3.5 g, 0.073 mole), a 50% suspension in mineral oil, was washed several times with anhydrous ether under a nitrogen atmosphere, 80 mL of anhydrous DMSO (distilled from CaH) was added and the mixture was heated to 80° for 45 minutes under a nitrogen atmosphere. The resulting mixture was cooled to room temperature, 32 g (0.07 mole) of (4-pentenyl)triphenylphosphonium iodide (105) dissolved in 100 mL of warm anhydrous DMSO was added to the NaH-DMSO, The resulting red solution was stirred at room temperature for 30 minutes. A solution of 7.5 g (0.065 mole) of 6-hepten-2-one (104) in an equal volume of DMSO was added in a dropwise manner. The final solution was stirred at room temperature for 18 hours and 100 mL of water was added. The mixture was extracted three times with 50-mL portions of pentane. The pentane extracts were combined and washed once with 50 mL of saturated aqueous solution of sodium chloride and then dried over anhydrous magnesium sulfate. Most of the pentane was removed by simple distillation at atmospheric pressure and the pot residue was subjected to simple vacuum distillation. A colorless liquid, b.p. 50° (10 mm), was obtained in a quantity of 5.0 g (0.031 mole). GLC analysis using column C at 120° showed the product was a mixture of cis- and trans-6-methyl-1,5,10-undecatriene; NMR (CCl₄) δ 5.55-6.00 (m, 2H), 4.80-5.40 (m, 5H), 1.89-2.20 (m, 8H), 1.58-1.80 (m, 3H), 1.30-1.60 (m, 2H).

1,6-Heptadien-4-ol (106)

A solution of allylmagnesium bromide was prepared from 121 g (1.0 mole) of allylbromide, 32 g (1.5 mole) of magnesium turnings in 500 mL of anhydrous diethyl ether under a nitrogen atmosphere. The allylbromide was dissolved in an equal volume of anhydrous ether and added over a six-hour period to the magnesium turnings maintained at ice bath temperature. After completion of the addition, the Grignard solution was stirred for two hours at ice bath temperature. Dropwise addition of 37 g (0.50 mole) of ethyl formate was accomplished while the Grignard solution was immersed in an ice bath. After being stirred for an additional two hours, the cold reaction mixture was quenched by the cautious addition of cold saturated aqueous ammonium chloride solution. The ether layer was washed with saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered. Most of the ether was removed by use of a rotary evaporator. Simple vacuum distillation of the resultant liquid provided 32 g (0.3 mole) of 1,6-heptadien-4-ol (106) b.p. $34-36^{\circ}$ (4 mm). The NMR spectrum of 106 was identical to that of an authentic sample; NMR (CCl_4) δ 5.60-6.06 (m, 2H), 4.93-5.24 (m, 4H), 3.49-3.78 (m, 1H), 2.01-2.46 (m, 4H), 1.95 (s, 1H, shifted to $\delta=1.60$ at 60°)

4-Chloro-1,6-heptadiene (107)

A mixture of 35 g (0.13 mole) of triphenylphosphine and 13 g (0.12 mole) of 1,6-heptadien-4-ol (106) was dissolved in 300 mL of anhydrous carbon tetrachloride. The solution was refluxed for 14 hours

under a nitrogen atmosphere. A white precipitate formed while the solution was refluxed. The mixture was cooled to room temperature and 300 mL of pentane was added to precipitate the bulk of the triphenylphosphine oxide. The mixture was filtered, and the filtrate was subjected to simple distillation at atmospheric pressure to remove the pentane.

The pot residue was subjected to simple vacuum distillation. Eight grams (0.061 mole) of 4-chloro-1,6-heptadiene (107), b.p. 42° (2 mm), was obtained; NMR (CCl_4) δ 5.64-6.10 (m, 2H), 5.50-5.30 (m, 4H), 3.75-4.05 (5 peaks, $J=6\text{Hz}$, 1H), 2.40-2.65 (m, 4H). Anal. Calcd for $\text{C}_7\text{H}_{11}\text{Cl}$: C, 64.37; H, 8.49; Cl, 27.14. Found: C, 64.60; H, 8.69; Cl, 26.84.

4-Allyl-1,6-heptadiene (108)

Magnesium turnings (2 g; 0.09 mole) in 100 mL of diethyl ether under nitrogen was activated by addition of 1 g of ethylbromide followed by a small piece of iodine. The mixture was stirred at room temperature until vigorous reaction was observed. To the reaction vessel was added dropwise 5 g (0.04 mole) of 4-chloro-1,6-heptadiene (107). After the addition of the chloride, the mixture was stirred under refluxing conditions for 4 days. The organometallic was decanted from the excess metal under a nitrogen atmosphere. Following the addition of 5 g (0.04 mole) of allylbromide, the mixture was stirred under reflux conditions for a period of 24 hours.

The reaction vessel was immersed in an ice bath, and saturated aqueous ammonium chloride was added dropwise. The ether layer was washed with saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered. After the ether was

removed by simple distillation at atmospheric pressure, the higher boiling material (3.1 g) was vacuum transferred. Preparative scale GLC using column D at 130° resulted in the collection of 1.1 g (0.01 mole) of 4-allyl-1,6-heptadiene (retention time 3.5 minutes); NMR (CCl_4) δ 5.52-5.98 (m, 3H), 4.82-5.20 (m, 6H), 1.93-2.28 (m, 6H), 1.53 (heptet, $J=7\text{Hz}$, 1H). Anal. Calcd for $\text{C}_{10}\text{H}_{16}$: C, 88.16; H, 11.84. Found: C, 87.96; H, 11.74.

1,8-Nonadien-5-ol (109)

An ethereal solution of 3-butenylmagnesium bromide was prepared from 12 g (0.089 mole) of 4-bromo-1-butene and 3.4 g (0.14 mole) of magnesium turnings at 0° under a nitrogen atmosphere.

To the Grignard reagent, 7 g (0.083 mole) of 4-pentenal [prepared by the method of A. Voila et.al. (75)] diluted with 10 mL of anhydrous ether was added dropwise. The mixture was stirred for three hours at 0° after the addition was completed. The reaction was worked-up by the dropwise addition of 100 mL of saturated aqueous ammonium chloride solution. The aqueous layer was washed twice with 50-mL portions of diethyl ether. The ethereal solutions were combined, dried over anhydrous magnesium sulfate, and filtered. Most of the solvent was removed by use of a rotary evaporator and the remaining liquid was subjected to simple vacuum distillation which resulted in the isolation of 8.1 g (0.058 mole) of a clear liquid b.p. 65° (3 mm). This liquid was assigned the structure of 1,8-nonadien-5-ol; NMR (CCl_4) δ 5.50-6.02 (m, 2H), 4.80-5.21 (m, 4H), 3.54 (5 peaks, $J=6\text{Hz}$, 1H), 2.52 (s, 1H), 1.91-2.71 (m, 4H), 1.33-1.75 (m, 4H). Anal. Calcd for

$C_9H_{16}O$: C, 77.09; H, 11.50; O, 11.41 . Found: C, 76.99; H, 11.46.

1,8-Nonadien-5-one (110)

Chromic acid solution was prepared by cautious dropwise addition of 5 mL of concentrated sulfuric acid to a solution containing 7.0 g (0.07 mole) of chromium trioxide dissolved in 25 mL of water. The chromic acid was added dropwise to a well-stirred solution consisting of 7.0 g (0.05 mole) of 1,8-nonadien-5-ol (109) in 100 mL of acetone. The temperature of the reaction mixture was maintained at under 25° by use of a cold water bath. The addition of the chromic acid solution was stopped after the appearance of the orange color of the reagent which persisted for 25 minutes. The excess oxidizing agent was destroyed by the addition of 1 mL of isopropyl alcohol. The acetone solution was decanted into another flask leaving behind residual green salts. Neutralization of the solution was accomplished by addition of solid sodium bicarbonate. The mixture was filtered and most of the acetone was removed by means of a rotary evaporator. To the material remaining was added 100 mL of ether. The ethereal solution was washed twice with 50-mL portions of saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered. Most of the solvent was removed by use of a rotary evaporator. The remaining liquid was subjected to simple vacuum distillation which provided 4.5 g (0.033 mole) of clear liquid b.p. 54° (3 mm). The structure of the product was assigned 1,8-nonadien-5-one; NMR (CCl_4) δ 5.57-6.00 (m, 2H), 4.83-5.13 (m, 4H), 2.12-2.60 (m, 8H). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21; O, 11.58 . Found: C, 78.00; H, 10.18 .

5-Methylene-1,8-nonadiene (111)

A solution of methylenetriphenylphosphorane in 100 mL of warm DMSO was prepared by the standard Wittig reaction procedure using 3.0 g (0.06 mole) of sodium hydride (50% suspension in mineral oil) and 20.0 g (0.06 mole) of methyltriphenylphosphonium bromide under a nitrogen atmosphere.

To the ylid was added 6.0 g (0.04 mole) of 1,8-nonadien-5-one (110) and the flask contents were stirred for 1.5 hours at room temperature. The solution was poured into 100 mL of cold water. The resulting mixture was extracted three times with 30-mL portions of pentane. The pentane solution was washed once with 50 mL of saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered. Most of the pentane was removed by means of a rotary evaporator. The remaining liquid was subjected to vacuum transfer from which 3.85 g (0.028 mole) of pure 5-methylene-1,8-nonadiene was isolated by preparative scale GLC using column E at 90°; NMR (CCl_4) δ 5.58-6.00 (m, 2H), 4.85-5.15 (m, 4H), 4.74 (s, 2H), 1.96-2.39 (m, 8H). Anal. Calcd for $\text{C}_{10}\text{H}_{16}$: C, 88.16; H, 11.84. Found: C, 88.41; H, 11.80.

Methylenecycloheptane (112)

A solution of methylenetriphenylphosphorane in 200 mL of anhydrous DMSO was prepared by the standard Wittig reaction procedure using 4.0 g (0.128 mole) of sodium hydride (50% suspension in mineral oil) and 32 g (0.04 mole) of methyltriphenylphosphonium bromide under

a nitrogen atmosphere.

To the ylid was added 7.0 g (0.06 mole) of cycloheptanone. The mixture was stirred for three hours at room temperature after the addition. Fifty milliliters of clear liquid was vacuum transferred from the reaction mixture and collected in a cold trap cooled by a Dry ice-acetone bath. The distillate was dissolved in 100 mL of cold water and extracted three times with 30-mL portions of pentane. The pentane extracts were combined and washed once with 50 mL of saturated aqueous sodium chloride solution. Pentane was removed by simple distillation under atmospheric pressure. The product was obtained by simple distillation at atmospheric pressure, b.p. 120° , in a quantity of 5.5 g (0.05 mole); NMR (CCl_4) δ 4.65 (broad s, 2H), 2.15-2.40 (broad s, 4H), 1.44-1.76 (broad s, 8H). Anal. Calcd for C_8H_{14} : C, 87.19; H, 12.81. Found: C, 86.85; H, 13.19.

1,9-Decadien-5-ol (113)

This substance was prepared from the reaction of 4-pentenyl-magnesium bromide [prepared from 20 g (0.14 mole) of 5-bromo-1-pentene and 6.4 g (0.27 mole) of magnesium turnings in 100 mL of anhydrous diethyl ether] and 11.6 g (0.13 mole) of 4-pentenal in a manner analogous to the preparation of 1,8-nonadien-5-ol (109).

Vacuum distillation afforded 14.5 g (0.094 mole) of clear liquid b.p. $85-93^{\circ}$ (3-4 mm); NMR (CCl_4) δ 5.57-6.02 (m, 2H), 4.83-5.14 (m, 4H), 3.40-3.88 (m, 2H), 1.85-2.30 (m, 4H), 1.20-1.74 (m, 6H). Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}$: C, 77.87; H, 11.75; O, 10.38. Found: C, 77.76; H, 11.80.

1,9-Decadien-5-one (114)

The reaction procedure involved the oxidation of 10.0 g (0.065 mole) of 1,9-decadien-5-ol (113) under the same conditions employed in the preparation of 1,8-nonadien-5-one (110).

The product (6.5 g; 0.04 mole) was isolated by simple vacuum distillation b.p. 65-72° (0.5-1.0 mm); NMR (CCl₄) δ 5.52-6.00 (m, 2H), 8.84-5.16 (m, 4H), 1.90-2.58 (m, 8H), 1.46-1.82 (m, 2H). Anal. Calcd for C₁₀H₁₆O: C, 78.91; H, 10.59; O, 10.50. Found: C, 78.75, H; 10.58.

5-Methylene-1,9-decadiene (115)

Following the reaction procedure described for the preparation of 5-methylene-1,8-nonadiene (111), 4.0 g (0.03 mole) of 5-methylene-1,9-decadiene was obtained by simple vacuum distillation b.p. 45° (2 mm) from 6.0 g (0.04 mole) of 1,9-decadien-5-one (114). The NMR spectrum was consistent with the assigned structure. NMR (CCl₄) δ 5.57-6.00 (m, 2H), 4.84-5.16 (m, 4H), 4.72 (s, 2H), 1.92-2.34 (m, 8H), 1.34-1.70 (m, 2H). Anal. Calcd for C₁₁H₁₈: C, 87.94; H, 12.06. Found: C, 87.97; H, 11.95.

1,10-Undecadien-6-ol (116)

A solution of 4-pentenylmagnesium bromide was prepared from 22.0 g (0.148 mole) of 5-bromo-1-pentene and 5.5 g (0.226 mole) of magnesium turnings in 200 mL of anhydrous diethyl ether in the same fashion as described for the preparation of 3-butenylmagnesium bromide.

To the Grignard solution maintained at 0° was added dropwise 5.47 g (0.074 mole) of ethyl formate. The mixture was stirred for

1.5 hours at 0° after completion of addition and then 100 mL of saturated aqueous ammonium chloride solution was added dropwise. The organic layer was washed once with saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered. After removal of solvent by means of a rotary evaporator, the remaining liquid was vacuum distilled. A clear liquid (11.85 g; 0.07 mole) was obtained b.p. $90-95^{\circ}$ (3 mm), whose NMR spectrum confirmed the structure as 1,10-undecadien-6-ol (116); NMR (CCl_4) δ 5.55-6.00 (m, 2H), 4.83-5.16 (m, 4H), 3.33-3.72 (m, 1H), 2.64 (broad s, 1H), 1.86-2.28 (m, 4H), 1.18-1.72 (m, 8H). Anal. Calcd for $\text{C}_{11}\text{H}_{20}\text{O}$: C, 78.51; H, 11.98; O, 9.51. Found: C, 78.46; H, 11.94.

1,10-Undecadien-6-one (117)

The same procedure employed in the oxidation of 1,8-nonadien-5-ol (109) to 1,8-nonadien-5-one (110) was used. The reaction resulted in the conversion of 11.0 g (0.07 mole) of 1,10-undecadien-6-ol (116) into 9.3 g (0.056 mole) of 1,10-undecadien-6-one (117). The product was purified by simple vacuum distillation b.p. $75-80^{\circ}$ (3 mm): NMR (CCl_4) δ 5.52-5.98 (m, 2H), 4.52-4.18 (m, 4H), 2.31 (t, $J=6.5\text{Hz}$, 4H), 1.89-2.18 (m, 4H), 1.45-1.82 (m, 4H). Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}$: C, 79.41; H, 10.91; O, 9.68. Found: C, 79.25; H, 10.86.

6-Methylene-1,10-undecadiene (118)

The standard procedure for the Wittig reaction for the preparation of 5-methylene-1,8-nonadiene (111) was used to convert 7.5 g (0.05 mole) of 1,10-undecadien-6-one (117) into 5.3 g (0.03 mole) of

6-methylene-1,10-undecadiene (118). In the reaction, 100 mL of anhydrous DMSO, 3.5 g (0.07 mole) of sodium hydride (50% suspension in mineral oil), and 25 g (0.071 mole) of methyltriphenylphosphonium bromide were used. The product was purified by preparative scale GLC using column C at 110°; NMR (CCl_4) δ 5.55-6.00 (m, 2H), 4.83-5.10 (m, 4H), 4.69 (s, 2H), 1.90-2.32 (m, 8H), 1.28-1.76 (m, 4H). Anal. Calcd for $\text{C}_{12}\text{H}_{20}$: C, 87.73; H, 12.27. Found: C, 87.81; H, 12.27.

3-(4-Pentenyl)-cyclohexanone (119)

About 10% of a solution containing of 15 g (0.01 mole) of 5-bromo-1-pentene in 30 mL of anhydrous diethyl ether was added to 2.8 g (0.4 mole) of lithium metal in 70 mL of anhydrous ether under a nitrogen atmosphere. Once reaction was observed, the reaction vessel was immersed in an ice bath and the remainder of the bromide was added in a slow dropwise fashion. The mixture was stirred at 0° for 30 minutes following the addition. The reaction vessel was cooled in a Dry Ice-acetone bath and 11.6 g (0.08 mole) of cuprous bromide was added. The flask contents were permitted to warm until the mixture turned deep black. The reaction vessel was reimmersed in the Dry Ice-acetone bath followed by the dropwise addition of 3.8 g (0.04 mole) of 2-cyclohexenone. Stirring was continued for one additional hour at low temperature and then the black solution was poured into 200 mL of cold saturated aqueous ammonium chloride solution with vigorous swirling (cautious, the excess lithium metal was not allowed to pour into the aqueous solution). The organic layer was washed with saturated aqueous sodium chloride solution and dried over anhydrous

sodium sulfate. After a filtration process, the ether was removed by use of a rotary evaporator. Vacuum distillation of the remaining liquid resulted in the isolation of 4.5 g (0.03 mole) of 3-(4-pentenyl)-cyclohexanone b.p. 75-80° (0.5 mm); NMR (CCl_4) δ 5.53-6.00 (m, 1H), 4.82-5.15 (m, 2H), 1.11-2.50 (m, 15H). Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}$: C, 79.47; H, 10.91; O, 9.62. Found: C, 79.53; H, 10.90.

1-(4-Pentenyl)-3-methylenecyclohexane (120)

The standard Wittig reaction procedure [preparation of 5-methylene-1,8-nonadiene (111)] was employed to convert 4.3 g (0.026 mole) of 3-(4-pentenyl)-cyclohexanone, 15 g (0.043 mole) of methyltriphenylphosphonium bromide, and 2.30 g (0.043 mole) of sodium hydride (50% suspension in mineral oil) into 2.20 g (0.013 mole) of 1-(4-pentenyl)-3-methylenecyclohexane (120), b.p. 52° (0.5 mm); NMR (CCl_4) δ 5.54-5.98 (m, 1H), 4.81-5.11 (m, 2H), 4.54 (s, 2H), 0.91-2.42 (m, 15H). Anal. Calcd for $\text{C}_{12}\text{H}_{20}$: C, 87.73; H, 12.27. Found: C, 87.50; H, 11.98.

1,6-Heptadien-3-ol (121)

To a 500 mL 3-necked round bottomed flask equipped with a reflux condenser, a thermometer, and an addition funnel, 20 g (0.82 mole) of magnesium turnings and 200 mL of anhydrous THF were added. The flask kept under a nitrogen atmosphere followed by addition of 0.5 mL of ethyl bromide. Fifty grams (0.41 mole) of vinyl bromide was added dropwise. The mixture was kept stirring at 40-45° by means of a cold water bath since the reaction was highly exothermic. After

completion of the addition, the mixture was heated to 80° for one hour.

To the vinylmagnesium bromide solution, 33 g (0.39 mole) of 4-pentenal, which was prepared by the method of A. Voila et.al. (75), in an equal volume of anhydrous diethyl ether was added in a dropwise manner while the Grignard solution was cooled in an ice bath.

The mixture was stirred at room temperature for one hour after the completion of the addition. Saturated aqueous ammonium chloride was added cautiously to quench the organometallic compound. The organic layer was separated, washed once with 50 mL of saturated aqueous sodium chloride, dried over anhydrous magnesium sulfate, and filtered. The ether was removed by simple distillation at atmospheric pressure and the product was purified by simple vacuum distillation. A clear liquid b.p. 48° (1 mm) which weighed 30 g (0.27 mole) was obtained and possessed spectral properties consistent with those expected for 1,6-heptadien-3-ol (121); NMR (CCl_4) δ 5.58-6.03 (m, 2H), 4.83-5.32 (m, 4H), 3.91-4.17 (m, 1H), 3.73 (s, 1H), 1.98-2.28 (m, 2H), 1.41-1.74 (m, 2H). Anal. Calcd for $\text{C}_7\text{H}_{12}\text{O}$: C, 78.95; H, 10.78. Found: C, 78.78; H, 10.72.

7-Chloro-1,5-heptadiene (122) and
3-Chloro-1,6-heptadiene (123)

Thionyl chloride (20.2 g; 0.17 mole) was dissolved in 150 mL of anhydrous diethyl ether under a nitrogen atmosphere. A solution of 18.0 g (0.101 mole) of 1,6-heptadien-3-ol (121) in 100 mL of anhydrous diethyl ether was added dropwise to the thionyl chloride solution. The flask contents were stirred at room temperature for 3.5 hours. The solvent was removed by use of a rotary evaporator

and the remaining liquid was subjected to simple vacuum distillation. The distillate collected b.p. 48° - 55° (10 mm) consisted of two compounds in a ratio of 1 : 6 . GLC analysis with column F at 100° revealed the presence of two components . The major product was purified by preparative scale GLC and was assigned 7-chloro-1,5-heptadiene (122) by NMR spectral analysis: NMR (CCl_4) δ 5.42-6.07 (m, 3H), 4.89-5.21 (m, 2H), 3.97 (d, $J=6\text{Hz}$, 2H), 2.08-2.42 (m, 4H). The structure of the minor product was assigned 3-chloro-1,6-heptadiene (123) by analysis of the NMR spectrum of the initial product mixture; NMR [CCl_4 , mixture of 122 and 123], δ 5.42-6.07 (m), 4.89-5.21 (m,) 3.22-3.55 (m), 3.97 (d, $J=6\text{Hz}$), 2.08-2.42 (m), 1.55-2.00 (m); IR (neat) 3050, 2900, 2820, 1650, 1625, 1280, 985, 965, 910, 675 (cm^{-1}) .

1,5,9-Decatriene (124)

A Grignard reagent was prepared from 15 g (0.12 mole) of a mixture of 7-chloro-1,5-heptadiene (122) and 3-chloro-1,6-heptadiene (123) and 7 g (0.29 mole) of magnesium turnings in anhydrous diethyl ether under a nitrogen atmosphere. The procedure employed was essentially the same as that used for the preparation of allylmagnesium chloride [preparation of 1,6-heptadien-4-ol (106)] . The Grignard reagent was decanted from the excess magnesium metal under nitrogen into another flask. Allyl bromide (28 g; 0.23 mole) was dissolved in an equal amount of diethyl ether and added dropwise into the Grignard solution maintained at 0° . The flask contents were well stirred and refluxed overnight. The reaction vessel was immersed in an ice bath

and an aqueous solution of saturated ammonium chloride was added cautiously in a dropwise fashion. The ethereal solution was washed with saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered. The ether was removed by simple distillation and the product (6 g; 0.04 mole) was obtained by vacuum distillation b.p. 40° (15 mm). The product was further purified by preparative scale GLC using column D at 110° ; NMR (CCl_4) δ 5.56-6.00 (m, 2H), 5.29-5.50 (m, 2H), 4.84-5.12 (m, 4H), 2.01-2.32 (m, 8H).
Anal. Calcd for $\text{C}_{10}\text{H}_{16}$: C, 88.16; H, 11.84 . Found: C, 87.91; H, 11.86.

1-Allyl-2-methylenecyclohexane (125)

The standard Wittig reaction [preparation of 5-methylene-1,8-nonadiene (111)] was used to convert 4.5 g (0.033 mole) of 2-allylcyclohexanone [prepared according to procedure of W. Howard et.al.(76)], 15 g (0.04 mole) of methyltriphenylphosphonium bromide, and 2.5 g (0.05 mole) of sodium hydride (50% in mineral oil) into 3.0 g (0.02 mole) of 1-allyl-2-methylenecyclohexane. The product was purified by preparative GLC using column D at 140° ; NMR (CCl_4) δ 5.55-6.00 (m, 1H), 4.86-5.16 (m, 2H), 4.64 (s, 1H), 4.58 (s, 1H), 1.00-2.54 (m, 11H).
Anal. Calcd for $\text{C}_{10}\text{H}_{16}$: C, 88.16; H, 11.84 . Found: C, 88.27; H, 11.90.

2-(3-Butenyl)-cyclohexanone (126)

To a solution of 20 mL of HMPA and 20 g (0.12 mole) of dicyclohexylamine in 100 mL of diethyl ether at 0° , 48 mL (0.12 mole) of n-butyllithium (2.5 M solution in hexane) was added in a dropwise manner for a period of 10 minutes. The mixture was stirred for 15

minutes at 0° and then 11.8 g (0.12 mole) of cyclohexanone was added dropwise over a 10-minute period. The solution was stirred for an additional 30 minutes at 0° and 16.2 g (0.12 mole) of 4-bromo-1-butene was added quickly at 0° . The solution was stirred at room temperature for 14 hours. The flask contents were poured into 150 mL of 3M HCl solution and filtered. The ethereal filtrate was washed twice with 100 mL of H_2O , twice with aqueous potassium carbonate solution, once with saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered. Most of the ether was removed by use of a rotary evaporator. The remaining liquid was subject to simple vacuum distillation. A colorless liquid weighing 3.4g (0.023 mole) was obtained b.p. $80-115^{\circ}$ (40-45 mm). An analytical sample of this product was produced by preparative scale GLC using column D at 110° ; NMR (CCl_4) δ 5.56-5.96 (m, 1H), 4.84-5.12 (m, 2H), 1.00-2.60 (m, 13H). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.51. Found: C, 79.07; H, 10.68.

1-(3-Butenyl)-2-methylenecyclohexane (127)

The standard Wittig reaction procedure [preparation of 5-methylene-1,8-nonadiene (111)] was used to convert 2.5 g (0.016 mole) of 2-(3-butenyl)-cyclohexanone, 10 g (0.03 mole) of methyltriphenylphosphonium bromide, and 1.5 g (0.031 mole) of sodium hydride (50% in mineral oil) into 1.8 g (0.02 mole) of 1-(3-butenyl)-2-methylenecyclohexane (127) in 100 mL of anhydrous DMSO. The product was further purified by preparative scale GLC with column A at 140° ; NMR (CCl_4) δ 5.56-5.96 (m, 1H), 4.84-5.12 (m, 2H), 1.00-2.60 (m, 13H). Anal. Calcd. for $C_{10}H_{16}O$: C, 78.90; H, 10.51; O, 10.60. Found: C, 79.07;

H, 10.68 .

5-Vinyl-1,8-nonadiene (128) and
1,5,10-undecatriene (129)

A solution of 3-butenylmagnesium bromide in anhydrous diethyl ether was prepared by dropwise addition of 8 g (0.06 mole) of 4-bromo-1-butene into a reaction vessel containing 3 g (0.13 mole) of magnesium turnings in 80 mL of ether under a nitrogen atmosphere. The Grignard reagent was decanted from excess magnesium under nitrogen, and 5 g (0.04 mole) of a mixture of 7-chloro-1,5-heptadiene (122) and 3-chloro-1,6-heptadiene (123) was added to the Grignard reagent in a dropwise fashion at room temperature. The resulting mixture was refluxed overnight. The reaction vessel was immersed in an ice bath and a saturated aqueous ammonium chloride solution was added cautiously to quench the organometallic compound. The ether layer was separated and washed once with 50 mL of saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered. The ether was removed by simple distillation at atmospheric pressure. The products, a 60 : 40 mixture of 5-vinyl-1,8-nonadiene (128) (0.8 g; 0.005 mole) and 1,5,10-undecatriene (129) (0.5 g, 0.003 mole), were isolated and purified by preparative scale GLC using column D at 140°: NMR (128) (CCl₄) δ 5.20-6.00 (m, 3H), 4.80-5.15 (m, 6H), 1.80-2.30 (m, 5H), 1.20-1.60 (m, 4H); NMR (129) (CCl₄) δ 5.35-6.00 (m, 4H), 4.84-5.10 (m, 4H), 1.85-2.25 (m, 8H), 1.30-1.60 (m, 2H).

cis-Hydrindan-2-ol (130)

Catalytic hydrogenation of 8 g (0.06 mole) of 2-indanol in 150 mL of 95% ethanol and 1 mL of acetic acid was accomplished with 3 g of 5% rhodium on aluminum oxide catalyst. Reduction was performed under a hydrogen pressure of 52 psi in a Parr Hydrogenation Apparatus for a period of 45 hours. The catalyst was filtered from the ethanol solution and washed with 50 mL of ethanol. Most of the ethanol was removed by simple distillation at atmospheric pressure. Vacuum distillation of the remaining oil afforded 7 g (0.051 mole) of cis-hydrindan-2-ol b.p. 92° (1 mm); NMR (CCl_4) δ 4.65 (s, 1H), 4.14-4.50 (m, 1H), 1.10-1.30 (m, 14H).

cis-Hydrindan-2-one (131)

Oxidation of 6 g (0.05 mole) of cis-hydrindan-2-ol (130) with chromium trioxide and sulfuric acid in acetone was conducted in the same manner as described in the preparation of 1,8-nonadien-5-one (110). The product (5.5 g; 0.04 mole) was obtained by simple vacuum distillation b.p. 58° (1 mm); NMR (CCl_4) δ 2.00-2.45 (m, 4H), 1.20-1.85 (m, 10H). Anal. Calcd for $\text{C}_8\text{H}_{14}\text{O}$: C, 78.21; H, 10.21. Found: C, 78.12, H, 10.37.

2-Methylene-cis-hydrindane (132)

The standard Wittig reaction procedure [preparation of 5-methylene-1,8-nonadiene (111)] was followed to prepare 3.5 g (0.026 mole)

of 2-methylene-cis-hydrindane (132) from 5.0 g (0.036 mole) of cis-hydrindan-2-one (131), 3.5 g (0.073 mole) of sodium hydride (50% in mineral oil), and 25 g (0.073 mole) of methyltriphenylphosphonium bromide in 200 mL of anhydrous DMSO. Preparative scale GLC with column A at 130° was used to isolate the pure 2-methylene-cis-hydrindane; NMR (CCl₄) δ 4.78-4.80 (m, 2H), 1.85-2.50 (m, 6H), 1.20-1.70 (broad s, 8H). Anal. Calcd for C₁₀H₁₆: C, 88.16; H, 11.84. Found: C, 88.06; H, 11.93.

1-Methyl-2-methylenecyclohexane (133)

This substance was prepared by the standard Wittig reaction procedure as described in the preparation of 5-methylene-1,8-nona-diene (111). The reaction converted 7.0 g (0.06 mole) of 2-methylcyclohexanone, 22 g (0.063 mole) of methyltriphenylphosphonium bromide, and 3.2 g (0.067 mole) of sodium hydride (50% in mineral oil) into 5.5 g (0.05 mole) of 1-methyl-2-methylenecyclohexane (133) in 120 mL of anhydrous DMSO. The product was purified by simple vacuum distillation b.p. 42° (30 mm): NMR (CCl₄) δ 4.50-4.70 (m, 2H), 1.18-2.50 (m, 9H), 1.20-1.18 (d, J=7Hz, 3H).

1,5,10-Dodecatriene (134)

To a mixture of 8.0 g (0.021 mole) of (4-pentenyl)triphenylphosphonium bromide in 80 mL of a 1 : 1 combination of anhydrous THF and diethyl ether, 9 mL (0.02 mole) of n-butyllithium (2.2M solution in hexane) was added in a dropwise manner under a nitrogen atmosphere. The flask contents were maintained at -78° during the addition. The

mixture was stirred well for 10 minutes after completion of the addition and then it was permitted to warm to room temperature. The reaction mixture turned into a deep red solution. The reaction vessel was then immersed in an ice bath. Two grams (0.018 mole) of 5-heptenal, which was prepared by the method of A. Viola et.al.(77), diluted with an equal volume of anhydrous diethyl ether was added to the reaction vessel in a dropwise manner. The mixture was stirred at room temperature for 2.5 hours after completion of the addition. The reaction vessel was reimmersed in the ice bath and 20 mL of saturated aqueous ammonium chloride solution was added. The mixture was extracted three times with 50 mL of diethyl ether which were combined. The ethereal solution was washed with 50 mL of H₂O, dried over anhydrous magnesium sulfate, and filtered. Most of the ether was removed by simple distillation under atmospheric pressure. The product was isolated and purified by preparative scale GLC using column A at 120°. Pure compound weighing 1.5 g (0.01 mole) was obtained; NMR (CCl₄) δ 5.56-6.00 (m, 1H), 5.16-5.54 (m, 4H), 4.84-5.12 (m, 2H), 1.80-2.30 (m, 8H), 1.20-1.74 (m, 5H). Anal. Calcd for C₁₂H₂₀: C, 87.73; H, 12.27 . Found: C, 87.69; H, 12.24.

cis- and trans-1-Chloro-4-methyl-
1,5-hexadiene (135)

A solution of 2-butenylmagnesium bromide was prepared by dropwise addition of 25 g (0.19 mole) of 1-bromo-2-butene to 6.0 g (0.25 mole) of magnesium turnings in 500 mL of anhydrous diethyl ether under a nitrogen atmosphere at 0°. The Grignard solution was decanted from excess magnesium metal under nitrogen. A solution of 14 g (0.13 mole) of 1,3-dichloropropene (mixture of cis- and trans-isomers) in 20 mL

of ether was added to the Grignard reagent in a dropwise manner. The reaction was refluxed for 18 hours. The reaction vessel was immersed to an ice bath and 100 mL of saturated aqueous ammonium chloride solution was added cautiously. The ether layer was separated, washed with 100 mL of saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered. Most of the ether was removed by simple distillation under atmospheric pressure. The remaining liquid was subjected to vacuum distillation. A clear liquid which weighed 18.5 g (0.14 mole) b.p. 85-95° (135 mm) was obtained. GLC analysis using column H at 100° indicated the product consisted of two components in a ratio of 1 : 2. The structures of the two product components were assigned by NMR spectral analysis after separation by preparative scale GLC (column H) at 100°. The major product was assigned the structure cis-1-chloro-4-methyl-1,5-hexadiene; NMR (CCl₄) δ 5.54-6.04 (m, 3H), 4.80-5.14 (m, 2H), 2.00-2.50 (m, 3H), 0.98-1.18 (d, J=7Hz, 3H). The structure of the minor product was assigned trans-1-chloro-4-methyl-1,5-hexadiene: NMR (CCl₄) δ 5.58-5.94 (m, 3H), 4.86-5.16 (m, 2H), 2.12-2.48 (m, 3H), 1.00-1.20 (d, J=7Hz, 3H). Elemental analysis was performed on a mixture of both isomers.

3-Methyl-1-hexen-5-yne (136)

To a solution of 4.70 g (0.05 mole) of diisopropylamine in 20 mL of anhydrous THF, 22.0 mL (0.05 mole) of n-butyllithium (2.2M in hexane) was added in a dropwise manner under a nitrogen atmosphere at -78°. After the addition was completed, the reaction mixture was permitted to warm to room temperature. The reaction vessel was immersed

in an ice bath which was followed by the dropwise addition of 3 g (0.023 mole) of a mixture of cis- and trans-1-chloro-4-methyl-1,5-hexadiene (135). The mixture was well stirred at room temperature for 10 hours. After the reaction vessel was immersed again in an ice bath, 30 mL of saturated aqueous ammonium chloride solution was added cautiously. The organic layer was washed three times with 30-mL portions of 0.1N HCl and then vacuum transferred. The product mixture was subjected to distillation using a spinning band distillation column. The distillate boiling lower than 70° was discarded. The residue was subjected to preparative scale GLC using column H at 120°. A clear liquid product which weighed 0.52 g (5.5 mmoles) was obtained from the preparative scale GLC. The structure of the product was assigned 3-methyl-1-hexen-5-yne (136); NMR (CCl₄) δ 5.65-6.02 (m, 1H), 4.90-5.15 (m, 2H), 2.10-2.56 (m, 3H), 1.89-1.90 (t, J=1.5Hz, 1H), 1.07-1.19 (d, J=6Hz, 3H).

General Method for Catalytic Cyclization of Polyenes with Diisobutylaluminum Hydride

All the cyclization reactions were done in a sealed tube with mineral oil or reagent grade anhydrous n-hexane as solvent. Any volatile components were removed from the mineral oil by heating it to 90° under 1 mm pressure. It was then stored under a nitrogen atmosphere. Unless otherwise specified, 0.1 equivalent of diisobutylaluminum hydride was used as a catalyst for the cyclization reaction. A premeasured quantity of polyene and solvent was introduced into a narrow-necked Pyrex tube with one end sealed. The glass tube was flushed with dry prepurified nitrogen for one minute and

diisobutylaluminum hydride was then added by means of syringe. The glass tube was immediately immersed in a Dry Ice-acetone bath while a flow of dry nitrogen was directed into the glass tube. The open end of the glass tube was covered securely with Parafilm. The tube was immediately pulled out from the Dry Ice-acetone bath and sealed by means of a torch. After warming to room temperature the sealed tube was immersed completely in an oil bath maintained at the desired temperature.

After the desired period of reaction time in the constant temperature oil bath, the sealed tube was removed and immersed in an ice bath. The sealed tube was opened and the tube contents were transferred to a small round bottomed flask. All volatile components were vacuum transferred and collected in a cold trap. For yield determination by GLC, a premeasured amount of internal standard was added to the vacuum transferred material. Analytical samples were obtained by preparative scale GLC.

Cyclization of 1,5-Hexadiene

A solution of 0.5 g (6.1 mmoles) of 1,5-hexadiene and 0.45 g (0.61 mmole) of diisobutylaluminum hydride (20% solution in n-hexane) in 5.0 mL of mineral oil was prepared in a sealed glass tube as described in the general procedure. The sealed tube was immersed in an oil bath at $110 \pm 5^\circ$ for 56 hours. GLC analysis of the vacuum transferred material using column B at 75° indicated that the 1,5-hexadiene had completely reacted and that only one product had formed. The product was isolated and purified by preparative scale GLC with the same column and conditions as described above. The structure of the

product was shown to be methylenecyclopentane by NMR spectral comparison to an authentic sample.

The reaction was repeated under the same conditions for yield determination. n-Decane (0.60 g; 4.22 mmol) was added as an internal standard and yield of 81% was determined using column B.

Cyclization of 1,6-Heptadiene

Similarly, 0.5 g (5.2 mmol) of 1,6-heptadiene was cyclized to methylenecyclohexane by reaction with 0.38 g (0.53 mmol) of diisobutylaluminum hydride (20% solution in n-hexane) in 5 mL of mineral oil at $100 \pm 5^\circ$ for a period of 48 hours in a sealed tube. GLC analysis of the vacuum transferred product using column I at 75° indicated that the starting material had completely reacted and one product had formed in 56% yield as determined by comparison with 0.62 g (4.36 mmol) of internal standard n-decane. The product was isolated by preparative scale GLC and its NMR spectrum was identical to that of an authentic sample of methylenecyclohexane.

Cyclization of 4-Vinylcyclohexene

Following the general procedure, the cyclization of 0.5 g (4.67 mmol) of 4-vinylcyclohexene with 0.30 g (0.42 mmol) of diisobutylaluminum hydride (20% solution in n-hexane) in 5.0 mL of mineral oil at 200° for 48 hours afforded a 61% yield of bicyclo[3.2.1]oct-2-ene. GLC analysis of the reaction mixture was accomplished with column J at 120° having 0.60 g (5.26 mmol) of n-octane as an internal standard. The product was purified and isolated by preparative scale

GLC using the same column and conditions as described above; NMR (CCl_4) δ 5.72-6.00 (m, 1H), 5.22-5.44 (m, 1H), 2.22-2.57 (m, 3H), 1.33-2.22 (m, 7H).

Cyclization of 5-Methylene-1,8-nonadiene (111)

One-half gram (3.67 mmoles) of 5-methylene-1,8-nonadiene (111) reacted with 0.32 g (0.45 mmole) of diisobutylaluminum hydride (20% in n-hexane solution) in 5.0 mL of mineral oil at $110 \pm 5^\circ$ for 48 hours. GLC analysis of the product mixture using column K at 100° revealed complete cyclization had taken place. The yield of product was calculated to be 78% using 0.50 g (4.38 mmoles) of n-octane as the internal standard. The product was isolated by preparative scale GLC using the same column and conditions as described above. The structure of the product was assigned that of 2-methylenespiro[4.4]-nonane; NMR (CCl_4) δ 4.72-4.86 (m, 2H), 2.10-2.46 (m, 4H), 1.30-1.82 (m, 10H). Anal. Calcd for C_9H_{16} : C, 88.16; H, 11.84. Found: C, 88.17; H, 11.84.

Cyclization of 5-Methylene-1,9-decadiene (115)

The general procedure was followed in which 0.50 g (3.33 mmoles) of 5-methylene-1,9-decadiene (115) was allowed to react with 0.37 g (0.52 mmole) of diisobutylaluminum hydride (20% solution in n-hexane) in 5.0 mL of n-hexane at 150° for 72 hours. GLC analysis of the product mixture with column F at 130° after 0.5 g (4.38 mmoles) of n-octane had been added showed the production of a single product in 37% yield. The product was purified by preparative scale GLC using

column K at 115° and assigned the structure of 7-methylenespiro[4.5]-decane as determined by NMR analysis: NMR (CCl_4) 4.50-4.80 (2m, with small coupling constant, 2H), 1.92-2.20 (m, 4H), 1.20-1.78 (m, 12H). Anal. Calcd for $\text{C}_{11}\text{H}_{18}$: C, 87.94; H, 12.06. Found: C, 87.84; H, 11.98 .

Cyclization of 6-Methylene-1,10-undecadiene (118)

In like fashion, 0.5 g (3.03 mmoles) of 6-methylene-1,10-undecadiene was allowed to react with 0.34 g (0.48 mmole) of diisobutylaluminum hydride (20% solution in n-hexane) in 5.0 mL of n-hexane at $150 \pm 5^{\circ}$ for 4 days. Column J was employed in the GLC analysis at 170° with 0.5 g (4.38 mmoles) of n-octane as an internal standard. The chromatogram revealed the presence of a small quantity of starting material (3.8%) along with two products. The major component consisted of 42% of the product composition and the minor component 11%. Purification of the products was accomplished by means of preparative scale GLC using the same column and temperature as described above. The major product was identified as 3-methylene-(4-pentenyl)cyclohexane by spectral analysis and independent synthesis. NMR spectral analysis alone was used to assign the minor product the structure 2-methylenespiro [5.5]undecane.

Major product: NMR (CCl_4) δ 5.56-6.00 (m, 1H), 4.82-5.11 (m, 2H), 4.58 (s, 2H), 1.04-2.44 (m, 15H). Anal. Calcd for $\text{C}_{12}\text{H}_{20}$: C, 87.73; H, 12.27 . Found: C, 87.50; H, 11.98 .

Minor product: NMR (CCl_4) δ 4.48-5.78 (2m, with small coupling constant, 2H), 1.90-2.20 (m, 4H), 1.16-1.70 (m, 14H) .

Cyclization of 1,5-Heptadiene

Following the general procedure, 1.0 g (10.42 mmol) of 1,5-heptadiene was allowed to react with 0.75 g (1.06 mmol) of diisobutylaluminum hydride (20% solution in n-hexane) in 5-mL of mineral oil at 170° for 12 hours. GLC analysis of the vacuum transferred material using column F at 80° indicated complete cyclization of the starting material and formation of only one product in 77% yield as determined by use of 0.52 g (4.06 mmol) of n-nonane as an internal standard. The product was isolated by preparative scale GLC using column C at 100°. Comparison of spectral properties to those of an authentic substance confirmed the product structure as ethylidene-cyclopentane.

Cyclization of 6-Methyl-1,5-heptadiene

One gram (9.09 mmol) of 6-methyl-1,5-heptadiene experienced reaction with 0.65 g (0.92 mmol) of diisobutylaluminum hydride (20% solution in n-hexane) in 5 mL of mineral oil at 160° for 16 hours. Volatile material was vacuum transferred according to the general procedure and subjected to GLC analysis using column F at 80°. Only one product was formed in 81% yield as determined by means of 0.50 g (4.39 mmol) of n-octane as internal standard. Column C at 100° was utilized in preparative scale GLC to obtain pure product. The NMR spectrum of the product, isopropylidenecyclopentane, satisfactorily corresponded to that expected for this material; NMR (CCl₄) δ 2.04-3.02 (m, 4H), 1.54-1.84 (m, 10H).

Cyclization of 1,5,9-Decatriene (124)

Reaction of 0.50 g (3.68 mmoles) of 1,5,9-decatriene (124) with 0.40 g (0.56 mmole) of diisobutylaluminum hydride (20% solution in n-hexane) was performed in 5.0 mL of anhydrous n-hexane at 150° for 18 hours following the general procedure. GLC analysis of the vacuum transferred reaction mixture with column D at 130° indicated a complete loss of the starting material and production of two products. n-Decane (0.50 g; 3.47 mmoles) was used as an internal standard and enabled the determination of a 55% yield for the major product (retention time of 9.2 minutes) and a 16% yield for the minor product (retention time of 7.5 minutes). The two products were separated by preparative scale GLC using the same column and temperature as described above. The structure of the major product was assigned that of cyclopentylidenecyclopentane based on NMR spectral analysis: NMR (CCl_4) δ 2.00-2.36 (broad s, 8H), 1.50-1.86 (m, 8H). Anal. Calcd for $\text{C}_{10}\text{H}_{16}$: C, 88.16; H, 11.84. Found: C, 88.13; H, 11.80.

The NMR spectrum of the minor component was consistent with that expected for 1-cyclopentylcyclopentene: NMR (CCl_4) δ 5.22-5.39 (m, 1H), 2.06-2.62 (m, 5H), 1.25-2.00 (m, 10H). Anal. Calcd for $\text{C}_{10}\text{H}_{16}$: C, 88.16; H, 11.84. Found: C, 88.28; H, 11.83.

Cyclization of 2-Methyl-1,5-hexadiene

Using the general procedure, 0.5 g (5.12 mmoles) of 2-methyl-1,5-hexadiene was permitted to react with 0.50 g (0.70 mmole) of diisobutylaluminum hydride (20% solution in n-hexane) in 5 mL of

mineral oil at 120° for 72 hours. GLC analysis of the vacuum transferred material using column F at 65° indicated a recovery of 40% of the starting material and only one product generated in a yield of 35% using 0.5 g (3.47 mmol) of n-decane as an internal standard. The product was isolated by preparative scale GLC using column D at 75°. Interpretation of the NMR spectrum showed the product to be 3-methylmethylenecyclopentane; NMR (CCl₄) δ 4.70-4.76 (m, 2H), 1.64-2.50 (m, 6H), 1.10-1.46 (m, 1H), 1.01 (d, J=7Hz, 3H).

Cyclization of 1,6-Octadiene (103)

In accordance with the general procedure, 0.5 g (4.55 mmol) of 1,6-octadiene (103) reacted with 0.32 g (0.45 mmol) of diisobutylaluminum hydride (20% solution in n-hexane) in 5-mL of mineral oil at 160° for 18 hours. The use of column E at 75° revealed the generation of a single product with a small quantity of starting material remaining. The yield of the product was determined to be 40% by comparison to 0.5 g (3.47 mmol) of n-decane which functioned as an internal standard. Preparative scale GLC under the same conditions relinquished the product which provided an NMR spectrum that was identical to an authentic sample of ethylidenecyclohexane.

Cyclization of 4-Allyl-1,6-heptadiene (108)

Reaction of 0.15 g (1.10 mmol) of 4-allyl-1,6-heptadiene with 0.12 g (0.17 mmol) of diisobutylaluminum hydride (20% solution in n-hexane) in 1.5 mL of mineral oil at 130° for 6 hours was performed following the general procedure. GLC analysis of the vacuum trans-

ferred product mixture with column G at 95° indicated that the starting material had not reacted completely and that one product had formed. The product was isolated by preparative scale GLC with the same column and conditions as described above. The NMR spectrum of the purified product was consistent with that expected for 1-allyl-3-methylene-cyclohexane; NMR (CCl_4) δ 5.54-6.00 (m, 1H), 4.73-5.16 (m, 2H), 4.62 (s, 2H), 1.06-2.62 (m, 11H).

The reaction was repeated using 0.30 g (2.20 mmoles) of 4-allyl-1,6-heptadiene, 0.25 g (0.34 mmole) of diisobutylaluminum hydride (20% solution in n-hexane) and 3.0 mL of mineral oil at 125° for 24 hours. GLC analysis (column G) revealed complete disappearance of the starting triene and the emergence of two products in a ratio of 1 : 1. The products were isolated and purified by preparative scale GLC (Column G). The first product to elute was 1-allyl-3-methylene-cyclohexane. The NMR spectrum of the second component was interpreted as being that of 3-methylenebicyclo [3.3.1]nonane; NMR (CCl_4) δ 4.55-4.65 (m, 2H), 1.00-2.60 (m, 14H); mass spectrum m/e 136.20 (Calcd for $\text{C}_{10}\text{H}_{16}$: 136.238)

The reaction was repeated again with 0.30 g (2.20 mmoles) of 4-allyl-1,6-heptadiene, 0.25 g (0.34 mmole) of diisobutylaluminum hydride and 5 mL of mineral oil at 125° for 48 hours. GLC analysis (column G) showed the production of only one product in 40% yield as determined through the addition of 0.18 g (1.41 mmoles) of n-nonane as an internal standard. Preparative scale GLC followed by NMR analysis of the product substantiated it as being 3-methylenebicyclo[3.3.1] nonane.

Cyclization of 1-Allyl-2-methylene-
cyclohexane (125)

Reaction of 0.25 g (1.84 mmoles) of 1-allyl-2-methylenecyclohexane (125) with 0.26 g (0.37 mmole) of diisobutylaluminum hydride (20% solution in n-hexane) in 4 mL of n-hexane at 120° for a period of 67 hours was conducted according to the general cyclization procedure. GLC analysis of the vacuum transferred product mixture using column H at 95° indicated formation of two products. The major product had a retention time of 36 minutes while the minor product had a retention of 26 minutes. Preparative scale GLC (column I at 95°) resulted in the isolation of both substances in a high state of purity. NMR spectral analysis and independent synthesis served to identify the major product as 2-methylene-cis-hydrindane; NMR (CCl₄) δ 4.78-4.92 (m, 2H), 1.90-2.40 (m, 6H), 1.22-1.73 (m, 8H). Anal. Calcd. for C₁₀H₁₆: C, 88.16; H, 11.84. Found: C, 88.06; H, 11.93 .

NMR analysis alone was relied upon in assigning the minor component the structure of 2-methylene-trans-hydrindane; NMR (CCl₄) δ 4.72-4.97 (m, 2H), 2.21-2.55 (m, 2H), 0.90-2.10 (m, 12H).

The percentage yields of the two products were ascertained by the use of column F at 70° after the addition of 0.25 g (1.95 mmoles) of n-nonane as internal standard. The major product, 2-methylene-cis-hydrindane, was generated in 40% yield, and the minor product, 2-methylene-trans-hydrindane, in 23% yield.

Cyclization of 2-(3-Butenyl)-methylene-
cyclohexane (127)

Following the general procedure, 0.25 g (1.67 mmoles) of 2-(3-butenyl)-methylenecyclohexane (127) was allowed to react with 0.24 g (0.34 mmole) of diisobutylaluminum hydride solution (20% solution in n-hexane) in 4.0 mL of n-hexane for a period of 72 hours at 120°. Analysis by GLC (column D at 135°) showed complete disappearance of starting material and the formation of two products. Addition of 0.20 g (1.56 mmoles) of n-nonane as an internal standard permitted the determination of percentage yield of the major product (retention 8.1 minutes) as 45% and of the minor product (retention time 9.8 minutes) as 15%. Separation and purification of the two products was accomplished by preparative GLC (column D). The structure of the major product was determined to be 2-methylene-trans-decalin by comparison of the NMR spectrum to that of a known sample; NMR δ (CCl₄) 4.47-4.66 (2m, with small coupling constant, 2H), 1.95-2.38 (m, 4H), 1.10-1.95 (m, 12H).

The same criterion was employed in ascertaining the constitution and stereochemistry of the minor component, 2-methylene-cis-decalin; NMR (CCl₄) δ 4.50-4.64 (m, 2H), 1.42-2.43 (m, 8H), 0.82-1.42 (m, 8H). Anal. Calcd for C₁₁H₁₈ (mixture of cis- and trans- isomers) : C, 87.93; H, 12.08 . Found: C, 88.10; H, 12.10 .

Cyclization of 3-Allylcyclohexene

The reaction of 0.50 g (4.1 mmoles) of 3-allylcyclohexene with 0.36 g (0.50 mmole) of diisobutylaluminum hydride (20% solution in

n-hexane) in 10 mL of n-hexane at 160° for a period of 6 hours was conducted in the same fashion described in the general procedure. GLC analysis of the vacuum transferred material using column H at 100° indicated that the starting material had completely reacted and that two products in a ratio of 3 : 1 were formed. The products were isolated and purified by preparative scale GLC with the same column and temperature as described above. NMR spectral analysis was used to identify the major product (retention time 23 minutes) as bicyclo[4.3.0]non-1-ene ; NMR (CCl_4) δ 5.34 (broad s, 1H), 0.82-2.46 (m, 13H). The structure of the minor product (retention time 23 minutes) was assigned that of cis-bicyclo[4.3.0]non-2-ene by NMR spectral analysis and subsequent chemical correlation involving the product of the same molecule; NMR (CCl_4) δ 5.63 (m, 2H), 1.10-2.52 (m, 12H).

The reaction was repeated with the same amounts of reagents and conducted at 160° for 1 hour 40 minutes. GLC analysis (column H) at 100° using 0.38 g (2.97 mmole) of n-nonane as internal standard revealed the presence of 54% unreacted starting material and 36.4% of a single product , cis-bicyclo[4.3.0]non-2-ene.

Reduction of Product Mixture from the Cyclization Reaction of 3-Allylcyclohexene

The product mixture from partial cyclization of 3-allylcyclohexene consisted of 54% unreacted starting material 3-allylcyclohexene and 36.4% 2-cis-bicyclo[4.3.0]nonene. Hydrogenation of 2 g (0.016 mole) of this mixture was done by use of 0.20 g of 5% rhodium on carbon catalyst in 45 mL of 95% ethanol. The pressure of hydrogen

was maintained at 52 psi in a Paar Hydrogenation Apparatus for a period of 24 hours. The mixture was filtered and the filtrate was subjected to simple distillation under atmospheric pressure. Most of the solvent was removed by the simple distillation and the remaining liquid was vacuum transferred. The reduction products were isolated and purified by preparative scale GLC using column G at 125°. The first compound to elute (retention time 2.6 minutes) was identified as n-propylcyclohexane: NMR (CCl_4) δ 1.05-1.90 (m, 15H), 0.85-0.98 (t, $J=8\text{Hz}$, 3H). The second component of retention time 3.5 minutes provided an NMR spectrum identical to that of cis-hydrindane which was prepared by independent synthesis; NMR (CCl_4) δ 1.20-2.00 (broad multiplet).

cis-Hydrindane (131)

Catalytic hydrogenation of 6 g (0.05 mole) of indene in 50 mL of 95% ethanol with 1.2 g of 5% rhodium on aluminum oxide in a Paar Hydrogenation Apparatus at 52 psi hydrogen pressure provided 4.0 g (0.033 mole) of cis-hydrindane after 48 hours of hydrogenation time. The ethanol solution was filtered away from the catalyst and 50 mL of saturated aqueous sodium chloride solution was added. The mixture was extracted three times with 30-mL portions of pentane which were then combined. Most of the pentane was removed by simple distillation at atmospheric pressure. The pure product (4 g; 0.032 mole) was obtained by simple vacuum distillation b.p. 45° (4 mm); NMR δ 1.20-2.00 (broad multiplet). Anal. Calcd for C_9H_{16} : C, 87.02; H, 12.98. Found: C, 87.14; H, 13.06 .

Unsuccessful Attempted Catalytic Cyclizations

No catalytic cyclization could be achieved with the following molecules under a variety of conditions within the realm of the general procedure: diallylether, 1,7-octadiene, 7-methyl-1,6-octadiene, and 4-vinyl-1,7-octadiene. An experiment involving 6-methyl-1,5,10-undecatriene resulted in the generation of a multitude of products which were not identified.

Cyclization of 1,5-Hexadiene with Dimethylaluminum Hydride

A solution of dimethylaluminum hydride in 50 mL of toluene was prepared under a nitrogen atmosphere from 8 g (0.022 mole) of dimethylaluminum chloride (20% solution in n-hexane), 1.1 g (0.023 mole) of sodium hydride (50% in mineral oil), and 1.5 g (0.002 mole) of diisobutylaluminum hydride solution (20% solution in n-hexane) following the procedure described by Zakharkin et.al.(62). To the dimethylaluminum hydride solution, 1.81 g (0.022 mole) of 1,5-hexadiene was added and the mixture was stirred at 50° for 15 hours. The reaction vessel was immersed in an ice bath and 20 mL of saturated aqueous ammonium chloride was added. The organic layer was separated, washed once with water, dried over anhydrous magnesium sulfate, and filtered. The product mixture was subjected to distillation under atmospheric pressure through a short Vigreux column. Material boiling below 100° was collected and subjected to GLC analysis using column M at 100°. This analysis revealed that the starting material

had completely reacted and only one product was formed in good yield. The product (retention time 4.2 minutes) was isolated and purified by preparative scale GLC (column M) and identified as methylcyclopentane by comparison of spectral properties to those of an authentic sample.

Cyclization of 1,5-Heptadiene with
Dimethylaluminum Hydride

A solution of dimethylaluminum hydride in 20 mL of anhydrous diphenylmethane was prepared under a nitrogen atmosphere from 8.00 g (0.022 mole) of dimethylaluminum chloride (20% solution in n-hexane), 1.1 g (0.023 mole) of sodium hydride (50% in mineral oil), and 1.5 g (0.002 mole) of diisobutylaluminum hydride following a procedure described in the literature (62). To the dimethylaluminum hydride solution, 1.86 g (0.019 mole) of 1,5-heptadiene was added, and the resulting solution was stirred at 80° for a period of 15 hours. To the reaction mixture, 3 mL of saturated aqueous ammonium chloride solution was added. The mixture was stirred for 20 minutes, dried over anhydrous magnesium sulfate, and filtered. The residue was washed three times with 10-mL portions of n-hexane, and the n-hexane was combined with the filtrate. The filtrate was vacuum transferred, and the volatile material was collected in a cold trap cooled by a Dry Ice-acetone bath. The collected product mixture was subjected to GLC analysis using column N at 65°, which indicated that all the starting material had completely reacted and two products had formed, with retention times of 4.2 minutes and 6.0 minutes, in a ratio 2:1. The

two products were isolated by preparative scale GLC with column G at 50°. The first component to elute was identified as ethylcyclopentane.

The second component to elute was the minor product and was identified by NMR spectral comparison to an authentic sample of ethylenecyclopentane.

Attempted Cyclization of 6-Methyl-1,5-heptadiene with Dimethylaluminum Hydride

A solution of dimethylaluminum hydride in 50 mL of anhydrous benzene was prepared under a nitrogen atmosphere from 8.0 g (0.022 mole) of dimethylaluminum chloride (20% solution in n-hexane), 1.1 g (0.023 mole) of sodium hydride (50% in mineral oil), and 1.5 g (0.002 mole) of diisobutylaluminum hydride (20% in n-hexane solution) following the procedure described in the literature (62). To the dimethylaluminum hydride solution was added 1.9 g (0.0173 mole) of 6-methyl-1,5-heptadiene. The reaction mixture was stirred at 80° for 18 hours. Then the reaction vessel was immersed into an ice bath and 25 mL of saturated aqueous ammonium chloride solution was added. The organic layer was separated, dried over anhydrous magnesium sulfate, and filtered. Most of the hexane and benzene were removed by distillation under atmosphere pressure through a short Vigreux column. The remaining solution was subjected to GLC analysis using column N at 65°. The GLC analysis revealed that the starting material had completely reacted and only one product was formed having a retention time of 6.5 minutes. The product was isolated by preparative scale GLC (column G at 100°)

and provided an NMR spectrum which was identical to that of an authentic sample of 2-methyl-2-heptene.

Cyclization of 1,5-Heptadiene with Diisobutylaluminum Hydride and Aluminum Chloride

To a solution of 0.50 g (5.2 mmol) of 1,5-heptadiene in 10 mL of anhydrous n-hexane, 3.90 g (5.49 mmol) of diisobutylaluminum hydride (20% in n-hexane solution) was added under a nitrogen atmosphere at room temperature. The resulting solution was stirred at 35° for a period of 18 hours which was followed by the solution being transferred to an addition funnel under nitrogen. The solution was added through the addition funnel in a dropwise manner to a suspension of 10 mL of n-hexane and 1.00 g (7.5 mmol) of anhydrous aluminum chloride (dried under high vacuum for 18 hours). The mixture was stirred at room temperature for 2.5 hours and the reaction vessel was immersed in a cold bath at -5°. To the reaction mixture, 5 mL of H₂O was added cautiously in a dropwise manner. The organic layer was separated, washed once with 10 mL of water, dried over anhydrous magnesium sulfate and filtered. GLC analysis of the filtrate using column M at 105° indicated complete disappearance of 1,5-heptadiene and the production of a single product in 76% yield as determined by comparison with 0.5 g (3.91 mmol) of n-nonane as internal standard. Preparative GLC (column M) resulted in the isolation of the product which was identified as ethylcyclopentane by NMR spectral analysis.

Attempted Cyclization of 6-Methyl-1,5-heptadiene with Diisobutylaluminum Hydride and Aluminum Chloride

To a solution of 1.5 g (13.64 mmol) of 6-methyl-1,5-heptadiene in 5.0 mL of anhydrous n-hexane was added 8.5 g (12.32 mmol) of diisobutylaluminum hydride (20% in n-hexane solution) under a nitrogen atmosphere. The mixture was stirred at 35° for a period of 12 hours. The reaction vessel was immersed in an ice bath and 1.5 g (11.3 mmol) of anhydrous aluminum chloride was added quickly. The mixture was stirred at 35° for one hour. The reaction vessel was cooled to -5° and 5.0 mL of water was added cautiously in a drop-wise manner. The organic layer was separated, dried over anhydrous magnesium sulfate, and filtered. The GLC analysis (column H at 160°) showed that the starting material had reacted completely and three products had been produced. The three products displayed retention times of 5 minutes, 6.3 minutes, and 7.2 minutes in a ratio of 3 : 1 : 2 respectively. The products of retention times 5 minutes and 7.2 minutes were isolated and purified by preparative scale GLC using column H. The structure of the major component proved to be that of 2-methylheptane by comparison to an authentic sample.

The structure of the product of longest retention time (7.2 minutes) was assigned that of cis-1,2-dimethylcyclohexane by comparison of its spectrum to that of a known sample of the molecule.

The material of retention time 6.2 minutes possessed a retention time identical to that of trans-1,2-dimethylcyclohexane.

Cyclization of 1,6-Heptadiene with
Diethylaluminum Hydride and
Aluminum Chloride

To a solution of 0.5 g (5.12 mmol) of 1,6-heptadiene in 15 mL of anhydrous n-hexane was added 2.1 g (6.0 mmol) of diethylaluminum hydride (25% in n-hexane solution) at room temperature under a nitrogen atmosphere. The solution was stirred at 35° for 18 hours. The reaction vessel was immersed in an ice bath and 1.00 g (7.5 mmol) of anhydrous aluminum chloride was added quickly. The reaction mixture was stirred at 60° for 5 hours followed by the same work up procedure used in the case of 6-methyl-1,5-heptadiene. GLC analysis of the filtrate using column M at 140° indicated that the starting material had completely reacted and two products had formed. The major component was generated in a 59% and the minor component in a yield of 30%. The two products were isolated by preparative scale GLC (column M) and the major product was identified as methylcyclohexane while the minor product proved to be n-heptane.

Cyclization of 1,5,10-Dodecatriene (134)
with Diethylaluminum Hydride and
Aluminum Chloride

To a solution of 0.20 g (1.22 mmol) of 1,5,10-dodecatriene (134) in 15 mL of anhydrous n-hexane was added 0.66 g (2.1 mmol) of diethylaluminum hydride (25% solution in n-hexane) under a nitrogen atmosphere at room temperature. The mixture was stirred at 60° for a period of 20 hours. The reaction vessel was immersed in an ice bath and 0.30 g (2.25 mmol) of anhydrous aluminum chloride was added all

at once. The mixture was heated to 65° for a period of 2.5 hours, the reaction vessel was immersed in a cold bath at -5° , and 5 mL of H_2O was added cautiously in a dropwise manner to quench the organometallic compound. The organic layer was separated, dried over anhydrous magnesium sulfate, and filtered. The filtrate was subjected to GLC analysis (column H at 160°) which revealed the presence of one dominant product as well as a group of minor components which accounted for less than 10% of the product composition. n-Decane (0.25g; 1.9 mmol) was added as an internal standard and used to determine an 81% yield for the major component. Preparative scale GLC using column A at 130° was used to isolate and purify the product. The structure of the product was assigned that of 1-cyclopentyl-2-ethylcyclopentane by NMR and mass spectral analysis; NMR (CCl_4) δ 1.00-2.10 (m, 19H), 0.76-1.00 (t, $J=7$ Hz, 3H); mass spectrum: $m/e = 166.30$ (calcd for $C_{12}H_{22}$: 166.308). Anal. Calcd for $C_{12}H_{22}$: C, 88.67; H, 13.33 . Found: C, 88.70; H, 13.30 .

Cyclization of 3-Methyl-1-hexen-5-yne (136)
with Diethylaluminum Hydride in
n-Hexane and Diethylether

To a solution of 0.25 g (2.66 mmol) of 3-methyl-1-hexen-5-yne and 0.5 g (6.76 mmol) of anhydrous diethylether in 2.0 mL of n-hexane was added 2.30 g (6.7 mmol) of diethylaluminum hydride (25% solution in n-hexane) under a nitrogen atmosphere. The mixture was stirred at 40° for a period of 40 hours. The reaction was worked-up in the same fashion as described for 1,5,10-undecatriene. The filtrate was subjected to GLC analysis using column M at 90° .

Only one product peak was observed on the chromatogram, and it possessed the same GLC retention as trans-1,2-dimethylcyclopentane.

Reduction of 1-Methyl-2-methylenecyclo-
hexane (133) with Diisobutylaluminum
Hydride

To a solution of 1.00 g (7.79 mmoles) of 1-methyl-2-methylenecyclohexane (133) in 5.0 mL of anhydrous n-hexane under a nitrogen atmosphere, was added 5.20 g (7.32 mmoles) of diisobutylaluminum hydride (20% solution in n-hexane). The resulting solution was stirred at 35° for a period of 18 hours. The reaction vessel was immersed in an ice bath and 5.0 mL of dilute hydrochloric acid (1.0N) was added to quench the organometallic compound. The organic layer was separated, dried over anhydrous magnesium sulfate and filtered. GLC analysis using column H at 130° indicated the presence of two products in a ratio of 1 : 1 with retention times of 11.0 minutes and 13.0 minutes. A small amount of starting material, 1-methyl-2-methylenecyclohexane (133) (retention time 15.0 minutes), was also observed. The two products were separated by preparative scale GLC (column H). The first component to elute proved to be cis-1,2-dimethylcyclohexane and the second component, trans-1,2-dimethylcyclohexane, as determined by comparison of NMR spectra with those of authentic samples.

Cyclization of 2-Methyl-1,5-hexadiene
with Diisobutylaluminum Hydride

To a solution of 0.5 g (8.33 mmoles) of 2-methyl-1,5-hexadiene in 10 mL of n-hexane was added 5.2 g (8.03 mmoles) of diisobutylaluminum hydride (20% solution in n-hexane) under a nitrogen atmosphere.

The resulting solution was refluxed for a period of 18 hours. The reaction vessel was immersed in a cold bath at -5° and 10 mL of saturated aqueous ammonium chloride solution was added cautiously. The organic layer was separated, dried over anhydrous magnesium sulfate, and filtered. Most of the n-hexane in the filtrate was removed by distillation under atmospheric pressure through a short Vigreux column. The remaining solution was subjected to GLC analysis using column O at 50° . Two product peaks were observed having retention times of 13.5 minutes and 15.0 minutes in a 60 : 40 ratio. The two products were isolated by preparative scale GLC using column M at 65° . The major product was identified as 1,1-dimethylcyclopentane and the minor component as 1,3-dimethylcyclopentane.

PART 2. REDUCTIONS USING LOW-VALENT TITANIUM AND ZIRCONIUM COMPLEXES

I. Introduction

Although titanium is one of the more abundant metals in the earth's crust (0.6%) its chemistry is little known compared to that of many other metals (78). The most predominant form of titanium is the 4^+ oxidation state: TiO_2 is used as a commercial white pigment and inexpensive TiCl_4 functions as "Smoke" by sky-writers since it is rapidly hydrolyzed. Titanium also has well-defined 2^+ and 3^+ oxidation states. Titanocene, which has titanium in a +2 oxidation state, is well known and is currently employed in nitrogen fixation studies (79). The 3^+ oxidation state is somewhat easier to work with and is commercially available as the trichloride.

Interest in the chemistry of both titanium and zirconium stems from their use in Ziegler-Natta catalysis. The insertion of an olefinic unit into a carbon-metal bond has considerable potential in organic synthesis as discussed in Part 1. Part 2 developed from reactions involving titanium and zirconium which led to reductions rather than cyclizations.

II. Historical

Low-valent titanium has had an interesting history as a reducing agent in organic chemistry: it was well known in the early 1900's but was then more or less forgotten until a decade ago. Knecht and Hibbert, for example, published a series of early papers (80) on the ability of aqueous TiCl_3 solution to reduce nitro arenes to amino arenes. They showed that the reaction was useful, not only as a preparative synthetic method but also as an analytical tool for the quantitative determination of aromatic nitro group in unknown substances (81). The same authors showed a short time later that aqueous TiCl_3 was capable of effecting rapid reduction of quinones to hydroquinones (82). In 1922, Macbeth demonstrated a further aspect of the reducing power of Ti(III) when he showed that both N-Br and N-Cl bonds in a variety of substrates were readily reduced (83).

Still other reports appearing occasionally in the literature demonstrated that cinnamic acid type double bonds could be reduced to the saturated analogs (84); azo groups were reduced to hydrazines (85).

Recently, J.E. McMurry and his coworkers published a series of papers and demonstrated that low valent titanium can be used to reduce epoxides (86), to induce coupling of allylic and benzylic alcohols (87), to induce reductive coupling of carbonyls to provide olefins (88), to reduce oximes, α -halo ketones and many more (89). In some cases, TiCl_3 was used as the source of low-valent titanium, while in other cases, the low-valent titanium was generated from the reaction of TiCl_4 with reducing reagents (87).

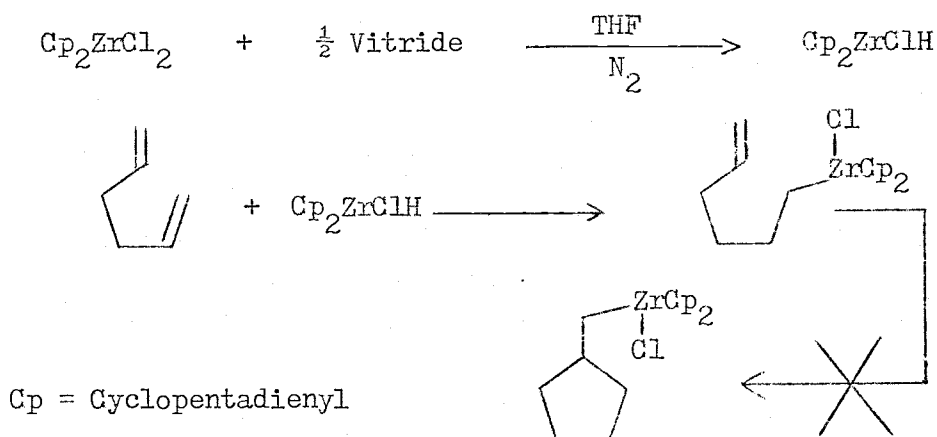
Although in many cases titanium and zirconium form similar types of compounds, they differ markedly from each other in some aspects of their chemical behavior. The methyl derivatives of zirconium, for example, are far more sensitive to hydrolysis than the corresponding compounds of titanium (90) whereas the latter are more susceptible to thermal decomposition. Much of the difference in chemical behavior between zirconium and titanium can be traced to the ease of reduction of the latter.

Reductions of alkenes and alkynes through hydrozirconation with di-(η^5 -cyclopentadienyl)chlorozirconium hydride were demonstrated to be synthetically useful reactions. The reaction has been employed in achieving synthetic objectives in a fashion similar to hydroboration (91). Reactions using low-valent titanium and zirconium compounds which might be synthetically useful were explored.

III. Results and Discussion

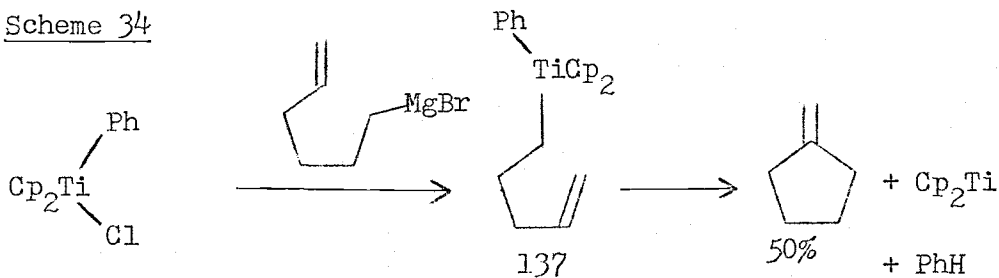
The combination of hydrozirconation and olefin insertion reaction can theoretically result in carbocyclization. But unfortunately, no cyclic product was found from the reaction of 1,5-hexadiene with $\text{di}(\eta^5\text{-cyclopentadienyl})\text{chlorozirconium hydride}$ (Scheme 33).

Scheme 33



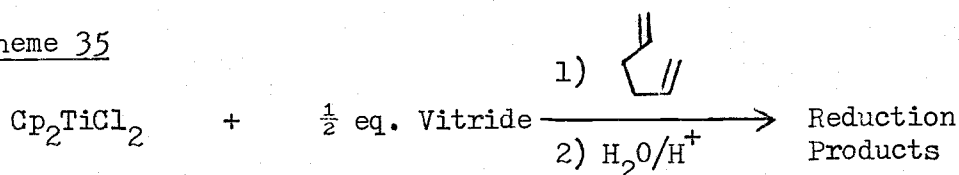
Since the cyclization reaction of the organozirconium compound met with failure, organotitanium compounds were investigated. Intramolecular cyclization of the 5-hexenyltitanium(IV) complex 137 had been successfully carried out giving a 50% yield of the carbocyclic product as described in Scheme 34 (92).

Scheme 34



Hydrotitanation of polyenes followed by olefin insertion into the titanium-carbon σ -bond was attempted, but, reminiscent of the hydrozirconation case, no carbocyclic product was produced in the reaction. Instead facile reduction of the polyenes took place (Scheme 35).

Scheme 35



It can be appreciated from Scheme 35 that the combination of a titanium (IV) complex and a hydride reducing reagent can accomplish hydrogenation of isolated carbon-carbon multiple bonds. Since this reaction had not been reported in the literature before, it was explored in more detail for possible synthetic applicability. Titanium tetrachloride was employed instead of di(n^5 -cyclopentadienyl)titanium dichloride in the reaction because of cost considerations. A convenient method for reductions of alkynes and alkenes by a combination of LiAlH_4 and TiCl_4 was developed. The reducing reagent was generated in situ from the dropwise addition of titanium tetrachloride to an ethereal solution containing lithium aluminum hydride and the unsaturated hydrocarbon. The results of reduction using molar quantities of LiAlH_4 and TiCl_4 are provided in Table 5. The yields were determined by measurement of relative peak areas on the gas-liquid phase chromatogram using *n*-decane as an internal standard. The molar ratio of unsaturated hydrocarbon to LiAlH_4 - TiCl_4 was optimized to obtain the highest yield of the desired reduction product with the minimum amount of hydrogen source.

Table 5. Yields of Reduction Products^a — Reduction of Alkynes and Monosubstituted Alkenes with $\text{LiAlH}_4\text{-TiCl}_4$

Alkene or Alkyne	Moles of Alkene or Alkyne Used	Moles of $\text{LiAlH}_4\text{-TiCl}_4$ Used	Temp.	Major Product	Yield
1-Octene	0.045	0.068	0°C	n-Octane ^b	92%
1-Octyne	0.045	0.110	0°C	n-Octane ^c	81%
4-Octyne	0.045	0.045	0°C	<u>cis-4-Octene</u> <u>trans-4-Octene</u> n-Octane	59% ^d <23% 13%
4-Octyne	0.045	0.045	-40°C	<u>cis-4-Octene</u> <u>trans-4-Octene</u> n-Octane	73% < 7% ^d 11%

^aAll reactions were performed under nitrogen.

^bA small amount (2.3%) of 1-octene remained unreduced.

^cA small amount (3.0%) of 1-octene was also present.

^dThe two isomeric 4-octenes were not completely resolved on the GLC.

Of the alkenes subjected to reduction conditions only mono-substituted double bonds were reduced with any reasonably efficient use of the hydrogen source. Disubstituted alkenes were reduced only partially even in the presence of a considerable excess of reducing agent. Only 36% of cyclooctene was reduced to cyclooctane under reaction conditions involving a 5 molar excess of $\text{LiAlH}_4\text{-TiCl}_4$. Although methylenecyclohexane was reduced somewhat faster than cyclooctene (30%

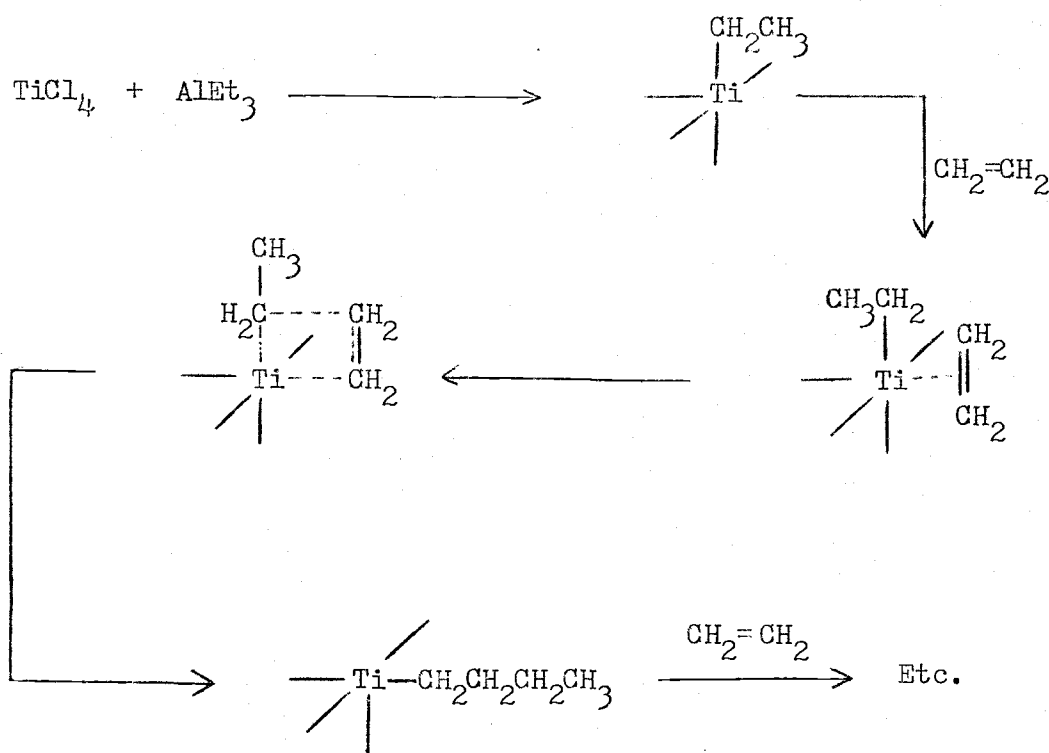
conversion into methylcyclohexane using a 10% molar excess of LiAlH_4 - TiCl_4), continued exploration into the reaction of additional alkenes was not pursued. The sluggishness of cyclooctene toward reduction suggested that a monosubstituted alkene would be selectively consumed in the presence of a more highly substituted alkene. A fair degree of selective reduction was realized in a competitive experiment involving equal molar quantities of 1-octene and cyclooctene with a 10% molar excess of LiAlH_4 - TiCl_4 . Under these conditions 95% of 1-octene was converted into n-octane, whereas only 10% of the cyclooctene was consumed.

Terminal alkynes were also reduced quite readily all the way to the alkane. Attempts to adjust conditions by limiting the amount of reducing agent in hopes of stopping at the terminal alkene stage inevitably resulted in isolation of a mixture of alkene and alkane. The rate of reaction of a monosubstituted alkene was apparently competitive with that of a terminal alkyne.

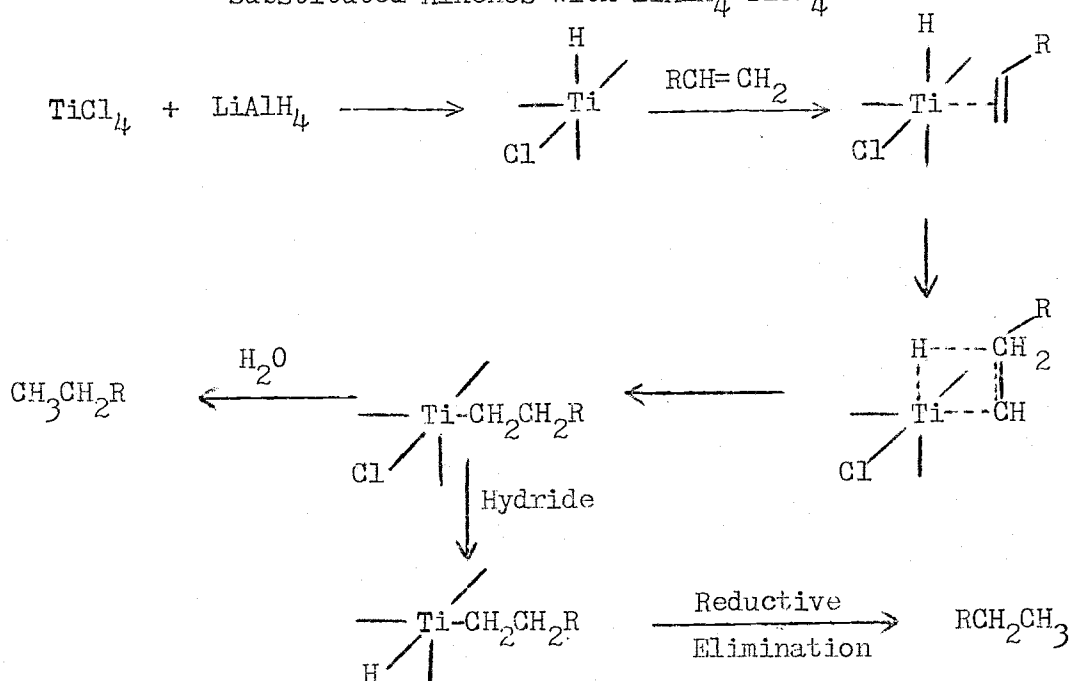
An internal alkyne is completely reduced with an equal molar amount of LiAlH_4 - TiCl_4 mainly to the alkene stage. As shown in Table 5, the stereochemistry of the 4-octene product depends markedly on temperature. At -40°C the percentage trans-4-octene produced was considerably less than that obtained at 0°C . This difference was matched almost exactly by a corresponding increase in the percentage cis isomer formed at the lower temperature. However, continued lowering of temperature (-78°C) appeared not to affect the cis/trans ratio further. The reaction represents a reasonably stereoselective synthesis of a cis- double bond from an appropriate internal alkyne.

Although no mechanistic study was involved, a plausible mechanism for the reduction reaction can be proposed as similar to the suggested mechanism of olefin polymerization using the Ziegler-Natta catalyst (combination of trialkylaluminum and TiCl_4) (93), in which titanium (IV) was reduced to a low-valent titanium by trialkylaluminum. A vacant site on the low-valent titanium allows the complexation of titanium with the π -bond of the olefin.

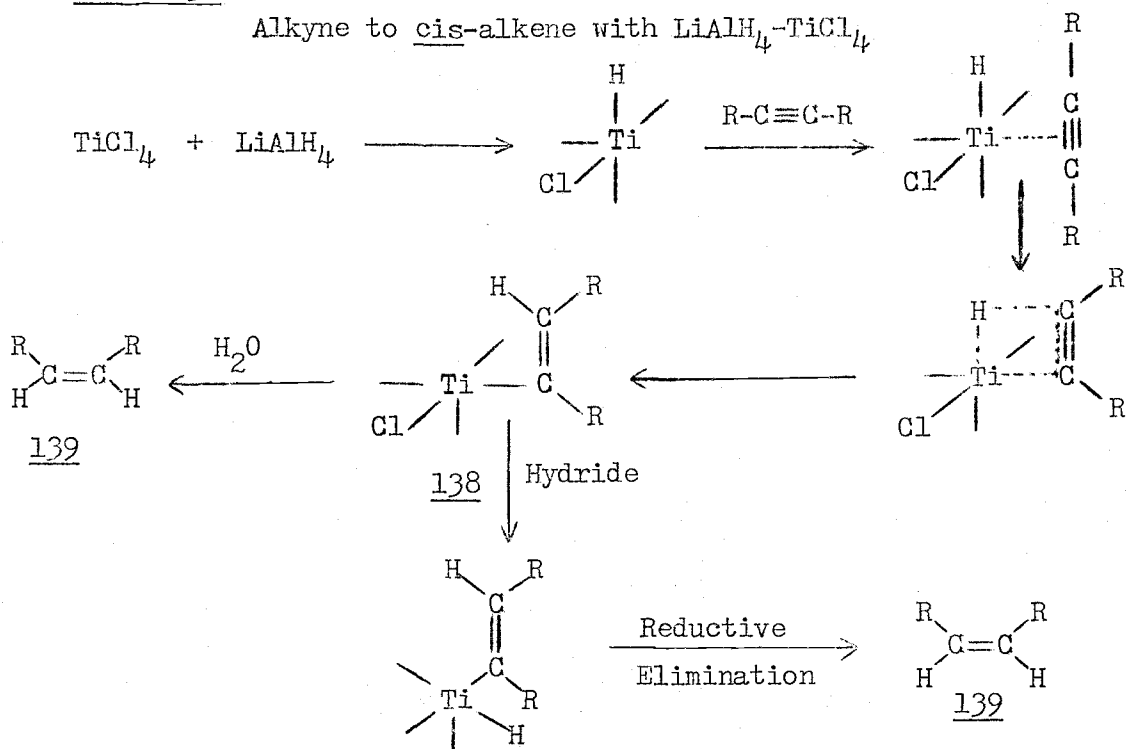
Scheme 36 Proposed Mechanism of Ethylene Polymerization with Ziegler-Natta Catalyst (94)



Scheme 37 Plausible Mechanism for the Reduction of Mono-substituted Alkenes with $\text{LiAlH}_4\text{-TiCl}_4$

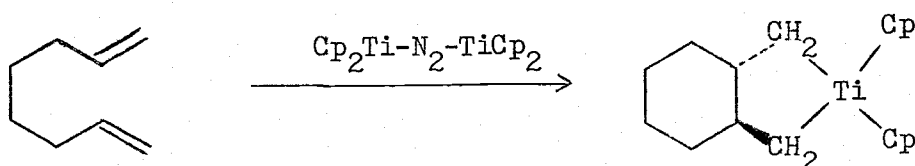


Scheme 38 Plausible Mechanism for Reduction of Internal Alkyne to cis-alkene with $\text{LiAlH}_4\text{-TiCl}_4$

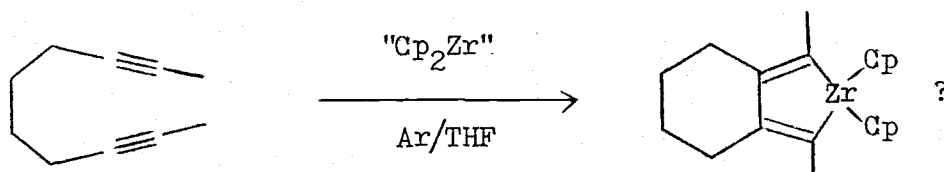


Intermediate 138 either experienced hydrolysis with retention of configuration (95) resulting in formation of cis-alkene 139 or underwent reductive elimination to relinquish the same stereochemical outcome.

Whitesides has recently reported an intramolecular cyclization of 1,7-octadiene by reaction with titanocene [generated from $(\text{Cp}_2\text{Ti})_2\text{N}_2$] through oxidative coupling. The yield was extremely low (96).



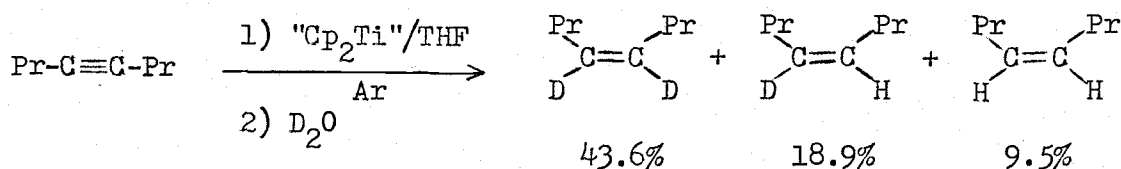
Zirconocene and titanocene can be generated in situ by reaction of sodium-naphthalene with Cp_2ZrCl_2 or Cp_2TiCl_2 in THF (97). Attempts to isolate the oxidative coupling product from the reaction of 2,8-decadiyne with zirconocene generated by the above mentioned method were unsuccessful. A pale yellow solid was obtained from the reaction but proved difficult to purify.



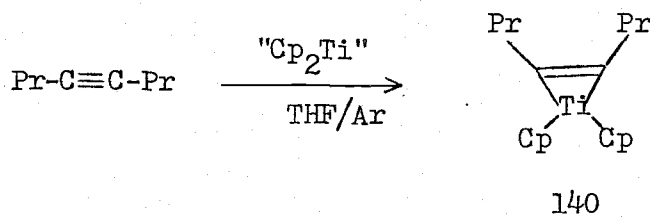
With the combination of Cp_2TiCl_2 , sodium, and naphthalene 1,8-octadiene gave only trace amounts of carbocyclization. Instead, simple reduction of the terminal double bonds took place readily (31).

When 4-octyne was allowed to react with Cp_2TiCl_4 and sodium naphthalene at -40°C in THF under an argon atmosphere, cis-4-octene

was produced in 73% yield after H_2O quenching. Low ionization energy mass spectral analysis of the product obtained from D_2O quenching showed 61% dideuteration, while the NMR spectrum revealed the location of the deuterium atoms to be virtually exclusively vinylic.



Although other possibilities exist, the results are clearly compatible with the formation of a rather stable metallocyclopropene 140.

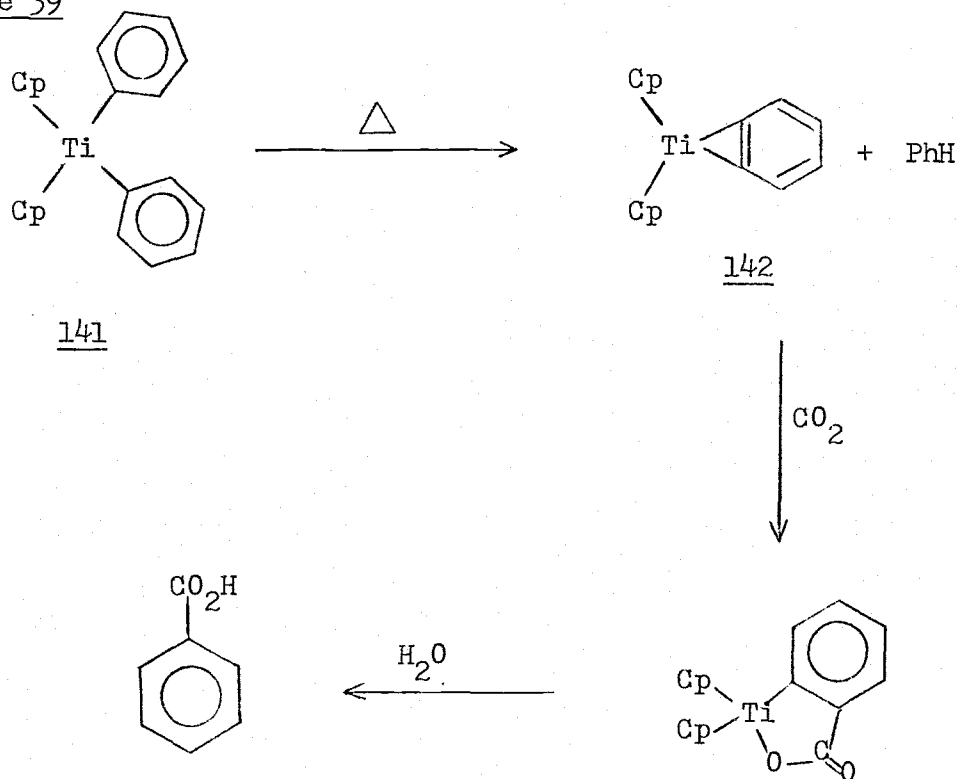


The metallocyclopropene intermediate 140 experienced hydrolysis in D_2O with retention of configuration (95) producing 4,5-dideutero-cis-4-octene. The monodeuterated product and the non-deuterated product might have resulted from an early stage hydrogen abstraction from solvent or the cyclopentadienide ring of the titanium complex.

A control reaction was performed under the same conditions in the absence of Cp_2TiCl_2 and the 4-octyne remained unchanged.

The existence of a titanocyclopropene was also proposed as an intermediate from pyrolysis reaction of 141 (98). The metallocyclopropene intermediate 142 experienced carbon dioxide insertion to produce benzoic acid after hydrolysis (Scheme 39).

Scheme 39



IV. Experimental

Reduction of 1-Octene with Lithium Aluminum Hydride and Titanium Tetrachloride

A mixture of 5.0 g (0.045 mole) of 1-octene and 3.2 g (0.52 mole) of lithium aluminum hydride in 50 mL of anhydrous diethyl ether was stirred under a nitrogen atmosphere at 0°. Nine and a half grams (0.05 mole) of titanium tetrachloride was added cautiously through an addition funnel in a dropwise manner. The resulting mixture was stirred for an additional 30 minutes followed by addition of 50 mL of saturated aqueous ammonium chloride solution. The ether layer was separated and washed with water, dried over magnesium sulfate, and filtered. The filtrate was analyzed by GLC using column I at 75°. Two grams (0.014 mole) of n-decane was added as an internal standard for yield determination. The yield of the product from the reaction was determined to be 92%. A NMR sample of the product was isolated by preparative scale GLC using the same conditions as described above. The product was determined to be n-octane by comparison of its NMR spectrum with that of a known sample of n-octane. A small quantity of unreacted 1-octene (2.3%) was recovered from the reaction.

Reduction of 1-Octyne with Lithium Aluminum Hydride and Titanium Tetrachloride

Similarly, 5.0 g (0.045 mole) of 1-octyne was reduced to n-octane by use of 6.6 g (0.11 mole) of lithium aluminum hydride and 20 g (0.11

mole) of titanium tetrachloride in 50 mL of anhydrous diethyl ether under a nitrogen atmosphere. GLC analysis of the product mixture using column I at 75° confirmed an 81% yield of n-octane and a 3.0% yield of 1-octene. n-Decane was used as internal standard for yield determination from the GLC analysis.

Reduction of 4-Octyne with Lithium Aluminum Hydride and Titanium Tetrachloride

In similar fashion, 5.0 g (0.045 mole) of 4-octyne was reduced to a mixture of cis-4-octene, trans-4-octene and n-octane by use 2.80 g (0.045 mole) of lithium aluminum hydride and 8.55 g (0.045 mole) of titanium tetrachloride in 50 mL of anhydrous ether under a nitrogen atmosphere. GLC analysis of the product mixture using column I at 75° confirmed a 59% of cis-4-octene, less than a 23% yield of trans-4-octene, and a 13% yield of n-octane. n-Decane was used as an internal standard.

When the reduction was conducted at -40°, the same quantities of reactants afforded a 78% yield of cis-4-octene, less than a 7% yield of trans-4-octene, and an 11% yield of n-octane.

The products from the reduction were isolated and purified by preparative scale GLC using column I at 75°. NMR spectra were obtained for each product and the structures of the products were assigned by comparison to the NMR spectra of known samples.

Reduction of Methylenecyclohexane with Lithium Aluminum Hydride-Titanium Tetrachloride

Under conditions already described for 1-octene, 2.0 g (0.02

mole) of methylenecyclohexane was reduced by the combination of 0.85 g (0.022 mole) of lithium aluminum hydride and 4.2 g (0.022 mole) of titanium tetrachloride in 50 mL of anhydrous diethyl ether under a nitrogen atmosphere. GLC analysis (column I at 75°) indicated that 31% of methylenecyclohexane was reduced to methylcyclohexane while 69% of the starting methylenecyclohexane remained unchanged.

The reduction product was isolated and purified by preparative scale GLC using column I at 75°. The NMR spectrum of the product was identical to that of a known sample of methylcyclohexane.

Competitive Reduction of 1-Octene vs
Cyclooctene with Lithium Aluminum
Hydride-Titanium Tetrachloride

A mixture of 2.5 g (0.022 mole) of 1-octene and 2.5 g (0.022 mole) of cyclooctene in 50 mL of anhydrous diethyl ether was reduced by 0.95 g (0.025 mole) of lithium aluminum hydride and 4.75 g (0.025 mole) of titanium tetrachloride under a nitrogen atmosphere under the same conditions as described for 1-octene. The resulting reaction mixture was subjected to GLC analysis (column I) at 75°. From relative peak areas, it was found that 95% of the 1-octene was converted into n-octane, while only 10% of cyclooctene was consumed and reduced to cyclooctane.

Reduction of 4-Octyne with Titanocene

A solution of 3.3 g (26 mmoles) of naphthalene in 50 mL of anhydrous THF was stirred under an argon atmosphere at 0° in the presence of a small piece of clean sodium metal (0.60 g; 26 mmoles).

A blue solution formed slowly which indicated the formation of the naphthalene radical anion. The solution was stirred for one hour until all the sodium metal dissolved. To this solution was added 1.32 g (12.0 mmoles) of 4-octyne and the flask contents were stirred for one-half hour. Three grams (12.24 mmoles) of di(n^5 -cyclopentadienyl) titanium dichloride was added to the reaction mixture all at once. The mixture was stirred for 3.5 hours at 0° followed by the cautious, dropwise addition of 2 mL of anhydrous methanol. After being stirred for an additional hour, the volatile components were vacuum transferred from the reaction mixture. GLC analysis of the clear transferred liquid with column D at 110° indicated that the starting material had reacted completely. Only one product peak was observed on the chromatogram. The product was isolated and purified by preparative scale GLC (column D) at 110°. The NMR spectrum was obtained and was identical to the NMR spectrum of a known sample of cis-4-octene. GLC analysis of the product mixture using column I indicated that the purity of the product was greater than 95% cis-4-octene and less than 5% trans-4-octene.

The reaction was repeated for yield determination. The same amounts of reactants were used and 0.50 g (3.91 mmoles) of n-nonane was added to the reaction mixture as an internal standard. From the relative peak areas of GLC analysis with column G at 90°, an overall yield of 72.5% of cis-4-octene was determined.

Reduction of 4-Octyne with Titanocene,
Quenching with Deuterium Oxide

A solution of 1.55 g (10.0 mmoles) of naphthalene in 30 mL of

anhydrous THF was stirred under an argon atmosphere at 0° and 0.30 g (13 mmol) of sodium metal was added. The resulting blue solution was stirred for one hour until all the sodium dissolved. To this solution was added 0.45 g (4.1 mmol) of 4-octyne and the reaction vessel was then immersed in a Dry Ice-acetone bath. The solution was stirred in the Dry Ice-acetone bath for 0.5 hour and 1.1 g (4.49 mmol) of $\text{di}(\eta^5\text{-cyclopentadienyl})\text{titanium dichloride}$ was added quickly. The resulting mixture was stirred for 6 hours at -78° . The reaction vessel was removed from the Dry Ice-acetone bath and immersed in an ice bath. This was followed by the addition of 1 mL (50 mmol) of deuterium oxide. The final mixture was stirred at 0° for one hour and then the volatile components were vacuum transferred. GLC analysis of the clear liquid which was collected in the vacuum transfer using column D at 110° indicated all the 4-octyne had completely reacted and a single product peak was observed. The yield of the product was 72% as determined using n-nonane as internal standard. The product was isolated and purified by preparative scale GLC using column I; NMR (CCl_4) δ 5.24-5.45 (m), 1.90-2.15 (m), 1.20-1.60 (6 peaks, $J=7\text{Hz}$), 0.85-1.05 (t, $J=7\text{Hz}$). The ratio of the peak area at $\delta=5.24-5.45$ to the peak area at $\delta=0.85-2.15$ was found to be 1 : 40. The mass spectrum at 10 eV ionization potential gave a ratio of m/e 112 : 113 : 114 = 1.0 : 2.0 : 4.6. From the mass spectral information, it was determined that the product consisted of 43.6% 4,5-dideuterio-cis-4-octene, 18.9% 4-deuterio-cis-4-octene, and 9.5% cis-4-octene.

Control Reaction of the Naphthalene
Radical Anion with 4-Octyne

A naphthalene radical anion solution in anhydrous THF (30 mL) was prepared from the reaction of 1.55 g (10.0 mmol) of naphthalene with 0.3 g (13.0 mmol) of sodium metal at 0° under an argon atmosphere. To the radical anion solution was added 0.45 g (4.1 mmol) of 4-octyne and the reaction was stirred for 6 hours at 0°. To the flask contents was added 1 mL of H₂O. After being stirred for one additional hour, the reaction mixture was subjected to vacuum transfer. GLC analysis of the transferred liquid using column I indicated that the 4-octyne was unchanged and no 4-octene was observed.

Attempted cyclization of 1,5-hexadiene
Using Di-(η^5 -cyclopentadienyl)chloro-
zirconium Hydride as a Catalyst

Two grams (24.4 mmol) of 1,5-hexadiene was dissolved in 20 mL of anhydrous benzene which was followed by addition 500 mg (2 mmol) of di-(η^5 -cyclopentadienyl)chlorozirconium hydride [prepared by the method of J. Schwartz et. al. (91)] under a nitrogen atmosphere. The mixture was stirred and refluxed for 10 hours. The reaction mixture was subjected to vacuum transfer and a clear liquid was collected in a Dry Ice-acetone trap. GLC analysis of the liquid using column I at 75° indicated no cyclic product had been generated in the reaction and that the bulk of the 1,5-hexadiene had remained unchanged.

Attempted Cyclization of 1,5-Hexadiene
Using Di-(η^5 -cyclopentadienyl)chloro-
zirconium Hydride as a Reagent

A solution of 0.26 g (3.1 mmol) of 1,5-hexadiene and 0.80 g (3.1 mmol) of di-(η^5 -cyclopentadienyl)chlorozirconium hydride [prepared by the method of J. Schwartz et.al. (91)] in 14 mL of anhydrous benzene was refluxed for 6 hours under a nitrogen atmosphere. The reaction vessel was immersed in an ice bath and 20 mL of 5% hydrochloric acid was added. The benzene layer was separated, dried over anhydrous magnesium sulfate, and filtered. The filtrate was vacuum transferred and a clear liquid was collected in a Dry Ice-acetone trap. GLC analysis of the clear liquid using column I at 75° revealed the presence of two products which displayed GLC retention times identical to those of n-hexane (17%) and 1-hexene (42%). Also present was 40% unreacted starting material. The most likely cyclic product, methylcyclopentane, was shown not to be produced due to the absence of a substance of longer retention time.

Attempted Cyclization of 1,5-Hexadiene
Using Di-(η^5 -cyclopentadienyl)dichloro-
titanium and Vitride as a Reagent

A mixture of 1.0 g (12.2 mmol) of 1,5-hexadiene, 2.99 g (12.0 mmol) of di-(η^5 -cyclopentadienyl)dichlorotitanium, and 10 mL of anhydrous benzene at 0° was stirred under a nitrogen atmosphere. To the mixture was added 1.68 mL (6.0 mmol) of Vitride (70% solution in benzene) in a dropwise manner. The reaction mixture changed from deep red to deep green in color. The mixture was stirred for one hour

after completion of the addition. To the reaction mixture was added 25 mL of 5% hydrochloric acid. The benzene layer was separated, dried over calcium chloride, and filtered. The filtrate was subjected to vacuum transfer and a clear liquid was collected in a Dry Ice-acetone trap. GLC analysis of the clear liquid using column I at 75° revealed the presence of two products which displayed GLC retention times identical to those of n-hexane (major product) and 1-hexene (minor product). Also present was a small amount of unreacted starting material. The most likely cyclic product, methylcyclopentane, was shown not to be produced owing to the absence of a substance of longer retention time.

BIBLIOGRAPHY

1. B. J. Wakefield, "The Chemistry of Organolithium Compounds", Pergamon Press, New York, N.Y. 1974.
2. E. A. Hill, J. Organomet. Chem., 91, 123 (1975) and references therein.
3. (a) K. Ziegler, "Organometallic Chemistry", H. Zeiss, Ed., Reinhold Publishing Corp., New York, N.Y., 1960, P. 234.
(b) T. W. Dolzin and J. P. Oliver, J. Organomet. Chem., 78, 165 (1974).
(c) A. A. Antonov, C. F. Brodovskaya, N. S. Nanetkin, and V. I. Smetanyuk, Neflckhimiya, 15, 264 (1975)
4. C. A. Bertelo and J. Schwartz, J. Amer. Chem. Soc., 98, 262 (1976).
5. L. G. Cannell, ibid., 94, 6867 (1972).
6. J. St. Denis, T. Dolzin, and J. P. Oliver, ibid., 94, 8260 (1972).
7. (a) K. Sakai and O. Oda, Tetrahedron Lett., 4375 (1972).
(b) H. Arai and J. Halpern, Chem. Commun., 1571 (1971)
(c) J. A. Evans, D. R. Russel, A. Gright, and B. L. Shaw, ibid., 841 (1971)
8. P. W. Jolly and G. Wilke, "The Organic Chemistry of Nickel, Volume II", Academic Press, New York, N.Y., 1975.
9. (a) J. Y. Mirour, J. L. Roustan, C. Charrier, J. Collin, and J. Benaini, J. Organomet. Chem., 51, C24 (1973)
(b) N. Genco, D. Marten, S. Raghu, and M. Rosenblum, J. Amer. Chem. Soc., 98, 848 (1976)
10. (a) D. R. Coulson, J. Amer. Chem. Soc., 91, 200 (1969).
(b) E. Forsellini, G. Bombieri, B. Crociani, and T. Boschi, Chem. Commun., 1203 (1970).
11. J. K. Crandall, P. Battioni, J. T. Wehlacz, and R. Bindra, J. Amer. Chem. Soc., 97, 7171, (1975)
12. T. J. Marks and W. A. Wachter, ibid., 98, 703 (1976).

13. K. P. C. Vollhardt and R. L. Funk, J. Amer. Chem. Soc., 99, 5483 (1977).
14. J. E. Baldwin, J. C. S. Chem. Commun., 734 (1976).
15. J. E. Baldwin, J. Cutting, W. Dupont, L. Kruse, L. Silberman, and R. C. Thomas, ibid., 736 (1976).
16. J. E. Baldwin and J. A. Reiss, ibid., 77 (1977).
17. W. S. Johnson, Accounts of Chem. Res., 1, 1 (1968).
18. (a) G. Stork and A. W. Burgstahler, J. Amer. Chem. Soc., 77, 5068 (1955).
(b) P. A. Stadler, A. Eschenmoser, H. Schinz, and G. Stork, Helv. Chim. Acta, 40, 2191 (1957)
(c) A. Eschenmoser, L. Ruzicka, O. Jeger, and D. Arigoni, ibid., 38, 1890 (1955).
19. (a) K. E. Harding, J. L. Cooper and P. M. Puckett, J. Amer. Chem. Soc., 100, 993 (1978).
(b) R. A. Volkmann, G. C. Andrews, and W. S. Johnson, ibid., 97, 4777 (1975).
(c) R. L. Markezich, W. E. Willy, B. E. McCarry, and W. S. Johnson, ibid., 95, 4414 (1973).
(d) W. S. John, K. Wiedhaup, S. F. Brady, and G. L. Olson, ibid., 96, 3979 (1974).
(e) P. A. Bartlett and W. S. Johnson, ibid., 95, 7501 (1973).
(f) P. A. Bartlett, J. T. Brauman, W. S. Johnson, and R. A. Volkmann, ibid., 95, 7503 (1973).
(g) W. S. Johnson, N. P. Jensen, J. Hooz, and E. J. Leopold, ibid., 90, 5872, (1968).
20. R. C. Lamb, P. W. Ayers, and M. K. Toney, ibid., 85, 3483 (1963).
21. M. Julia, Accounts of Chem. Res., 4, 386 (1971).
22. M. Julia, Rec. Chem. Prog., 25, 3 (1964).
23. M. A. Silver, P. P. Shafer, J. E. Nordlander, C. Reechardt, and J. D. Roberts, J. Amer. Chem. Soc., 82, 2649 (1960).
24. R. Waack and M. A. Doran, ibid., 91, 2456 (1969)

25. E. A. Hill, H. G. Richey, Jr., and T. C. Rees, J. Org. Chem., 28, 2161 (1963).
26. J. Y. Mirour, J. L. Roustan, C. Charrier, J. Collin, and J. Benaini, J. Organomet. Chem., 51, C24 (1973)
27. K. Sakai, J. Ide, O. Oda and N. Nakamura, Tetrahedron Lett., 1287 (1972).
28. H. G. Richey, Jr., T. C. Rees, and E. A. Hill, ibid., 4297 (1966).
29. J. J. Eisch and G. R. Hask, J. Org. Chem., 31, 3419 (1966).
30. G. Hata and A. Miyake, J. Org. Chem., 28, 3237 (1963).
31. L. W. Bass and S. E. Wilson, Unpublished Results, Department of Chemistry, Oregon State University, Corvallis, Oregon.
32. S. W. Benson, "Thermochemical Kinetics", John Wiley & Sons, New York, N.Y. 1968.
33. E. A. Hill, R. J. Theissen, A. Daughy, and R. Miller, J. Org. Chem., 34, 3681 (1969).
34. G. Wilke and H. Miller, Ann., 629, 222 (1960)
35. G. Wittig and J. Otten, Tetrahedron Lett., 601 (1963)
36. H. Felkin, G. Swierczewski, and A. Tambute, ibid., 707 (1969).
37. J. Halpern and J. P. Maher, J. Amer. Chem. Soc., 86, 2331 (1964); 87, 5361 (1965).
38. P. B. Chock and J. Halpern, ibid., 91, 582 (1969).
39. M. Rosenblum, Accounts of Chem. Res., 7, 122 (1974).
40. E. A. Hill, R. J. Theissen, and K. Tancher, J. Org. Chem., 34, 3061 (1969).
41. E. A. Hill, R. J. Theissen, C. E. Cannon, R. Miller, R. B. Guthrie, and A. T. Chen, J. Org. Chem., 41, 1191 (1976)
42. S. E. Wilson, Tetrahedron Lett., 4561 (1975).
43. V. N. Drizd, Yu. A. Ustynyjuk, M. A. Tsel'iva, and L. B. Bmitriev, Zh. Obshch. Khim., 38, 2114 (1968).
44. K. Ziegler, H. G. Gellert, K. Zosel, W. Lehmkuhl, and W. Pfohl, Angew. Chem., 67, 424 (1954).

45. (a) K. Ziegler, E. Holzkamp, H. Brill, and H. Martin, Angew. Chem., 67, 541 (1955)
(b) G. Natta and I. Pasquio, Adv. in Catalysis, 11, 1 (1959).
46. (a) J. J. Eisch and C.K. Fichler, J. Amer. Chem. Soc., 96, 6815 (1974).
(b) J. J. Eisch and M. W. Foxton, J. Org. Chem., 36, 3520 (1971).
47. H. Pines and N. E. Hoffmann, J. Amer. Chem. Soc., 76, 4417 (1954).
48. K. Ziegler, H. G. Gellert, H. Martin, N. Nagel, and J. Schneider, Ann. Chem., 589, 91 (1954).
49. A. Stefani, Helv. Chim. Acta., 57, 1346 (1974).
50. K. Ziegler, Angew. Chem., 64, 323 (1952).
51. (a) K. Ziegler, H. G. Gellert, H. Lehmkuhl, W. Pfohl, and K. Zosel, Ann. Chem., 629, 1, (1960).
(b) K. Ziegler, W. R. Kroll, W. Larbig, and O. W. Steudel, Ann. Chem., 629, 53 (1960).
(c) K. Ziegler, K. Nagel, and W. Pfohl, Ann. Chem., 629, 210 (1960).
52. H. Lehmkuhl, Ann. Chem., 719, 40 (1968)
53. K. W. Egger and A. T. Cocks, Trans. Faraday Soc., 57, 2629 (1971)
54. K. W. Egger, International J. Chem. Kinetics, 1, 459 (1969).
55. (a) A. G. Bchering, Chem. Abstr., 60, 131645f (1964)
(b) V. P. Yur'ev, A. V. Kuchin, I. M. Salimgareeva, G. A. Kozhevnikova, V. I. Kleiner, and G. A. Tolstikov, Izvest. Akad. Nauk SSSR, 23, 2553, (1974); Bull. Acad. Sci. U.S.S.R., 23, 2460 (1974).
56. J. J. Eisch and G. Ronald, J. Org. Chem., 31, 3419 (1966).
57. K. W. Egger, Liebigs Ann. Chem., 521 (1975)
58. (a) W. S. Johnson, J. Amer. Chem. Soc., 75, 1498 (1953)
(b) N. L. Allinger and J. L. Coke, ibid., 82, 2553 (1960)
(c) K. R. Blanchard and P.V.R. Schleyer, J. Org. Chem., 28, 247 (1963).

59. G. Fraenkel, D. T. Dix, and M. Carlson, Tetrahedron Lett., 579 (1968).
60. J. J. Eisch and K. C. Kichter, J. Amer. Chem. Soc., 96, 6815 (1974).
61. I. Zakharkin and L. A. Savina, Zhurnal Obshchei Khimii, 35, 1142 (1965).
62. I. Zakharkin and I. M. Khonliner, Bull. Acad. Sci., USSR, Engl. Transl., 1768 (1961).
63. (a) A. V. Gross and J. M. Mavity, J. Org. Chem., 5, 106 (1940)
(b) H. Reinheckel and K. Haage, J. Prakt. Chem., 33, 70 (1966).
(c) T. Mole, Australian J. Chem., 16, 794 (1963)
64. J. Schwartz and D. B. Carr, J. Amer. Chem. Soc., 99, 638 (1977).
65. J. P. Oliver and T. W. Dolzine, ibid., 96, 1737 (1974).
66. (a) K. Ziegler and W. R. Kroll, Ann. Chem., 629, 167 (1960).
(b) K. Ziegler, Ger. Pat., 1,162,368; Chem. Abstr., 60, 15909c (1964).
67. J. J. Eisch, E. N. Barlinson, and E. Nicholas, J. Amer. Chem. Soc., 98, 753 (1976)
68. (a) G. H. Smith and F. J. Hamilton, J. Phys. Chem., 72, 3567 (1968)
(b) K. Starowieyski, S. Pasynkiewicz, and M. Boleslawski, J. Organometal. Chem., 10, 393 (1967)
69. G. Gaicomelli, R. Menicagli, and L. Lardicci, J. Org. Chem., 39, 1757 (1957).
70. W. L. Smith and T. Wartik, J. Inorg. Nucl. Chem., 29, 629 (1967).
71. G. Wilke and H. Muller, Annalen., 629, 222 (1960).
72. G. Zweifel and R. B. Steele, Tetrahedron Lett., 6021 (1966).
73. G. Zweifel, G. M. Clark, and R. Lynd, Chem. Commun., 1593 (1971).
74. H. Fleischaker and G. F. Wood, J. Amer. Chem. Soc., 78, 3436 (1956).

75. A. Viola and L. Levasseur, J. Amer. Chem. Soc., 87, 1150 (1965).
76. W. L. Howard and N. B. Lorette, Organic Syn., 42, 14 (1962)
77. A. Viola, J. Iorio, K. K. Chen, G. M. Glover, V. Nayak, and P. J. Kocienski, J. Amer. Chem. Soc., 89, 3462 (1967).
78. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd Ed., Interscience, New York, N.Y. 1972, p. 807-818.
79. E. E. van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Akemark, J. Amer. Chem. Soc., 91, 1551 (1969)
80. E. Knecht and E. Hibbert, Chem. Ber., 36, 166 (1903).
81. E. Knecht and E. Hibbert, Chem. Ber., 40, 3819 (1907).
82. E. Knecht and E. Hibbert, Chem. Ber., 43, 3455 (1910).
83. L. A. Black, E. L. Hirst and A. K. Macbeth, J. Chem. Soc., 121, 2527 (1922).
84. P. Karrer, Y. Yen, and T. Reichstein, Hevl. Chim. Acta, 13, 1308 (1930).
85. N. R. Large, F. J. Stubbs, and C. Hinshelwood, J. Chem. Soc., 2736 (1954).
86. J. E. McMurry and M. P. Fleming, J. Org. Chem., 40, 2555 (1975).
87. J. E. McMurry and M. Silvestri, ibid., 40, 2687 (1975).
88. J. E. McMurry and M. P. Fleming, J. Org. Chem., 41, 896 (1976).
89. J. E. McMurry, Accounts Chem. Res., 7, 281 (1974).
90. P. C. Wailes, R.S.P. Coutts, and H. Weigold, "Organometallic Chemistry of Titanium, Zirconium, and Hafnium", Academic Press Inc., New York, N.Y. 1974, Chapter 1.
91. D. W. Hart and J. Schwartz, J. Amer. Chem. Soc., 96, 8115 (1974).
92. S. E. Wilson, Unpublished Results, Department of Chemistry, Oregon State University, Corvallis, Oregon.
93. (a) G. Natta, Angew. Chem., 68, 393 (1959).
(b) K. Ziegler, Collection Czech. Chem. Commun. Suppl., 22, 295 (1957)
(c) J. C. W. Chien, J. Amer. Chem. Soc., 81, 86 (1959).

94. M. Hancock, M. N. Levy, and M. Tsutsui, "Organometallic Reactions, Volume 4", E. I. Becker and M. Tsutsui, Ed., Wiley-Interscience, New York, N.Y., 1972, p. 38.
95. (a) J. Dvorak, R. J. O'Brien, and W. Santo, Chem. Commun., 411 (1970).
- (b) I. S. Kolmnikov, T. S. Tobeeva, V. V. Gorbachevkaya, G. G. Aleksandrov, Yu. T. Struckhor, and M. E. Volpin, ibid., 972 (1971).
96. J. X. McDermott, M. E. Wilson, and G. M. Whitesides, J. Amer. Chem. Soc., 98, 6529 (1976).
97. G. W. Watl, J. L. Baye, and F. O. Drummond, ibid., 88, 1138 (1966).
98. (a) G. A. Razuvaev, N. V. Latyaeva, and L. I. Vyshinskaya, Zh. Obshh. Khim., 35, 169 (1965).
- (b) G. A. Razuvaev, N. V. Latyaeva, and L. I. Vyshinskaya, Dokl. Adad. Nauk SSSR, 134, 612 (1960).