

ABSTRACT

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Title: THE INTRAMOLECULAR ENE REACTION OF SOME
1, 2-DIALLYLCYCLOHEXANES

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Abstract approved by: _____
Elliot N. Marvell

The familiar equilibrium between 1,7-octadiene and cyclo-octene at temperatures exceeding 300° , indicates that an ene-retroene process could be used as a six atom ring expansion method. To test this possibility we prepared both cis and trans isomers of 1,2-diallyl-1,2-bis(trimethylsiloxy)cyclohexane and pyrolyzed this both in liquid and vapor phases. Reaction in either phase was clean leading essentially to a single product, 1,8-bis(trimethylsiloxy)bicyclo[6.4.0]dodec-2-ene, the ene product. This was not separated into cis and trans isomers either preparatively or analytically. This cis isomer of the reactant rearranges faster than the trans isomer. A minor by-product was identified as 7-spiro[6.5]dodecen-1-one, which apparently arises from 2-bicyclo[6.4.0]dodecen-1,8-diol through a pinacol rearrangement. This reaction must therefore result from the

presence of traces of moisture, though it is possible to account for the rearrangement without hydrolysis.

A sample of 1,2-diallyl-1-trimethylsiloxy cyclohexane was also prepared and rearranged. The product consisted of two isomers in a 9:1 ratio. The major isomer was 1-trimethylsiloxy-6-bicyclo [6.4.0] dodecene and the mirror isomer was the 2-ene. These results show that the 2-allyl group acts preferentially as the ene component, a result undoubtedly keyed by steric effects.

The Intramolecular Ene Reaction of Some
1,2-Diallylcyclohexanes

by

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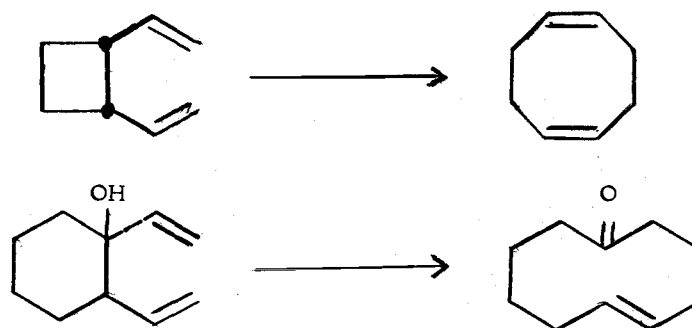
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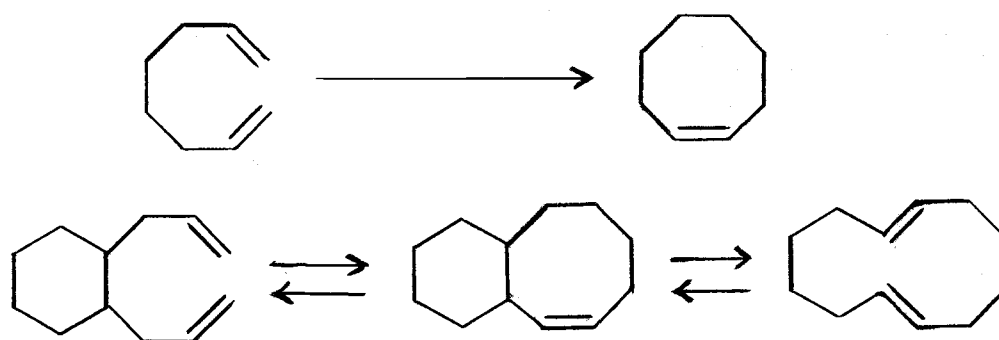
THE INTRAMOLECULAR ENE REACTION OF SOME 1,2-DIALLYLCYCLOHEXANES

INTRODUCTION

Ring expansion processes occupy an important place among the methods available for the controlled synthesis of alicyclic rings. The classic example is the carbonium ion rearrangement leading to a single carbon increase in size. One of the most interesting developments is the use of the Cope rearrangement to permit an increase of four atoms in one single step. Use of the oxy-Cope has extended the



value of this reaction to the formation of medium rings. Though it does not seem to have been recognized previously, the well-known equilibrium between 1,7-octadiene and cyclooctene is functionally adapted for a six atom ring expansion process (1, 2). The major problem herein rests with the reopening of the cyclooctene ring via the retro-ene process which must operate against an increase of enthalpy of ca. 20 kcal/mole, because a sigma bond is converted to a pi bond in the transaction. In this thesis some attempts to develop this

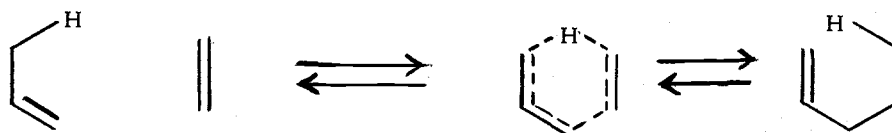


ene-retro-ene process into a useful six carbon ring expansion will be explored.

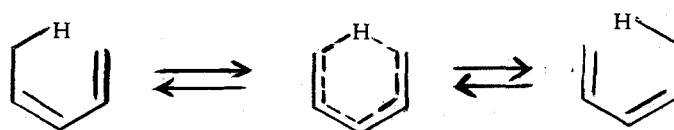
HISTORICAL

Introduction

Around the beginning of this century a number of reactions of olefins including such diverse reactions as those of olefins with formaldehyde, decarboxylation of β -ketoacids, pyrolysis of esters to form olefins and the pyrolytic decomposition of castor oil were discovered, but were not recognized as being related until the classic work of Alder (3) in 1943 described the general process called the ene reaction. This indirect substituting addition is a relative of the



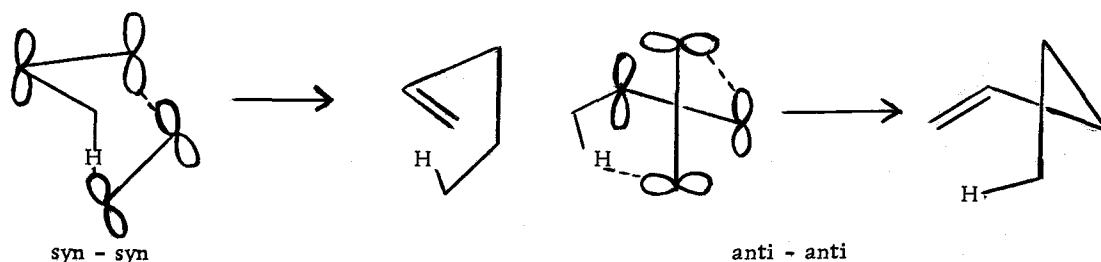
famous Diels-Alder reaction, and could be considered an intermolecular variant of the 1,5-hydrogen shift.



Excellent reviews of the ene reaction are available, so in this section a brief treatment of the mechanism will be presented, followed by the present knowledge of the selectivity features of the reaction. The largest part of the review will be devoted to intramolecular examples and retroene reactions since these are particularly pertinent to the work to be discussed in this thesis.

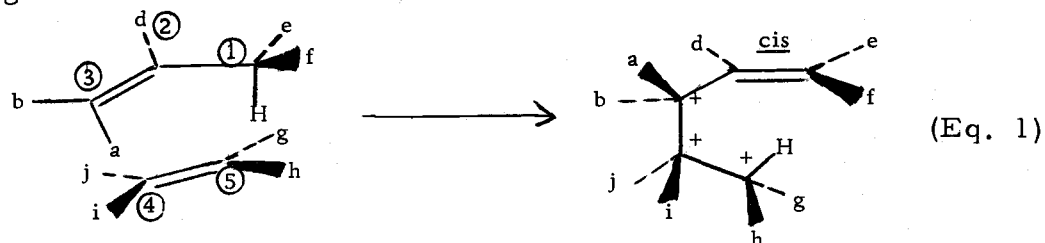
Mechanism

A concerted reaction proceeding via a cyclic six atom transition state was suggested by Koch (4) and independently by Arnold (5) as the mechanism for the ene reaction. A number of pieces of evidence support this suggestion. If the process is concerted, it is expected to conform to the Woodward-Hoffmann conservation of orbital symmetry theory (6). The syn-syn addition is allowed as is also the anti-anti addition. Clearly the anti-anti transition state is much

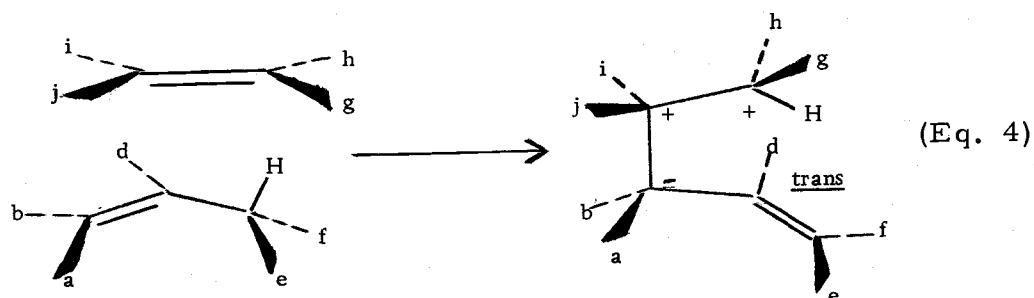
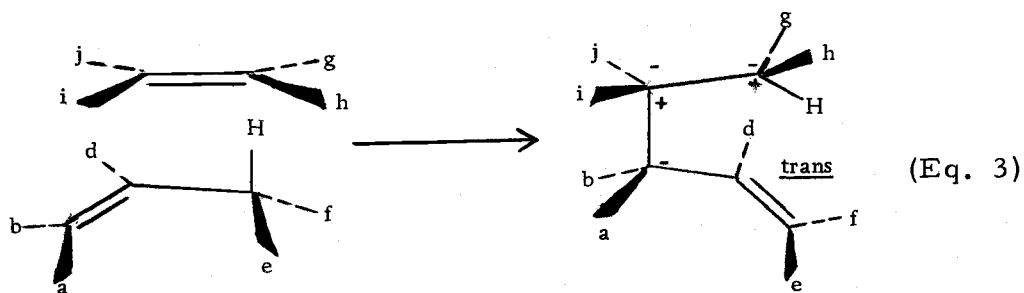
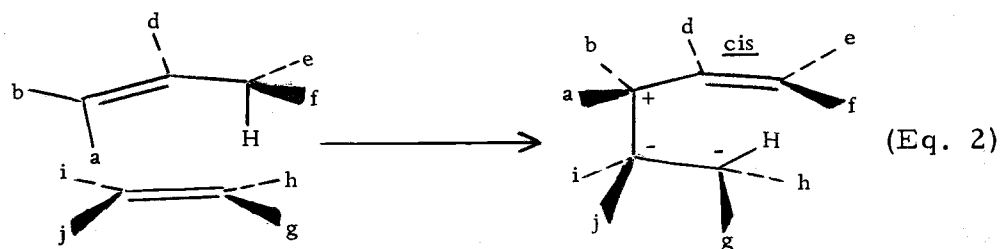


less likely on steric grounds and has not yet been observed. The syn-syn addition mode (sometimes called the cis addition process) is expected to restrict the possible stereochemical routes, leading to a considerable stereoselectivity (7).

The general ene reaction can convert reactants containing two double bonds and one hydrogen donor (potentially chiral) to products having three chiral centers and one double bond. There are thus



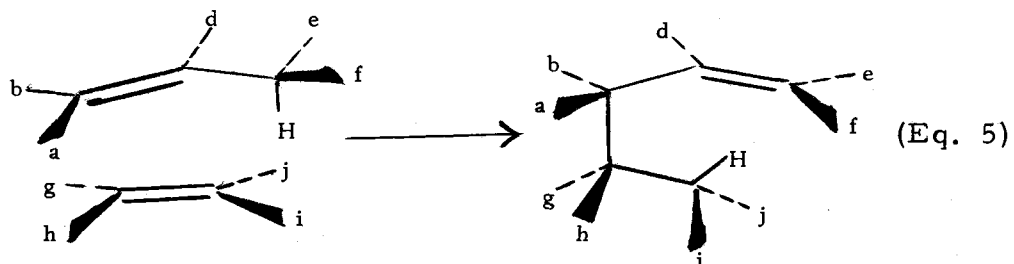
eight possible stereoisomers for reactants and sixteen for the products. However, for one pair of reactants using the syn-syn addition route there are four possible products, achieved via four different transition states. Along with the one above the other three are shown here. The problem relating to the switching of the side of the



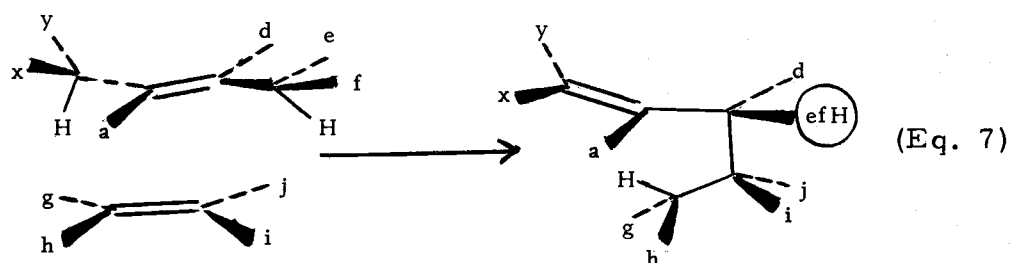
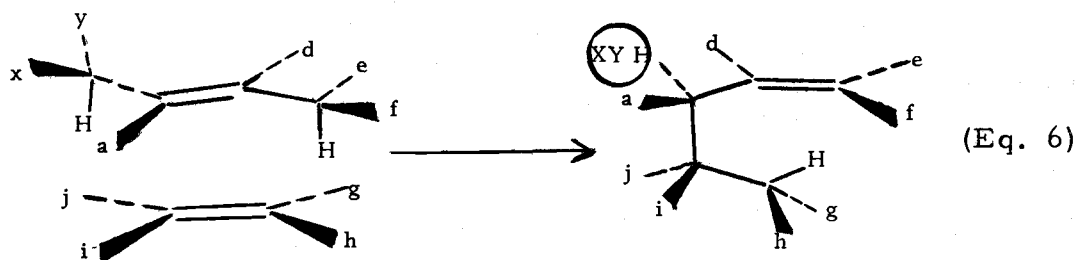
enophile to which addition occurs (Equation 1 or 2, 3 or 4) has been identified as the exo-endo problem. The question relating to which side of the ene can react, thus leading to an enantiomeric configuration

of the three chiral centers but with reversed double bond stereochemistry has not received a name and has not yet been studied.

In addition to the stereochemical problems noted above, there exist two regiochemical problems. If the enophile is unsymmetrical, the hydrogen could be transferred to either end, leading to structurally different products. For example, equation 5 represents a regio-



isomeric reaction to equation 1. Finally the ene component may have more than one atom having a hydrogen to transfer, again leading

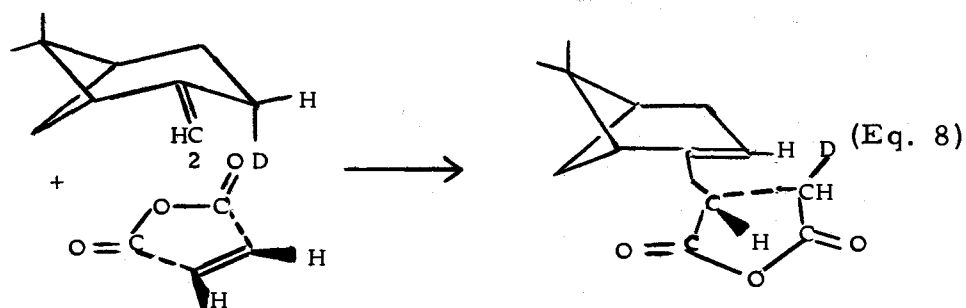


structurally different products, equations 6 and 7. Some of these problems have been examined experimentally, and the pertinent

material is noted below. Also some studies of the influence of substituents on the rates are included here, although relatively little is known about this question.

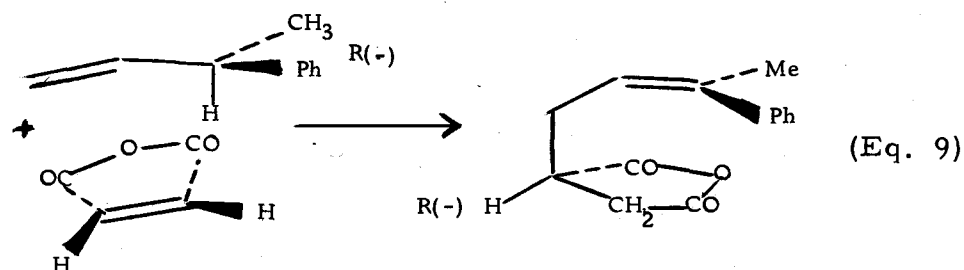
Stereochemical Studies

Recently Hill and his students (8) have shown that the hydrogen transferred is one aligned with its C-H bond parallel to the π orbitals in the ene (Equation 8). Arnold and his students (9) showed the same



result with some other enophiles in their studies with β -pinene.

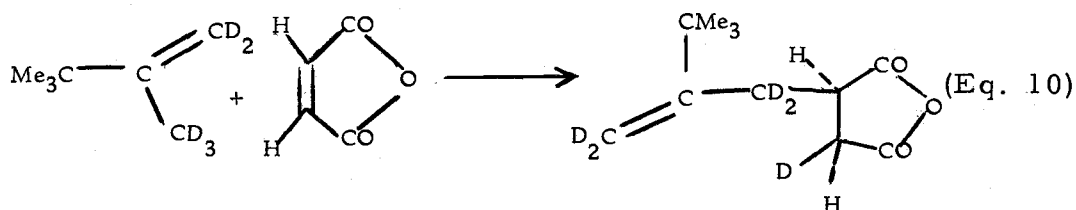
Earlier Hill and Rabinovitz (10) had shown that the hydrogen transfer should be simultaneous with C-C bond formation. Thus R(-) 3-phenyl-1-butene gave R(-) product (Equation 9) though the degree of



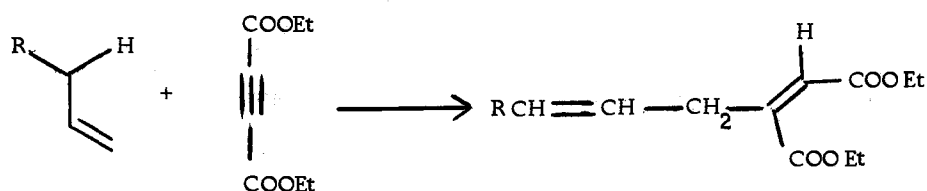
optical purity was unknown and the double bond geometry was not specified.

In 1971 Friedrich (11) showed that the cis-addition requirement

of the syn-syn allowed process was indeed verifiable experimentally.



The cis relationship of the two hydrogens on the ring in the product was determined by nmr but the stereoselectivity could not be shown to be better than 70% because of some scrambling. The result is in agreement with ene reactions with acetylenic enophiles, but there the



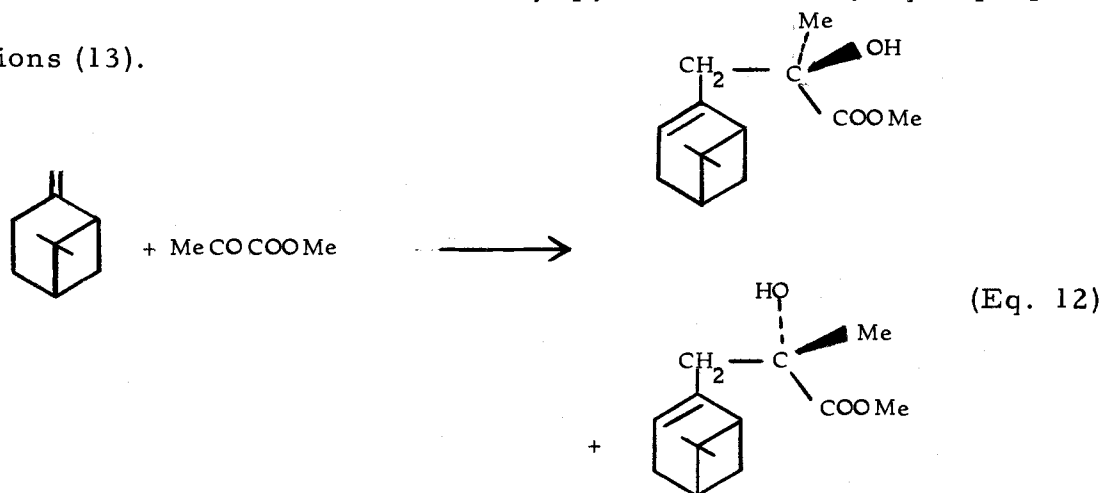
(Eq. 11)

reaction is 100% selective (5).

A few experiments related to the exo-endo question have been published. These lead to the conclusion that the endo arrangement is preferred, but that it is very sensitive to steric effects. The study of Hill above (8) showed that in the reaction between β -pinene and maleic anhydride the endo form is preferred over the exo by a factor somewhat greater than 3:1. Berson (12) in some earlier work showed that with cis-2-butene the endo form predominates by about a 4:1 ratio, while with trans-2-butene the ratio shrinks to 57:43.

Addition to the enophile can indeed take place from both sides,

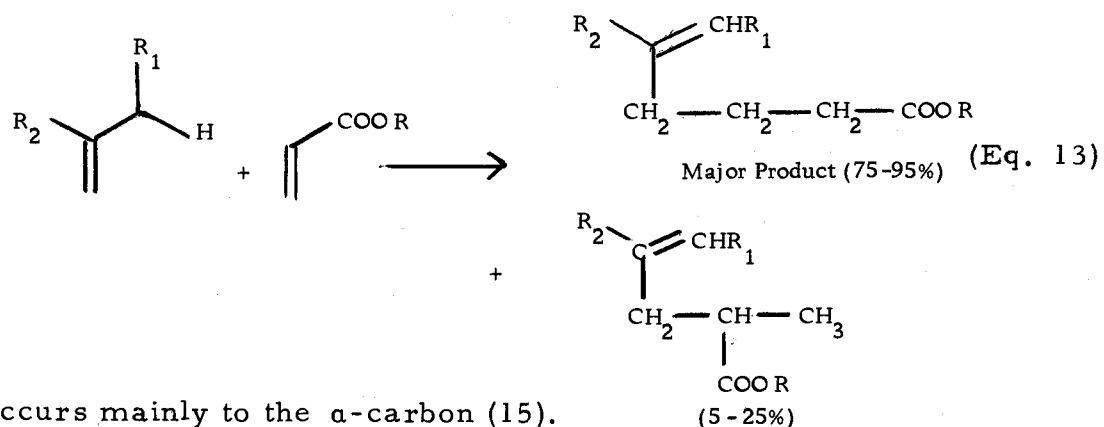
unless steric factors become dominant. Thus β -pinene forms two diastereomeric adducts with methyl pyruvate in nearly equal proportions (13).



Earlier studies had suggested this reaction gave only one of the two stereoisomers (14).

Regiochemical Studies

Most ene reactions involve either symmetrical enophiles or ones like a carbonyl group where the direction of reaction is dominated by energy considerations. However, a few reactions have been carried out with acrylic and propiolic esters, and transfer of the hydrogen



occurs mainly to the α -carbon (15).

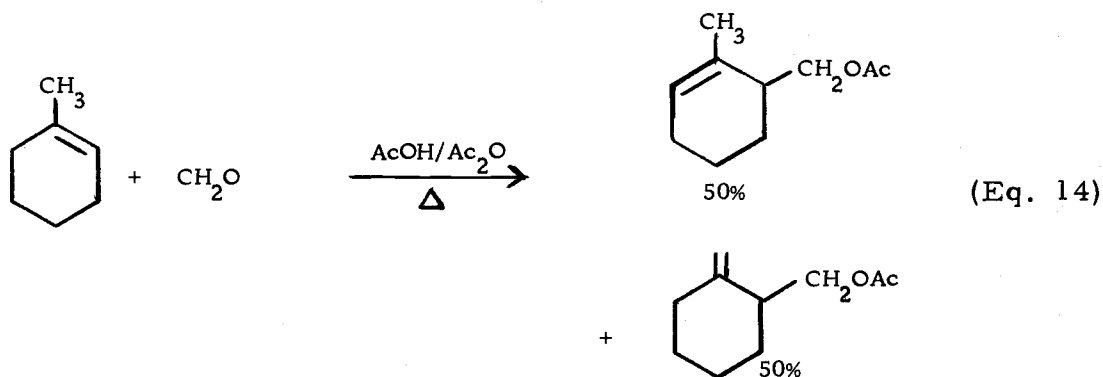
Somewhat more is known about the hydrogen which would be preferentially transferred, if more than one type of hydrogen is available. The results in Table 1 indicate that when non-competitive reactions are being considered (entries 1, 3 and 6), a primary hydrogen is transferred faster than a secondary, and that much faster than

Table 1. Reactions of some alkenes with diethyl azodicarboxylate.

Entry	Olefin	Rel. Rate	Rate Per H
1	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C} = \text{CH}_2 \\ \diagup \\ \text{CH}_3 \end{array}$	17.2	2.9
2	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{H} \\ \quad \quad \quad \diagdown \\ \quad \quad \quad \text{CH}_3 \end{array}$	3.73	.62
3	$\text{CH}_2 = \text{CH} - \text{CH}_2\text{CH}_3$	2.57	1.28* (2.1 [†] , 0.47 [‡])
4	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{CH}_3 \\ \quad \quad \quad \diagup \\ \quad \quad \quad \text{H} \end{array}$	1.00	.17
5	$\begin{array}{c} \text{CH}_2 \\ \diagdown \\ \text{C} - \text{CH}_2\text{CH}_3 \\ \diagup \\ \text{CH}_3 \end{array}$	3.64 1.8 prim. 1.84 sec.	.6 .92* (1.22 [†] , .62 [‡])
6	$\text{CH}_2 = \text{CH} - \text{CH} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{CH}_3 \end{array}$	Very slow	Very slow

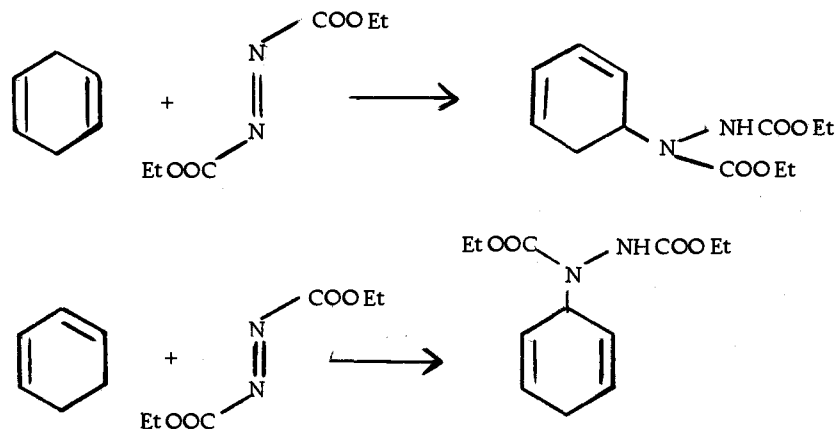
* The two H's of the CH₂ do not react at the same rate. † leads to trans d.b. in product. ‡ leads to cis d.b. in product.

a tertiary (16). However in a competitive system (entry 5), that result does not hold, since on a per hydrogen basis the secondary hydrogens now react as fast as or faster than the primary. Steric factors around the carbon which forms a new C-C bond and the stability of the forming double bond also appear to play an important role. Equation 14 supports the same conclusion since one (presum-



ably axial) hydrogen of a secondary type can compete equally with three of the primary type (16, 17).

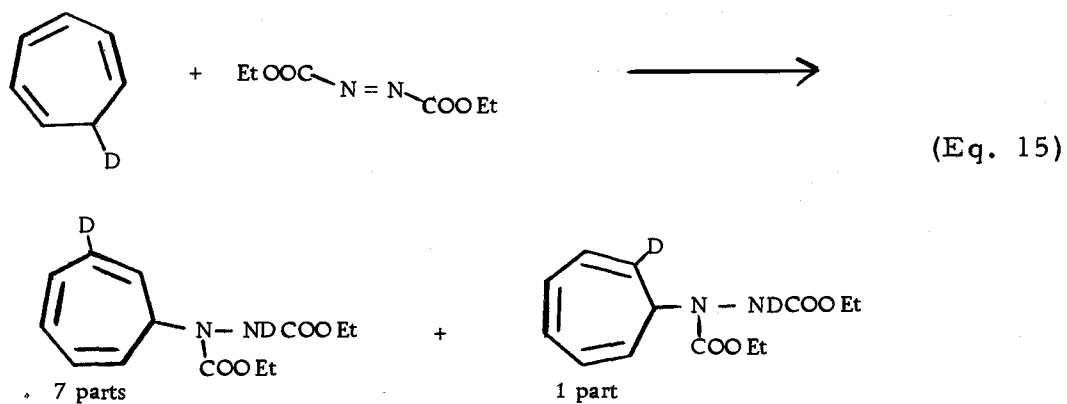
Further allylic activation does not appear to help speed hydrogen donation, since 1,4-cyclohexadiene reacts 15 times slower than



does the 1,3-isomer (18).

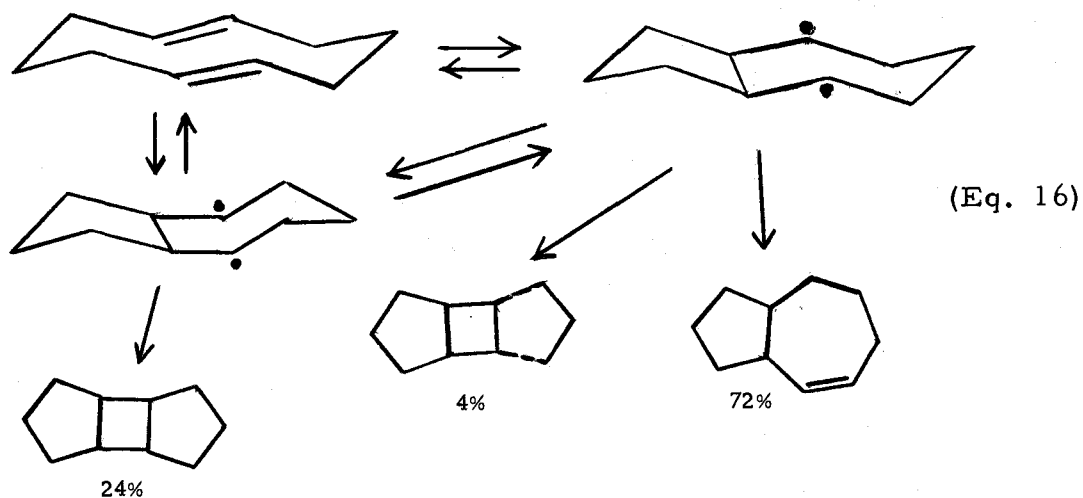
Miscellaneous Mechanistic Results

The concerted reaction can proceed via a ten electron as well as a six electron system. In the reaction of equation 15 both products



were shown to have no deuterium at C_3 or C_4 (19)

When steric factors preclude the formation of the concerted transition state, reaction can occur via a diradical intermediate (20). For example, trans,trans-1,6-cyclodecadiene reacts via a diradical (Equation 16). The rigidity of this ring precludes reaction via a concerted process.

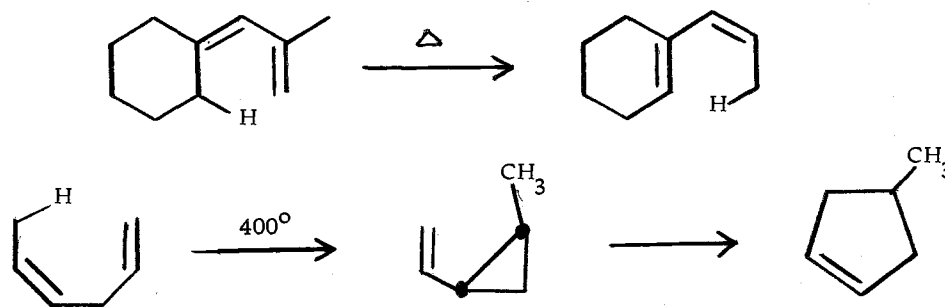


The Intramolecular Ene Reaction

It is to be expected that molecules containing both the HC - C = C and C = C moieties properly situated would undergo an internal ene reaction, thus leading to ring formation. Here we will review the characteristics of the intramolecular ene reaction.

1,3-, 1,4- and 1,5-Dienes

In this group only the cis-1,3-dienes which undergo a 1,5 hydrogen shift, a rather special form of the intramolecular ene reaction, and cis-1,4 dienes will participate in the intramolecular reaction. Neither trans-1,3- or trans-1,4-dienes can attain the proper geometry to permit reaction, and 1,5-dienes generally is-

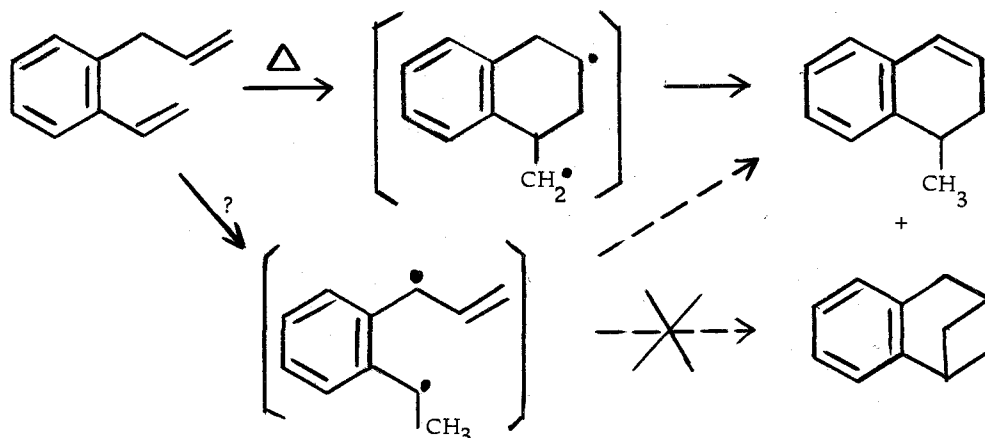


omerize via the Cope rearrangement (20, 7). All of these reactions, 1,5-hydrogen shifts (4, 20), homo-1,5-hydrogen shifts (21), and the Cope rearrangement (22) have been reviewed.

1,6-Dienes

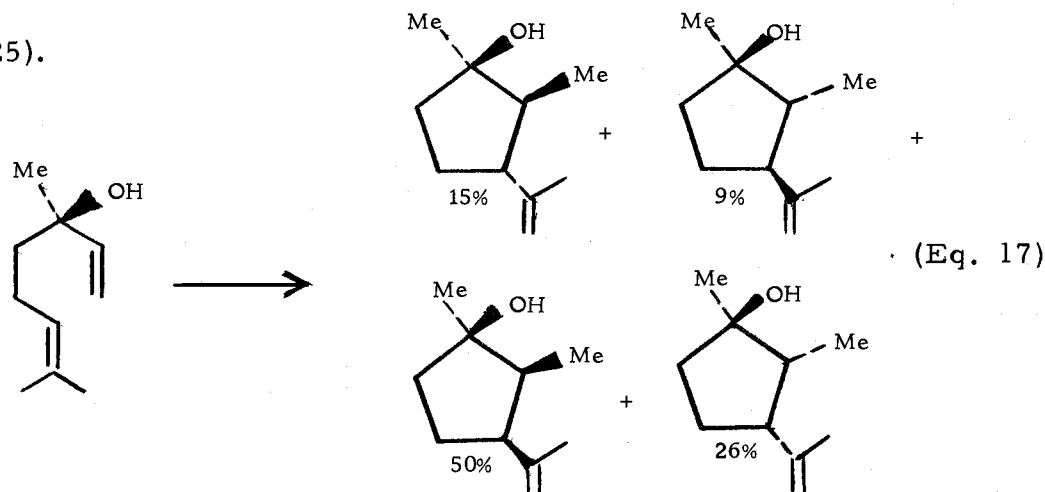
The unadorned 1,6-heptadiene does not cyclize at temperatures

up to 500° (23), but the more rigid 1,6-diene, o-allylstyrene, will

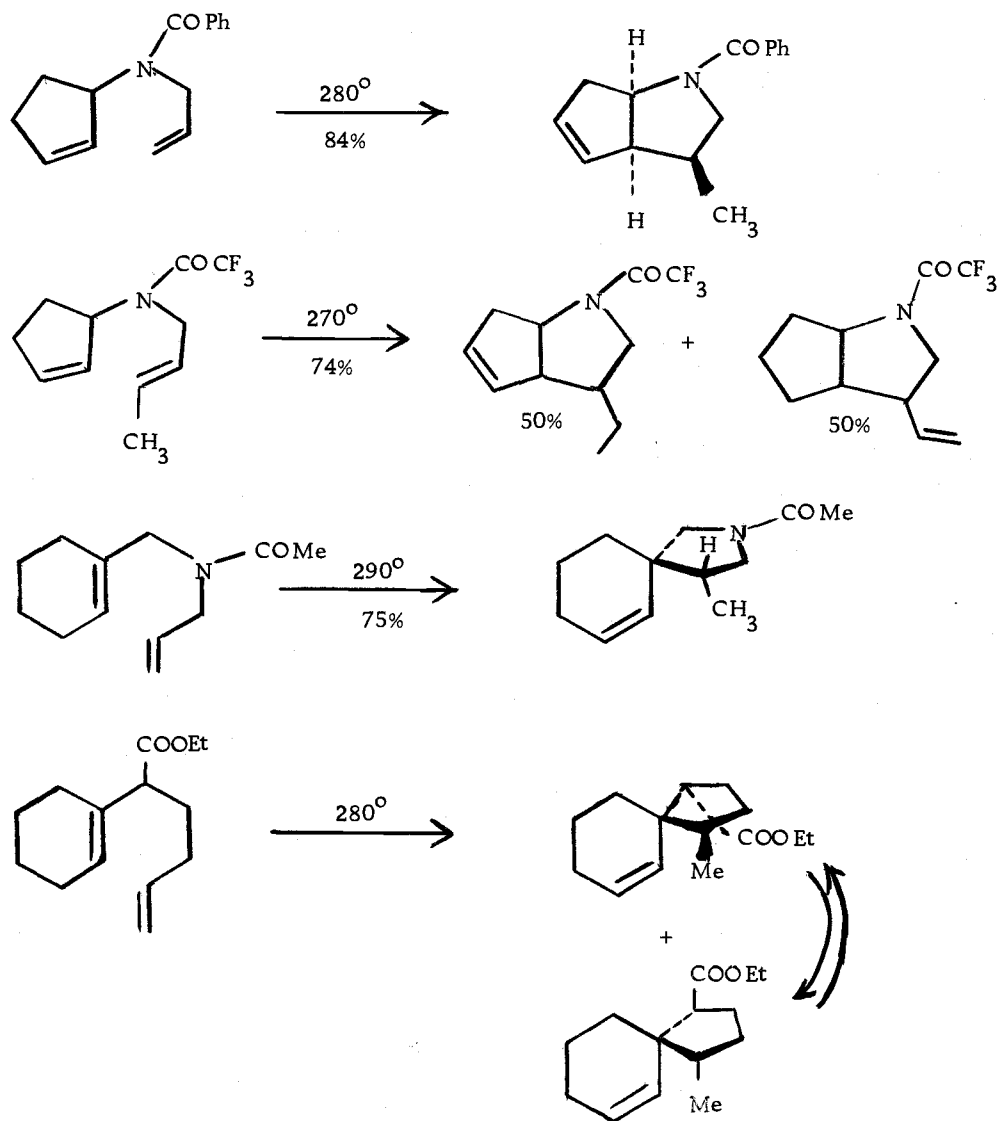


cyclize, albeit via a diradical (24). The authors suggested the non-stabilized diradical as the source of both observed products, though an initial hydrogen transfer would lead to the more stable product via a stabilized diradical.

With one added carbon the 1,6-diene system can achieve a concerted ene transition state and 1,6-octadiene gives cis-2-vinyl-1-methylcyclopentane. The cis stereochemistry for the product is generally preferred, but is not necessarily exclusive. Other substituents may influence the stereochemistry as is illustrated by equation 17 (25).



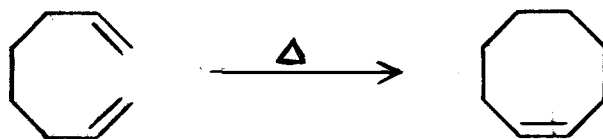
Oppolzer has used the cyclization of 1,6-dienes very effectively in synthesis. Several examples are shown here using both a nitrogen-



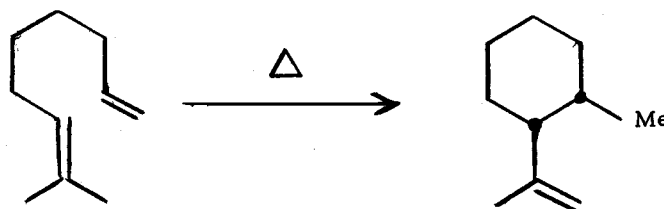
containing and an all carbon 1,6-diene (26, 27).

1,7-Dienes

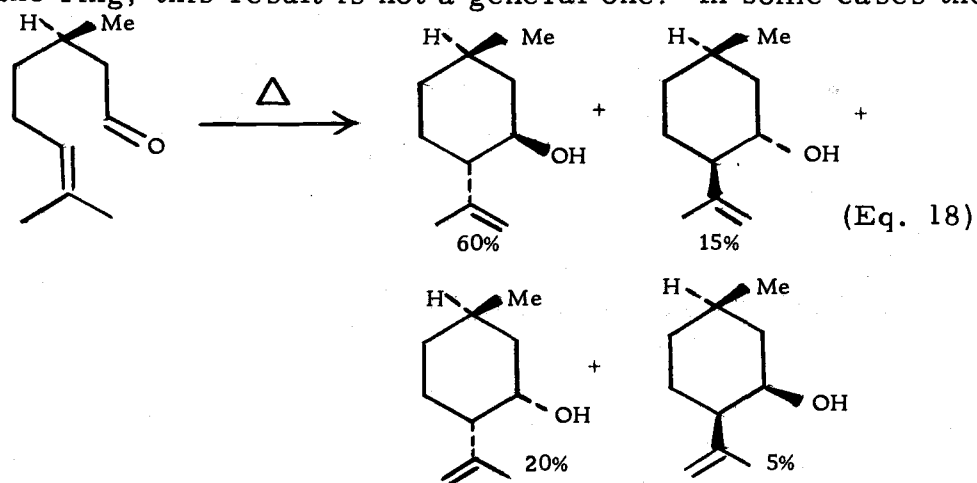
The simplest possible 1,7-diene, 1,7-octadiene, is in equilibrium with cyclooctene at temperatures above 320° (2). However,



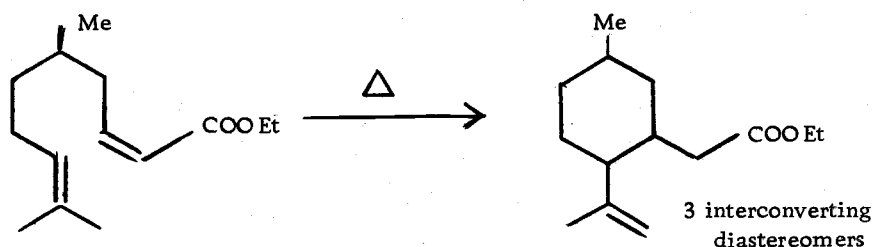
1,7-nonadienes cyclize preferentially to substituted cyclohexanes (28).



Though the initial example gave a cis orientation of the groups on the cyclohexane ring, this result is not a general one. In some cases the



reaction may be reversible at the temperature needed to carry out cyclization, and the resultant stereochemistry is not determined by



the rates of formation of the individual stereoisomers (29).

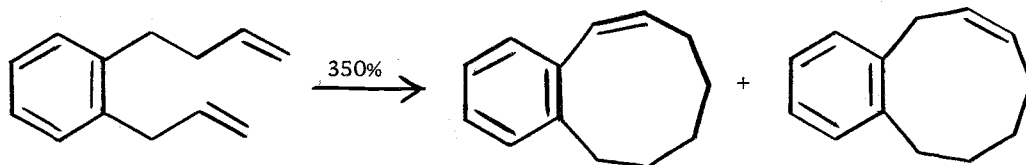
No examples of substituted 1,7-octadienes which form

substituted cyclooctenes were uncovered in our literature search.

1,8-Dienes

Normally ring formation from an acyclic diene is expected to proceed spontaneously since the conversion of a pi bond to a sigma bond leads to a gain of ca. 20 kcal./mole in enthalpy. However, the strain energy of medium rings tends to reduce this advantage, and at the relatively high temperatures needed for these reactions, combined entropic and strain effects may render ring opening a preferred process. Thus trans-cyclononene is converted to 85% 1,8-nonadiene at 500°. The cis-isomer however gave only 20% of ring cleavage at the same temperature.

Lambert and Napoli pyrolyzed 4-(o-allylphenyl)-1-butene and obtained two benzocyclononadienes (30). About equal amounts of the



two isomers were formed indicating each double bond can act as the ene component about equally readily.

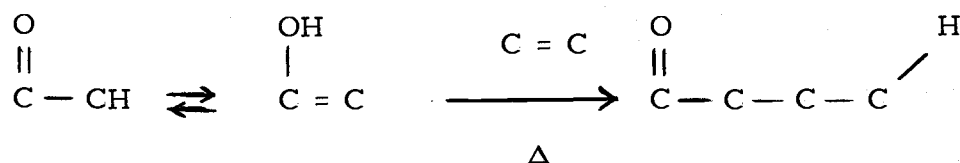
1,9-Dienes

Only one example appears to be known of a 1,9-diene-cyclodecene reaction. Reinacher (31) showed that cis-cyclodecene is converted to 80% 1,9-decadiene at 580°. A similar reaction was run by

Crandall and Watkins (32) who studied a series of cycloalkenes at 720°, and showed that generally ring cleavage occurred to give an α, ω -diene, and to a lesser extent a ring contraction to a vinylcycloalkane also took place. The authors suggested that both concerted and biradical routes could be involved.

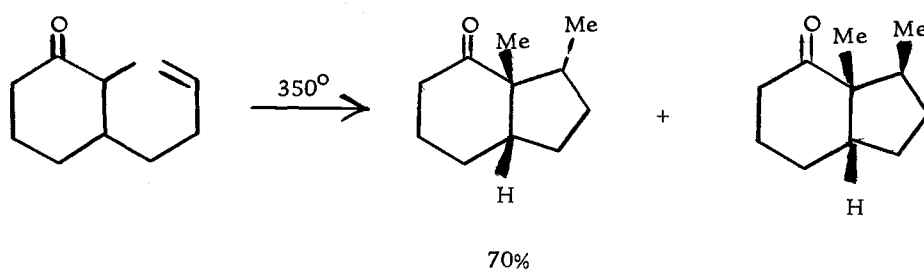
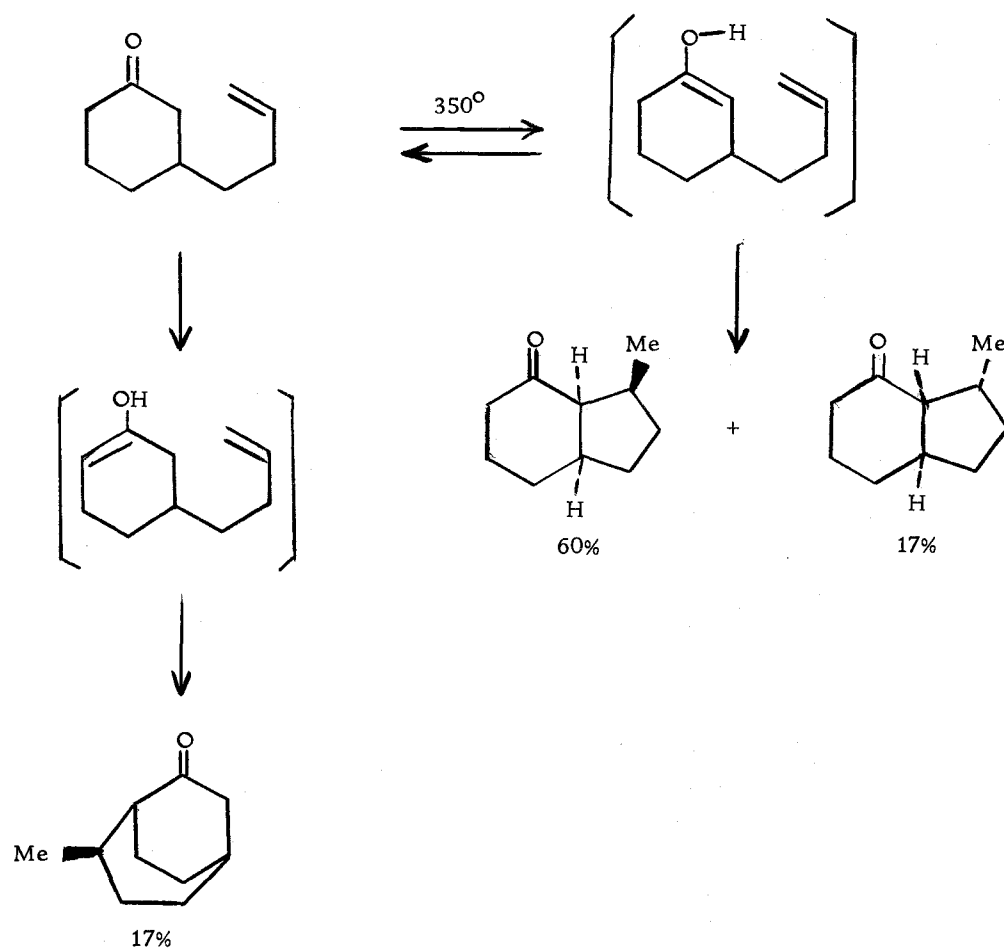
The Enolene Reaction

In the examples discussed above the carbonyl group served as the enophilic component in all cases. However the conversion of a keto group to an enol permits the enol to serve as the ene component. This reaction has been called the "enolene" reaction. Generally it



takes place only with intramolecular examples, and it has been reviewed recently (37). Conia and his students (33) have surveyed the synthetic utility of the "enolene" reaction in considerable detail.

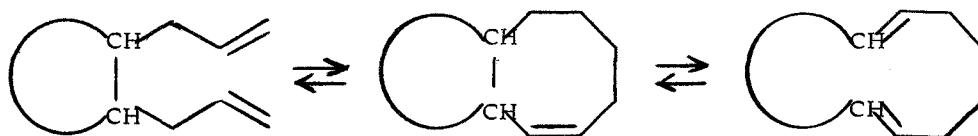
Several examples are shown below. Normally the cis-ring juncture occurs in these cases, though if the carbon α to the ketone bears a hydrogen epimerization can occur. The cis isomer presumably arises because the pseudoequatorial butenyl group approaches the enol along the p-orbital leading to formation of an axial C-C bond (34).



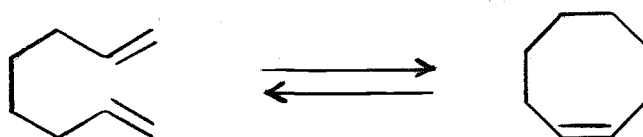
DISCUSSION

Introduction

The ene reaction appears potentially useful in synthesis for the generation of new carbon-carbon bonds and chiral centers, while the retroene reaction provides a route for cleavage of a carbon-carbon bond. Combination of the ene and retroene reactions in an intramolecular example could lead to a ring expansion of six carbons if



the equilibrium constant were favorable. A simple calculation from bond energies indicates that cis-cyclooctene is more stable (ΔH) than

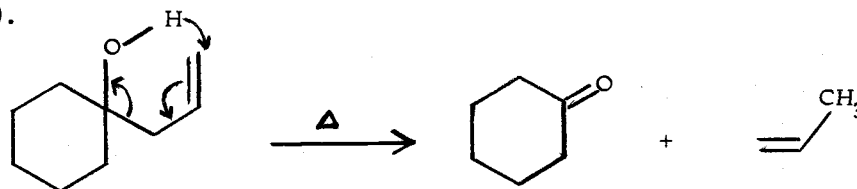


1,7-octadiene by about 17 kcal./mole. This value takes into account the conversion of a pi to a sigma bond ($\Delta H \sim -20$ kcal./mole), of a terminal to an internal double bond ($\Delta H = -2.5$ kcal./mole), and the strain energy of cis-cyclooctene (4.9 kcal./mole)(35). Thus unless something is done to offset this ΔH value, the retroene reaction will not proceed, and the bicyclic product would be the exclusive result. In the present case trimethylsiloxy groups will be used to help offset this advantage of the bicyclic intermediate, since enol ethers have

double bonds about 5 kcal./mole more stable than normal pi bonds (35).

Part A: Disiloxy Derivatives

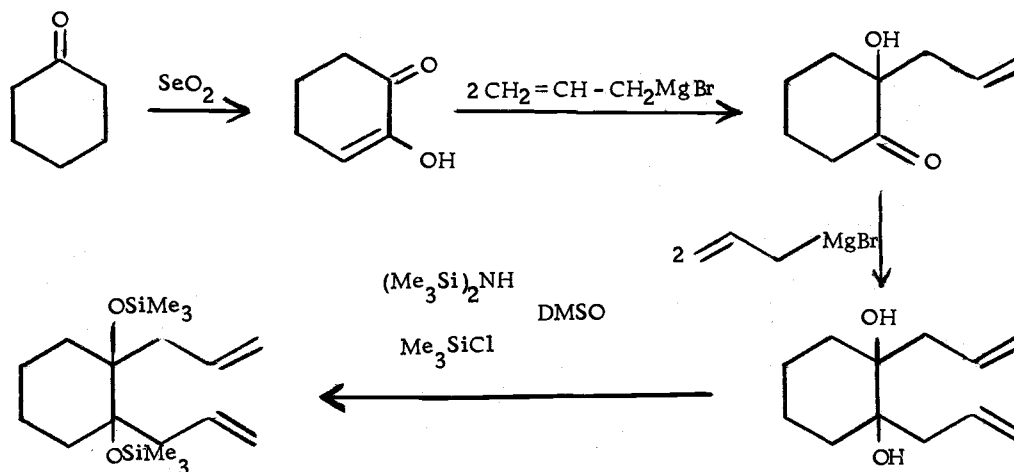
The first attempt to use the ene-retroene route to ring expansion was made with 1,2-diallyl-1,2-bis(trimethylsiloxy)cyclohexane. The trimethylsilyl ether was used in place of a simple hydroxyl group to prevent β -hydroxyolefin cleavage from becoming the main thermal reaction. (37).



Synthesis

The required 1,2-diallyl-1,2-bis(trimethylsiloxy)cyclohexane was prepared in four steps from cyclohexanone as is shown in scheme 1. All of the reactions proceed without difficulty except for the

Scheme 1



silylation step, which caused problems until it was found that running the reaction at room temperature instead of at ca. 100° as previous authors (38) had recommended for preparation of silyl ethers of tertiary alcohols permitted isolation of a nearly quantitative yield.

The 1,2-diallyl-1,2-cyclohexanediol can exist as cis and trans isomers, and it is not clear whether the synthesis should give a predominance of one or the other of these. The synthetic material was not separable on several glc columns, but no great effort was expended in this direction, since in the course of trying to silylate this diol, we found that the bis-(trimethylsilyl) derivatives separated readily. The silylation process eventually gave an almost quantitative yield, and this liquid product was separated into two isomers in a ratio of 62:38. We feel this also represents, to a good approximation, the ratio of isomers in the diol mixture as well.

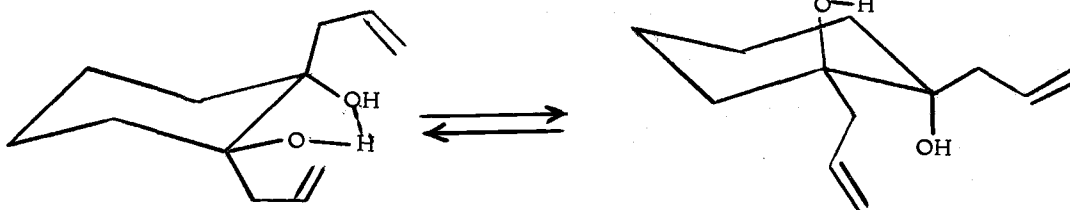
Direct isolation of one of the diol isomers in small amount proved possible by cooling a mixture of the two to 0°. About 7% of the mixture crystallized and could be separated by filtration. This isomer melted at 89 - 91°, and preparation of the bis-(trimethylsilyl) derivative from the solid diol gave only the derivative present in lesser amount (38%). Separation of the silyl derivative into the two isomers by glc, and hydrolysis of the major isomer gave a liquid diol which solidified at 0°, but melted below room temperature. We shall refer to the two diols and their two silyl derivatives as the major

(liquid diol) and minor (solid diol) isomers.

Structure Determination

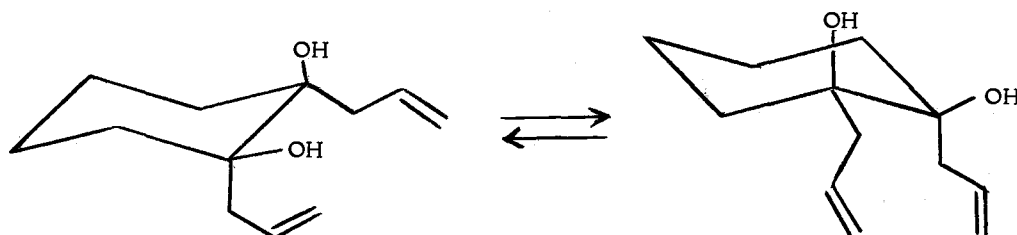
To ascertain which of the two isolated compounds corresponds to the trans and which to the cis isomer, we used both nmr and infrared methods.

a. NMR Studies. The trans diol can exist in two conformations. That conformer with the two hydroxyls axial should be the



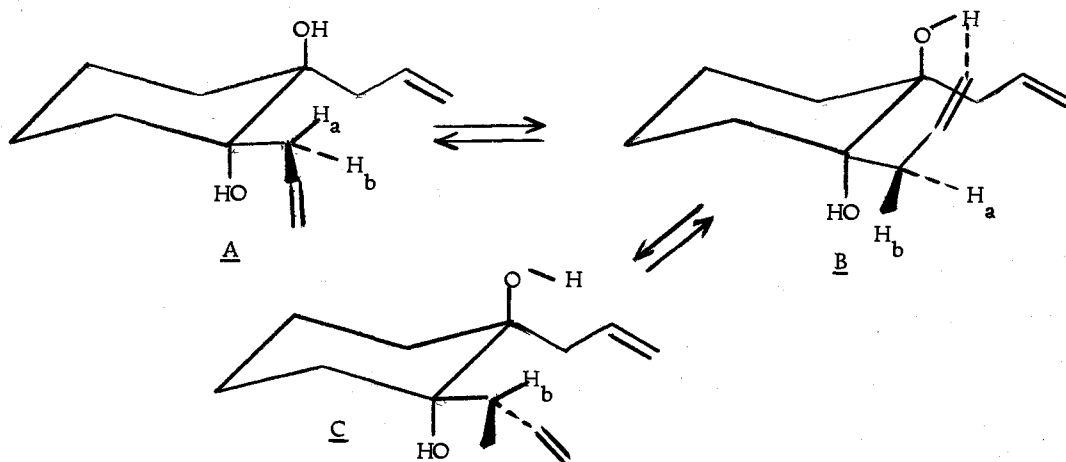
more favorable one, and using 1.85 kcal./mole (ΔG conf. for ethyl), 0.8 kcal./mole for the skew interaction between the allyl groups and 0.6 kcal./mole for the hydrogen bond between two equatorial hydroxyls (35), the conformational equilibrium constant at 25° can be estimated to be 10. Thus the room temperature nmr spectrum is expected to be dominated by the conformer with both allyl groups in equatorial positions.

Contrarily the cis-diol exists as an equal mixture of two conformers each having one allyl group in an axial and one in an

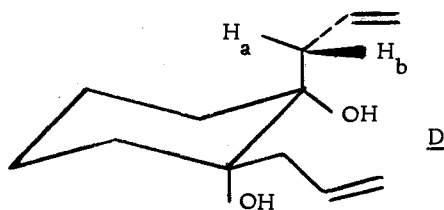


equatorial position. Thus the room temperature nmr spectrum has equal contributions from the two conformers.

In both isomers the CH_2 group of the allyl moieties lies next to a chiral center and the two H's are therefore diastereotopic. However the rotational forms for these groups are not the same for the two isomers. The trans isomer with two equatorial allyls has three



rotational forms for each allyl group (A, B and C). Of these A is the favored form and C is least probable, being the only one which may not be populated in any appreciable amount. On the other hand the cis isomer with an axial allyl group should find only one rotational form for the axial allyl group (D), which is populated.



The minor isomer of the diol (solid) has a nmr spectrum with the methylene groups of the allyls appearing as the A part of an $\text{A}_2\text{XYY}'$ pattern ($J_{\text{AX}} = 7$, $J_{\text{AY}} = 0.6$, $J_{\text{AY}'} = 0$). Thus the two

hydrogens are accidentally equivalent. The major isomer, by contrast, has the methylene spectrum as the AB part of an ABX pattern ($J_{AB} = 14$, $J_{AX} = 6.3$, $J_{BX} = 7.5$), and the two hydrogens are clearly separated ($\Delta\nu = 19$ Hz). This led us to assign the minor isomer as the trans and the major one as the cis forms, an assignment which ultimately proved correct but was really only a fortuitous happenstance.

Realization that this assignment was based on an illusion occurred quickly. Conversion of the diols to silyl derivatives would be expected to render the conformation B of the trans isomer less likely, and hence to enhance the likelihood of a separation of the two hydrogens of that methylene group. The cis isomer should remain unchanged. We were consequently most chagrined to find that the minor isomer indeed shows a ABX pattern, but the major isomer now has so little separation between the two methylene hydrogens that analysis is no longer possible. Fortunately however when the nmr spectra for the two silyl derivatives were run at -40° , distinction was again possible. The minor isomer shows one singlet for the eighteen hydrogens of the six silyl methyls, and the allyl methylenes appear as a very broad smear. The major isomer on the other hand has two singlets for the silyl methyl protons and the allyl methylenes now exhibit a complex pattern from which one can extract couplings of 14.5 and 7.7 for one of the protons. Clearly the two allyl groups

and the two trimethylsiloxy groups are structurally different at this temperature in accord with expectations for the cis stereoisomer.

b. Infrared Studies. Intramolecular hydrogen bonding differences between stereoisomeric 1,2-diols can be used to distinguish cis and trans isomers (39). The non-associated O-H bond has a stretching frequency between 3600 - 3650 which is a strong sharp band. Formation of an intramolecular hydrogen bond lowers the frequency of this bond, and the extent is related to the strength of the hydrogen bond. Thus stereoisomers often have predictable differences in

$$\Delta \tilde{\nu} = \tilde{\nu}_{\text{OH}}^{\text{free}} - \tilde{\nu}_{\text{OH}}^{\text{bond}}$$

For 1,2-cyclohexanediols the diaxial conformer of the trans isomer cannot form an internal hydrogen bond, but the diequatorial conformer can, while the (a,e) form of the cis isomer also forms a hydrogen bond. The steric requirements for the hydrogen bond cause the chair form of the cyclohexane ring to distort, and in the (e,e) trans isomer the chair assumes a deeper pucker forcing the axial groups closer together, while the (a,e) cis isomer tends to flatten the chair toward planarity. Since the latter distortion is more favorable, the relation $\Delta \tilde{\nu}_{\text{cis}} > \Delta \tilde{\nu}_{\text{tr}}$ is a rather general one.

A very dilute solution of the minor isomer of the diol in carbon tetrachloride has $\tilde{\nu}_{\text{OH}}^{\text{free}} = 3613(\text{sh})$ and $\tilde{\nu}_{\text{OH}}^{\text{bond}} = 3576$ so $\Delta \tilde{\nu} = 37 \text{ cm}^{-1}$.

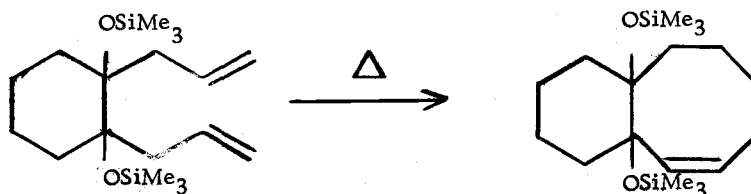
The major isomer under the same conditions has $\tilde{\nu}_{\text{OH}}^{\text{free}} = 3605$ and $\tilde{\nu}_{\text{OH}}^{\text{bond}} = 3560$ so $\Delta\tilde{\nu} = 45 \text{ cm}^{-1}$. These results support the conclusion that the major diol is the cis isomer, but since a double bond can act as a receptor for a hydrogen bond, this conclusion is most tenuous. For this reason the two isomers were reduced to give the two isomeric 1,2-dipropyl-1,2-cyclohexanediols. The minor isomer gave a 1,2-dipropyl-diol m.p. $122 - 23^{\circ}$, which showed only a free OH bond at 3613 cm^{-1} . The major isomer reduced to a dipropyl diol (m.p. $54 - 6^{\circ}$) which had $\tilde{\nu}_{\text{OH}}^{\text{free}} = 3608$, $\tilde{\nu}_{\text{OH}}^{\text{bond}} = 3560$ and $\Delta\tilde{\nu} = 48 \text{ cm}^{-1}$. The cis isomer has been reported previously to melt at 71.5° (40).

All of these results lead then to the same structural assignments, the major synthetic 1,2-diallyl-1,2-cyclohexanediol (62%, liquid) is the cis isomer, and the minor product (38%, solid) is the trans isomer. This conclusion is also in accord with the rates of thermal ene reactions expected and found (see below). It is reassuring that all of the data lead to a consistent interpretation.

Thermal Reactions

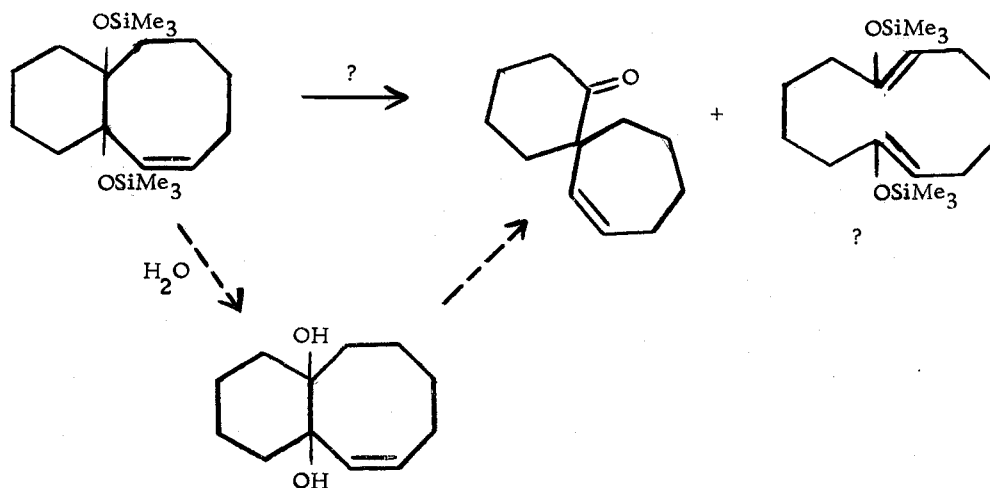
All studies of the thermal reactions of the 1,2-diallyl-1,2-bis(trimethylsiloxy) cyclohexanes were carried out with the mixture of both cis and trans isomers. Reaction was carried out both in the liquid phase (methylcyclohexane as solvent) and in the vapor phase.

Both methods gave a relatively clean reaction leading to one main product. This product has been identified (see below) as 1,8-bis



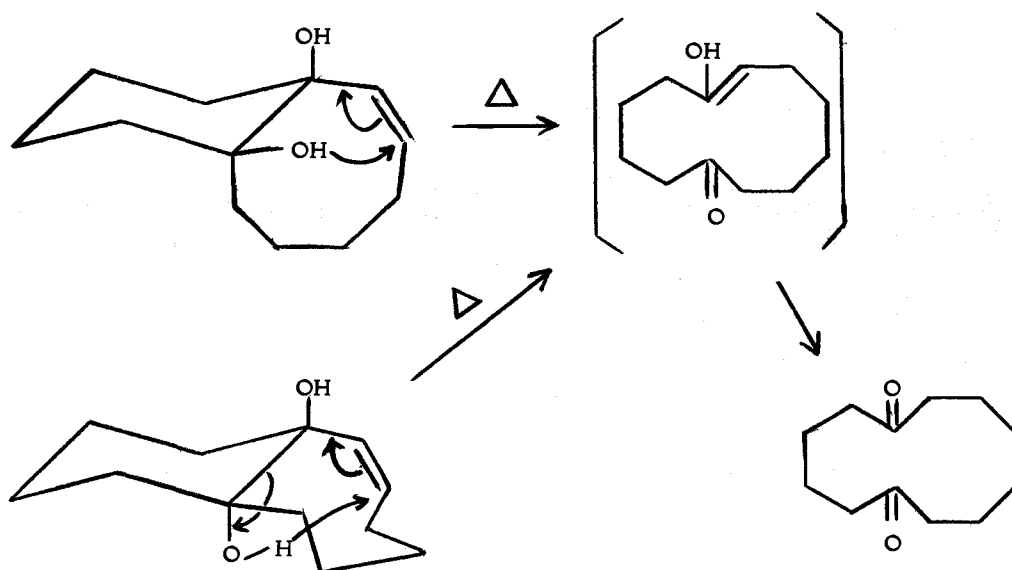
(trimethylsilyloxy) bicycle [6.4.0] dodec-2-ene. Despite the expectation that both cis and trans isomers of the product should be formed, we have not yet been able to separate this liquid product.

The expected ene reaction to form the *cis*-cyclooctene ring thus occurs readily and cleanly at 275 - 300^o in solution, though the reaction is relatively slow. A small increase in temperature leads to formation of at least two additional products, one of which has been identified as 7-spiro [6.5] dodecen-1-one. The second may be the retroene product 1,8-bis (trimethylsilyloxy)-1,7-cyclododecadiene but no adequate evidence permitting an assignment has been obtained.



The origin of the pinacol rearrangement product is obscure, though it may be formed via 2-bicyclo [6.4.0] dodecen-1,8-diol which appears as a result of the presence of adventitious moisture. This idea is in accord with the formation of this spiro ketone in some, but not all runs made under apparently identical conditions. Apparently vapor phase reaction at higher temperatures will be necessary for the study of the retroene ring expansion.

One attempt was made to develop an alternative route to the twelve membered ring. Models suggest that both the cis and trans forms of the bicyclic diol should undergo a ready β -hydroxy olefin



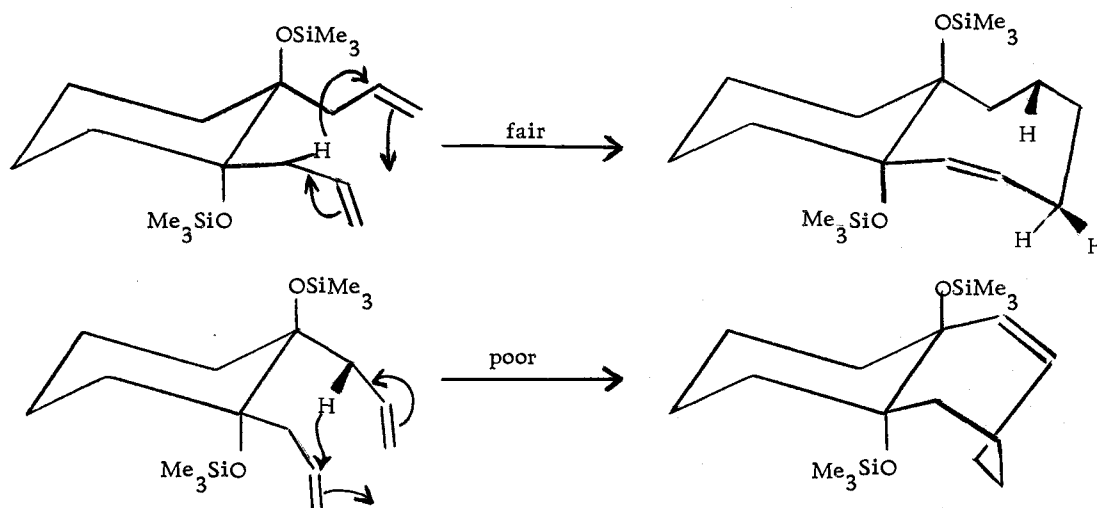
cleavage to give 1,6-cyclododecadione. Unfortunately however the pinacol rearrangement intervened and only 7-spiro [6.5] dodecen-1-1 one was formed. Whether this rearrangement was a surface catalyzed reaction was not ascertained.

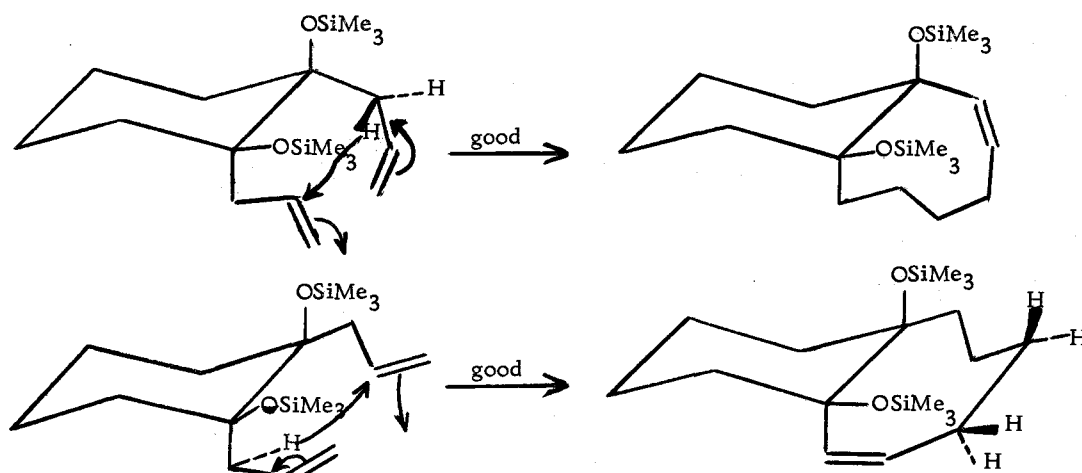
Rates of the Thermal Reaction

Early in the study of the thermal ene reaction of 1,2-bis (trimethylsiloxy)-1,2-diallylcyclohexane, we noted that the cis isomer reacted faster than the trans. While no attempt was made to determine accurate rate constants, several runs were made in solution at temperatures near to 300° which suggest the half life for the cis isomer is about 24 hrs. at that temperature and that for the trans isomer is about 72 hrs. These lead to rough rate constants of $7 \times 10^{-6} \text{ sec}^{-1}$ for the cis isomer and $2 \times 10^{-6} \text{ sec}^{-1}$ for the trans, assuming that both react by first order processes.

This result agrees with predictions made from models, assuming that the ene reaction is concerted, that the proton transferred has its bond parallel to the p-orbitals of the double bond of the ene reactant, and that the double bond being formed must be cis (cis-cyclooctene). Given these restrictions one can readily see that

Trans



Cis

in all cases the transition state has the forming cyclooctene ring positioned so that one axial position on the cyclohexane ring is subject to severe steric hindrance, in both possible routes from the trans isomer, and in neither case when the cis isomer is involved. Clearly the cis isomer should react considerably faster than the trans via a concerted ene reaction.

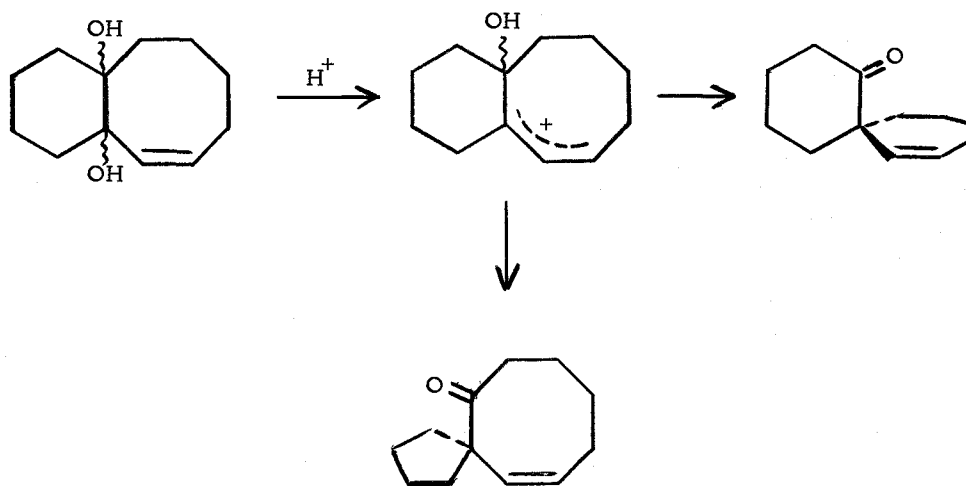
Structure of the Products

The major product obtained by heating 1,2-bis (trimethylsilyloxy)-1,2-diallylcyclohexane shows spectral properties consistent with those expected for the ene product, 1,8-bis (trimethylsilyloxy) bicyclo [6.4.0] dodec-2-ene. In particular the eighteen silyl methyl protons are still present but the original singlet is split into two nine proton singlets, and the six olefinic protons of the two allyl groups in the reactant are replaced by two olefinic protons which appear as the AB portion of an ABX_2 pattern with $J_{AB} = 11$, $J_{AX} = 0$, $J_{BX} = 7$. The

coupling between the two olefinic protons is exactly that expected for a cis-cyclooctene moiety (41, 42).

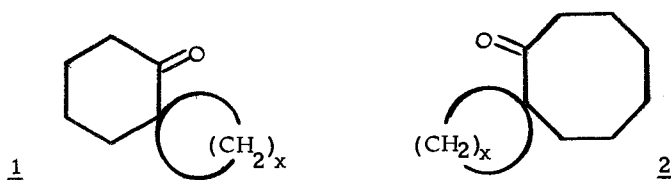
Removal of the protecting silyl groups by hydrolysis gives a diol which was not separated into the cis and trans isomers on the glc column used. The mixture was treated directly with dilute methanolic hydrochloric acid. The only product isolated from this reaction was an unsaturated ketone of non-conjugated type. The carbonyl bond in the infrared is at 1705 cm^{-1} , and the olefinic protons show a typical ABX_2 pattern with $J_{AB} = 11\text{ Hz}$, a value normal for seven or eight membered rings. This product is identical with the product obtained by heating the diol at 300° in methylcyclohexane solution, and also to one of the by-products obtained in some runs with the silyl derivative.

Pinacol rearrangement of 2-bicyclo [6.4.0] dodêcen-1,8-diol could lead to either spiro [5.6] dodec-7-en-1-one or spiro [4.7]



dodec-10-en-6-one. Neither of these compounds has been reported previously, but the saturated ketones are both known (43). Accordingly we reduced our unsaturated ketone, and prepared a 2,4-dinitrophenylhydrazone, m.p. 127° . Unfortunately both 1-spiro [5.6] dodecanone and 6-spiro [4.7] dodecanone form 2,4-dinitrophenylhydrazones which melt at $127 - 128^{\circ}$. No other derivatives are known. Sands (43) reported that the two saturated spiro ketones can be separated on a silicone column, and we found no evidence of more than a single compound in our product. The 2,4-dinitrophenylhydrazone of our product melted sharply at 127° , also indicating that only one spiro ketone was present. Since the spiro [5.6] dodecenone would be expected to form more readily because of relief of the strain of the cyclooctene ring, we have assigned our product that structure.

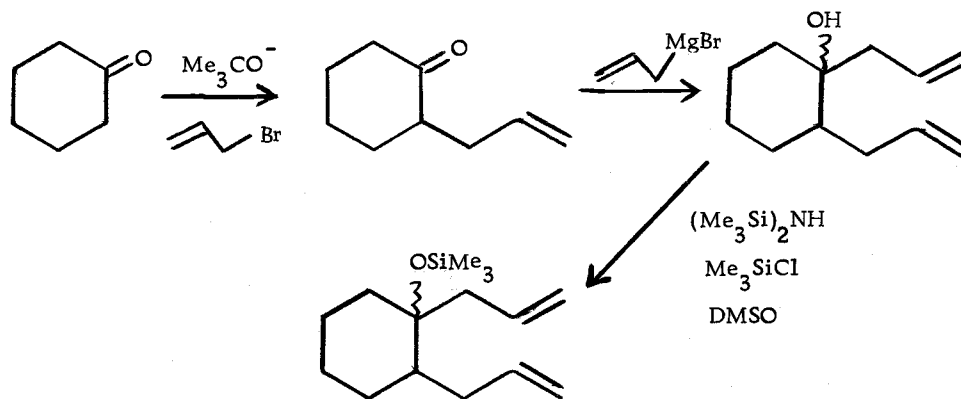
Partial confirmation of that assignment can be obtained from the infrared frequency of the carbonyl band. Krapcho and McCullogh (44) have shown that spiro ketones of type 1 have carbonyl frequencies



between 1708 - 1710 and of type 2 at 1698 cm^{-1} . Our ketone has the carbonyl band at 1705 cm^{-1} .

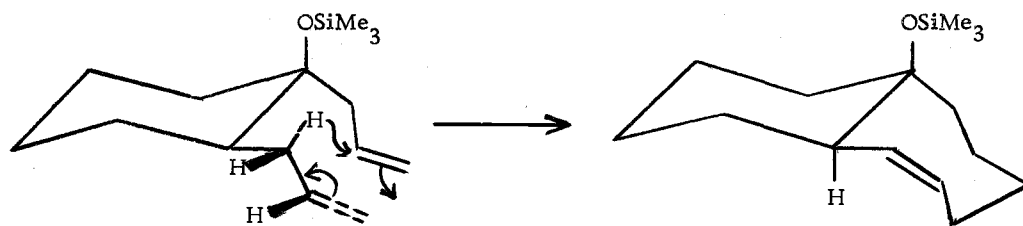
Part B: Monosiloxy Derivatives

A brief study of the readily accessible 1,2-diallyl-1-trimethylsiloxy cyclohexane was also carried out. The starting material was prepared from cyclohexanone as shown in the scheme below. No

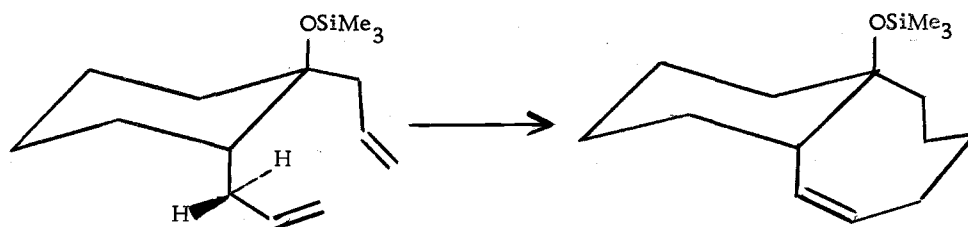
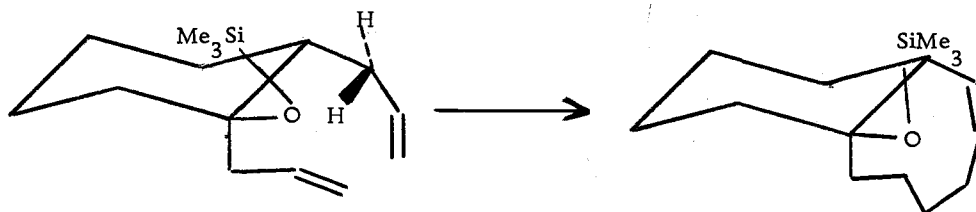


difficulty was noted in any step, but the possible cis and trans isomers which could be formed in the Grignard addition step were not separated under our glc conditions, either with the alcohol or the trimethylsilyl derivative.

The ene reaction of this mono siloxy compound is now of considerable interest since the two different allyl groups can act either as the enophilic or enoid components. Using the same assumptions as were noted in the disiloxy example, we find that a slight preference appears to exist for the allyl group on the hydroxyl bearing

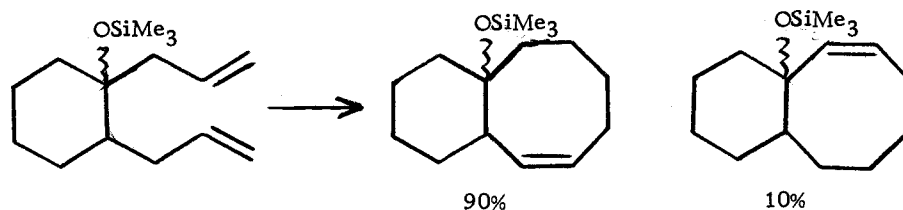


carbon to act as the enophile in the trans isomer of the reactant. The same preference appears to hold with the cis isomer as well, but the degree of preference appears considerably greater with the less



stable conformer having the trimethylsilyl and an allyl group both axial, than with the more stable conformer having only one axial group (allyl). In the latter case in fact both routes seem about equally probable. Therefore both cis and trans isomers of the reactant might be expected to show some, though apparently small, tendency for the same allyl group (on the oxygenated carbon) to act as the enophile.

Heating 1,2-diallyl-1-trimethylsiloxy cyclohexane in solution at 300° gave a liquid which was separable on glc into two fractions, a major one (90%) and a minor one (10%). Based on their nmr spectra and by analogy to the disiloxy derivatives, we have assigned both of these the bicyclo [6.4.0] dodecane skeleton. The nmr spectrum of the major isomer shows the AB part of an ABXY₂ pattern in the olefinic region, $J_{AB} = 11$, $J_{AX} = 8$, $J_{BY} = 7.3$, $J_{AY} \approx J_{BX} \approx 0$. Thus the main product must be 1-trimethylsiloxy-6-bicyclo [6.4.0]



dodecene, and the minor product is the isomeric 2-ene.

If each product is a mixture of cis and trans isomers, neither was readily separable by glc. The result, which shows an unexpectedly large selectivity, seems more in accord with the trans form of the reactant, and we suspect that the starting material contained mainly that isomer.

CONCLUSION

The pyrolysis of 1,2-diallyl-1,2-bis (trimethylsiloxy) cyclohexanes in either the liquid or the vapor phase gave one main product, 1,8-bis (trimethylsiloxy) bicyclo [6.4.0] dodec-2-ene. An increase in temperature led to the formation of an additional product, 7-spiro [6.5] dodecen-1-one, which is formally the result of a pinacol rearrangement of 2-bicyclo [6.4.0] dodecen-1,8-diol. The cis isomer of 1,2-bis (trimethylsiloxy)-1,2-diallyl cyclohexane reacted faster than the trans isomer.

Pyrolysis of 1,2-diallyl-1-trimethylsiloxy cyclohexane gave two products in a 9:1 ratio. The major isomer was identified as 1-trimethylsiloxy-6-bicyclo [6.4.0] dodecene, and the minor product was the 2-ene. Thus the allyl group at C₂ acts preferentially as the ene component in this case. Probably the cause is largely steric.

In these examples an ene reaction to close the cyclooctene ring, followed by a retroene reaction could lead to formation of a cyclo-dodecadiene. Despite this possibility the only further reaction observed was the formation of 7-spiro [6.5] dodecene-1-one. We attribute this to formation of 2-bicyclo [6.4.0] dodecen-1,8-diol, probably because of the presence of adventitious moisture, followed by a pinacol rearrangement induced by surface catalysis.

EXPERIMENTAL

The Pyrolysis Apparatus

The apparatus is in three major parts, the preheater (vaporizer), the heated column, and the receivers (condensers). The vaporizer consisted of a heated Pyrex chamber into which the reactant can be injected in controlled amount by a micrometer syringe. This preheater is connected to the main column by a short Pyrex tube heated by heating tape. The column is made of a 22 mm (id) Vycor tube heated by a spiral coil heater, and is carefully insulated and enclosed in a stainless steel case. The top, center and lower end of the column are equipped with thermo couples to monitor the temperature, and the heater is controlled by a thermostat operated from the central thermocouple. The column is packed with short pieces of quartz tubing and has a volume of 108 ml. The receivers are conventional in design and can be connected in series.

Prior to use the column was washed with acetone and then ether. The ether was evaporated with a nitrogen stream and the column was heated to 450^o for 2 hrs. Prepurified nitrogen was used as a carrier gas and the flow rate was measured by a soap bubble flow meter. The condensers were cooled with dry-ice.

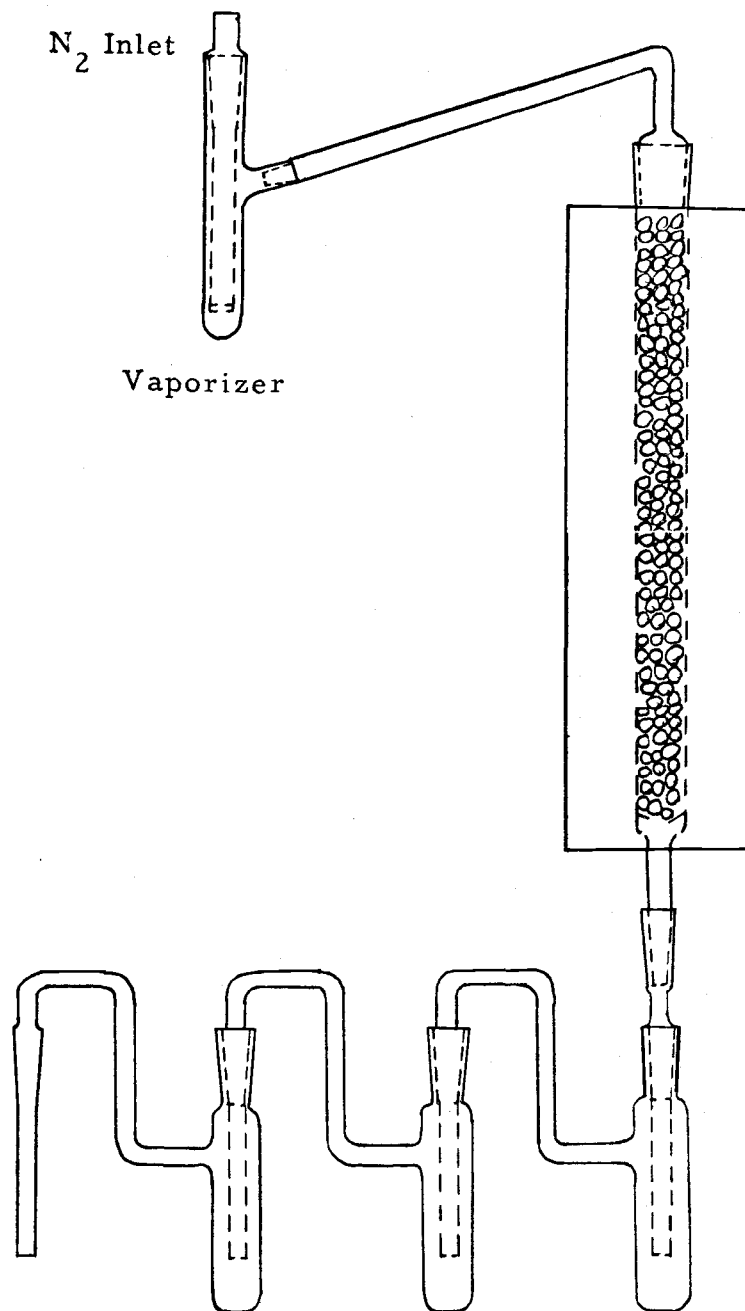


Figure 1. The pyrolysis apparatus.

2-Allyl-2-hydroxy cyclohexanone

This reaction was carried out under a nitrogen atmosphere and under rigorously dry conditions. A solution of allylmagnesium

bromide in ether was prepared (45) from 100 g (0.826 mole) of allyl bromide, 20 g (0.823 g-atom of magnesium in 250 ml. of ether.

This solution was transferred by nitrogen pressure to a dropping funnel and was added (9 hrs.) to a solution containing 31.8 g (0.284 mole) of 1,2-cyclohexanedione (46) in 250 ml of ether cooled in an ice bath. The reaction mixture was stirred 3 hrs. after the addition had been completed, and was then treated with saturated ammonium chloride solution. The product was taken up in ether, dried (MgSO_4), the ether removed and the product was distilled, b. p. $46 - 47^\circ$ (0.3 mm); 36.8 g (0.222 mole); 78% yield; n_mr (CCl_4) δ , 1.70 (m, 6H), 2.10 (m, 2H), 2.42 (m, 2H), 5.04 (d, 2H, J=12), 5.70 (m, 1H). Glc analysis on a 2% SE-30 chromosorb M. column at 135°C indicated this crude product was ca. 93% pure. It was used directly in the next step without further purification.

1,2-Diallyl-1,2-cyclohexanediol

This reaction was carried according to the procedure described for preparation of 2-allyl-2-hydroxycyclohexanone. A solution containing approximately 0.458 mole of allylmagnesium bromide was added to 29.5 g (0.178 mole) of 2-allyl-2-hydroxycyclohexanone. The product was isolated as described except that the crude product was not distilled. A yield of 35.8 g (0.174 mole) of liquid (97%) was obtained. Glc analysis on a 2% SE-30 on Chromosorb M column at 135°

indicated the crude material contained 95% of the diol. Under these conditions no separation of cis and trans isomers was achieved. An analytical sample was collected from glc; nm r (CCl_4 , D_2O added) δ , 1.45 (m, 8H), 2.22 (m, 4H, cis isomer), 2.42 (d, 4H, $J = 7\text{Hz}$, trans isomer), 5.12 (m, 4H), 5.85 (m, 2H).

Anal. Calc'd for $\text{C}_{12}\text{H}_{20}\text{O}_2$: C, 73.47; H, 10.20.

Found: C, 73.42; H, 10.30.

A. Trans Isomer

When this crude product was cooled to 0° , a small amount of solid material crystallized and the crystals were isolated by filtration and washed with hexane, m.p. $89-91^\circ$; nm r (CCl_4 , D_2O added) δ 1.5 (m, 8H), 2.40 (d, 4H, $J = 7\text{Hz}$), 5.10 (m, 4H), 5.85 (m, 2H); ir (CCl_4 soln. ca. 0.005M) 3613, 3576, $\Delta\tilde{\nu} = 37\text{ cm}^{-1}$. The crystals constituted about 7% of the total crude product.

A sample (300 mg) of the above solid was treated with hexamethyldisilazane and trimethylsilyl chloride as described for the preparation of the bis-trimethylsilyl ethers below. After work-up as described the silyl derivative from this preparation was shown to have the same retention time (internal standard) as the trans-1,2-diallyl-1,2-bis(trimethylsiloxy) cyclohexane.

B. Cis Isomer

A sample (150 mg) of the cis-1,2-diallyl-1,2-bis(trimethylsiloxy)cyclohexane (see below) was hydrolyzed with pyridinium hydrochloride as described for 2-bicyclo [6.4.0] dodecen-1,8-diol. The cis-1,2-diallyl-1,2-cyclohexanediol was isolated and purified by glc, nm r (CCl_4) δ , 1.2-1.9(broad m, 8H), 2.18 and 2.37 (AB part of ABX, $J_{AB} = 14$, $J_{AX} = 6.3$, $J_{BX} = 7.5$), 5.06 (m, 4H), 5.88 (m, 2H); ir (CCl_4 , 0.005 M) 3605 sh, 3560, $\Delta\tilde{\nu} = 45 \text{ cm}^{-1}$.

1,2-Diallyl-1,2-bis-(trimethylsiloxy) cyclohexane

A solution containing 4.0 g (0.019 mole) of 1,2-diallyl-1,2-cyclohexanediol in 32 ml. of anhydrous DMSO was mixed with 13.7 g (0.086 mole) of hexamethyldisilazane and 3.5 g (0.029 mole) of trimethylchlorosilane in a bottle sealed with a septum and flushed with nitrogen. The mixture was stirred at room temperature for 48 hrs. The two layers were separated and the lower layer (DMSO) was extracted with pentane. The extract was combined with the top layer, and this solution was washed with sodium bicarbonate solution and then with water. The solution was dried (MgSO_4), the solvent was removed, and the product was distilled in a semi-micro Hickman still at 150° (5×10^{-5} mm), 6.0 g (90%). Glc analysis on a 2% SE-30 on Chromosorb M column at 135° showed the product to be 99% pure and composed of 62% cis and 38% trans isomers. The cis and

trans isomers were separated by preparative glc.

Trans-Isomer

Nm r (CCl_4) δ , 0.16 (S, 18H), 1.25-1.90 (m, 8H), 2.36 and 2.54 (AB part of ABX, $J_{AB} = 14$, $J_{AX} = J_{BX} = 7$), 4.97 (m, 4H), 5.85 (m, 2H).

Anal. Calc'd. for $\text{C}_{18}\text{H}_{36}\text{O}_2\text{Si}_2$: C, 63.49; H, 10.58.

Found: C, 63.70; H, 10.81

Cis-Isomer

Nm r (CCl_4) δ , 0.16 (S, 18H), 1.57 (m, 8H), 2.35 (m, 4H), 4.99 (m, 4H), 5.83 (m, 2H).

Anal. Calc'd. for $\text{C}_{18}\text{H}_{36}\text{O}_2\text{Si}_2$: C, 63.49; H, 10.58

Found: C, 63.67; H, 10.80

1,8-Bis (trimethylsiloxy) bicyclo [6.4.0] dodec-2-ene

A. Pyrolysis in Solution

A solution containing 3.0 g (8.7 mmoles) of 1,2-diallyl-1,2-bis (trimethylsiloxy) cyclohexane in 30 ml of methylcyclohexane was degassed and sealed in a carefully cleaned bottle (washed with dilute NH_4OH , distilled water and dried in an oven). The bottle was placed in a 500 ml. hydrogenation bomb and 30 ml. of methylcyclohexane was added to the bomb to equalize the pressure. The bomb was sealed and heated at $300 \pm 10^\circ \text{C}$ for 90 hrs. After the solvent had been removed

by distillation, 2.63 g of crude product (88%) was recovered. Glc analysis on a 2% SE-30 column at 180° showed that this material contained 80% (2.1 g, 70%) of 1,8-bis-(trimethylsiloxy) bicyclo [6.4.0] dodec-2-ene, and 20% of the trans-isomer of the starting material. A pure sample of product collected from the glc showed nm r (CCl₄) δ, 0.17 (s, 18H), 1.09 - 2.25 (m, 16H), 5.47 and 5.71 (AB part of ABX₂, J_{AB} = 11, J_{AX} = 0, J_{BX} = 7).

Anal. Calc'd. for C₁₈H₃₆O₂Si₂: c, 63.49; H, 10.58.

Found: C, 63.25; H, 10.50.

A sample which was heated at 325° for 66 hrs. gave 64% of the bicyclo [6.4.0] product and two additional products which eluted from the SE-30 column earlier than that product. One (12%) had an nm r spectrum which matched that of spiro [5.6] dodec-7-en-1-one (see below). The second (7%) was collected from the glc, nm r (CCl₄) δ 0.9 (m, 2H), 1.46 (m, 10H), 2.16 (m, 4H), 5.66 (m, 2H).

B. Pyrolysis in the Vapor Phase

Two grams (5.9 m moles) of 1,2-diallyl-1,2-bis-(trimethylsiloxy) cyclohexane was placed in the vaporizer with an oil bath at 85° C while the connection between the column and vaporizer was held at 100° C with a heating tape. Prepurified nitrogen was used as a carrier gas at 55 ml./min. flow rate. The column was maintained at 390° C and residence time in the column was approximately

50 secs. Heating was continued for ca. 1 hour and 10 min. after which 0.6 g of dark polymer remained in the vaporizer. The product was washed from the column and the receivers with pentane and the pentane was evaporated. Glc analysis of this mixture showed it to contain 30% of 1,8-bis-(trimethylsiloxy) dodec-2-ene, 38% of the cis-isomer and 21% of the trans-isomer of the reactant.

2-Bicyclo [6.4.0] dodecen-1,8-diol

A. Acid Hydrolysis

One gram (2.35 mmoles) of 1,8-bis-(trimethylsiloxy) bicyclo [6.4.0] dodec-2-ene was dissolved in 75 ml of methanol containing 0.65 g of pyridine and 0.5 ml of concentrated hydrochloric acid. The mixture was stirred 24 hrs. at 25° and the acid was then neutralized. The methanol was evaporated in vacuo and the residue was taken up in ether. The ether solution was washed with water, dried (MgSO₄) and the ether was evaporated. The diol was purified by glc, 2% SE-30 column; nmr (CCl₄) δ, 1.2-2.1 (m, 15H), 3.1 (broad m, 1H), 5.73 (m, 2H).

Anal. Calc'd. for C₁₂H₂₀O₂: C, 73.47; H, 10.20.

Found: C, 73.67; H, 10.13

B. Basic Hydrolysis

A solution of 0.6 g of the trimethylsiloxy derivative in 25 ml. of

0.1 M sodium methoxide in methanol was refluxed 5 hrs. After the basic had been neutralized the diol was isolated as described above and gave 80% yield.

Spiro [5.6] dodec-7-en-1-one

A sample [150 mg, (0.69 mmole)] of 2-bicyclo [6.4.0] dodecen-1,8-diol purified by glc was dissolved in 75 ml. of methanol containing 0.3 ml. of concentrated hydrochloric acid. The solution was refluxed for 6 hrs., and the acid was neutralized with sodium bicarbonate. The methanol was removed by distillation, and the product was taken up with ether. The ether solution was dried (MgSO_4) and the ether was evaporated. Glc analysis (2% SE-30 at 135°) indicated the product contained 65% of the spiro-ketone. A sample trapped from the glc showed nmr (CCl_4) δ , 1.20-2.61 (m, 16H), 5.58 and 5.80 (AB part of ABX_2 , $J_{\text{AB}} = 11$, $J_{\text{AX}} = 6$, $J_{\text{BX}} = 0$) 2,4-dinitrophenylhydrazone melted at $103-105^\circ$.

1-Spiro [5.6] dodecanone

The crude product above [33 mg (0.12 mmole)] was hydrogenated in 6 ml. of ethanol over 4 mg of 5% platinum-on-charcoal catalyst at 0° . The catalyst was removed by filtration, and the solvent was evaporated in vacuo. The product was isolated by glc (2% SE-30 at 135°), nmr (CCl_4) δ , 1.10-2.13 (m, 18H), 2.29 (m, 2H).

A 2,4-dinitrophenylhydrazone melted at 128-129° (m.p. 127° C) (43).

1,2-Diallylcyclohexanol

This preparation was carried out according to the procedure described for 2-allyl-2-hydroxycyclohexanone. A solution containing about 0.027 mole of allylmagnesium bromide was added to 4.0 g (0.022 mole) of 2-allylcyclohexanone in 30 ml. of ether. The product was isolated as described, and the crude product was not distilled, 5.15 g (0.02 mole), 93%; glc analysis on a 2% SE-30 column at 135° indicated the crude product contained 94% of one product. Nmr (CCl_4 , D_2O added) δ , 0.98-1.90 (m, 9H), 2.18-2.50 (m, 4H), 5.18 (m, 4H), 5.58 (m, 2H).

Anal. Calc'd. for $\text{C}_{12}\text{H}_{20}\text{O}$: C, 80.00; H, 11.11

Found: C, 79.88; H, 11.20

1,2-Diallyl-1-trimethylsiloxy cyclohexane

A solution containing 1.88 g (0.010 mole) of 1,2-diallylcyclohexanol, 1.0 g (0.008 mole) of trimethylchlorosilane and 3.91 g (0.024 mole) of hexamethyldisilazane in 12 ml. of anhydrous DMSO was stirred under nitrogen for 49 hrs. The two layer mixture was separated, and the bottom layer (DMSO) was extracted with pentane. The pentane extract and upper layer were mixed, and the solution was washed with sodium bicarbonate and then with water and finally was

dried (MgSO_4). The product was isolated by distillation in a semi-micro Hickman still (bath temp. 150° at 5×10^{-5} mm), 2.44 g (93%). Glc analysis on a 2% SE-30 column at 135° showed a single product (99%) with no separation of cis or trans isomers. An analytical sample was collected from the glc, nmr (CCl_4) δ , 0.15 (s, 9H), 1.50 (broad m, 9H), 1.80-2.70 (broad m, 4H), 5.0 (m, 4H), 5.75 (m, 2H).

Anal. Calc'd. for $\text{C}_{15}\text{H}_{28}\text{OSi}$: C, 71.40; H, 11.11

Found: C, 71.19; H, 11.03

1-Trimethylsiloxy bicyclo [6.4.0] dodec-(2 and)-6-ene

The above 1,2-diallyl-1-trimethylsiloxy cyclohexane (0.9 g, 3.57 mmoles) in 30 ml. of methylcyclohexane was heated at $290 \pm 20^\circ$ for 76 hrs. in a sealed glass bottle placed in a steel hydrogenation bomb as described above. After removal of the solvent, 0.76 g of crude product (84%) was recovered. Glc analysis on a 2% SE-30 column at 115° showed two products were present in a ratio of 9:1. Samples of the two isomers were collected from the glc: minor isomer, nmr (CCl_4) δ , 0.3 (s, 9H), 1.3-2.15 (m, 14H), 2.35 (m, 2H), 2.85 (m, 1H), 5.85 (m, 2H); major isomer, nmr (CCl_4) δ , 0.06 (s, 9H), 1.06-1.96 (m, 15H), 2.16 (m, 2H), 5.20 and 5.66 (AB part of XABY₂, $J_{AB} = 11$, $J_{AX} = 8$, $J_{BY} = 7.3$).

6-Bicyclo [6.4.0] dodecen-1-ol

A solution of 0.1 g of the above silyl derivative in 35 ml. of 0.1 N sodium methoxide in methanol was refluxed 12 hrs. The base was neutralized, and the methanol was removed in vacuo. The residue was taken up in ether, and the solution was washed with water and then dried (MgSO_4). The ether was removed and the product was purified by glc (2% SE-30 column), nmr (CCl_4) δ , 1.15-2.0 (m, 15H), 2.0-2.5 (m, 2H), 5.34 and 5.55 (AB part of ABXY_2 , $J_{\text{AB}} = 11$, $J_{\text{AY}} = 7.8$, $J_{\text{BX}} = 8.2$).

Anal. Calc'd. for $\text{C}_{12}\text{H}_{20}\text{O}$: C, 80.00; H, 11.11

Found: C, 80.00; H, 11.22.

Trans-1,2-dipropyl-1,2-cyclohexanediol

The solid form of 1,2-diallyl-1,2-cyclohexanediol (300 mg, 1.53 mmole) was hydrogenated in 10 ml. of 100% ethanol over 35 mg of 5% platinum on charcoal catalyst at 0° . The catalyst was removed by filtration and the solvent was evaporated in vacuo. A crystalline solid was obtained 256 mg (83% yield) m.p. $122-23^\circ$. Glc analysis indicated one pure compound; nmr (CCl_4) δ , 1.0 (m, 6H), 1.55 (m, 16H), ir (CCl_4 , soln ca. 0.005 M), 3615 and 3574 sh, $\Delta\tilde{\nu} = 41 \text{ cm}^{-1}$, 0.00025 M, 3617 cm^{-1} only.

Cis-1,2-dipropyl-1,2-cyclohexanediol

1,2-diallyl-1,2-bis-(trimethylsiloxy) cyclohexane (the major isomer of the silyl derivative of diol, 100 mg. 0.294 m mole, isolated by glc) was hydrolyzed in 5 ml. of methanol containing 0.05 ml. of pyridine and 0.05 ml. of concentrated hydrochloric acid for 24 hrs. at 25°.

Thirty milligrams of cis-1,2-diallyl-1,2-cyclohexanediol was isolated by glc (2% SE-30 at 135°), and was hydrogenated in 2.5 ml. of 100% ethanol, over 4 mg. of 5% platinum-on-charcoal catalyst at 0°. The catalyst was removed by filtration and the solvent was obtained 10 mg. m.p. 54-6°, ir (CCl₄ solⁿ ca. 0.005 m), 3608 sh., 3560 cm⁻¹, $\Delta\tilde{\nu} = 48 \text{ cm}^{-1}$, nmr (CCl₄) δ 0.93 (m, 6H), 1.12 - 1.96 (m, 16H).

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