

AN ABSTRACT OF THE THESIS OF

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Title: Part 1 A PYROLYSIS OF CIS-1-TRIMETHYLSILOXY-
1-CYCLOPROPYL-3-CYCLONONENE

Part 2 THE THERMAL ISOMERIZATION OF 2-
PHENYL-1-TRIMETHYLSILOXY-1-
VINYLCYCLONONANE

Abstract approved:

Redacted for privacy

Dr. Richard W. Thies

Part 1

The pyrolysis of cis-1-trimethylsiloxy-1-cyclopropyl-3-cyclononene in the temperature range 285-350° is described. Instead of siloxy-Cope rearrangement, undesired desiloxylation took place.

Part 2

Gas-phase pyrolytic rearrangement of 2-phenyl-1-trimethylsiloxy-1-vinylcyclononane was investigated in a static system in the temperature range 213-330°. It was discovered that three major products resulted: cis- and tran-4-phenyl-1-trimethylsiloxy-1-cycloundecene and 4-phenyl-undecanone.

Although an appreciable amount of polymerization occurred at high temperature, it was not significant at low temperature.

A Pyrolysis of cis-1-Trimethylsiloxy-1-Cyclopropyl-3-
Cyclononene

The Thermal Isomerization of 2-Phenyl-1-Trimethylsiloxy-1-
Vinylcyclononane

by

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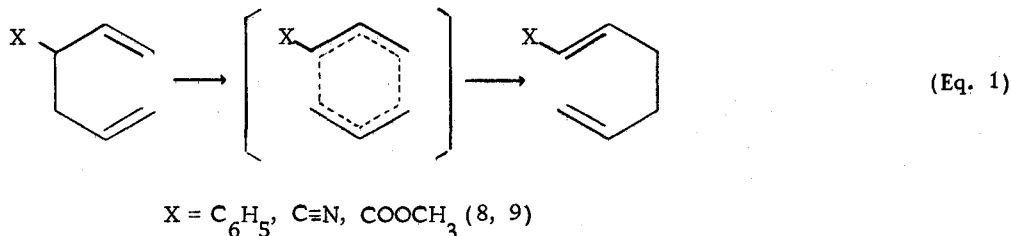
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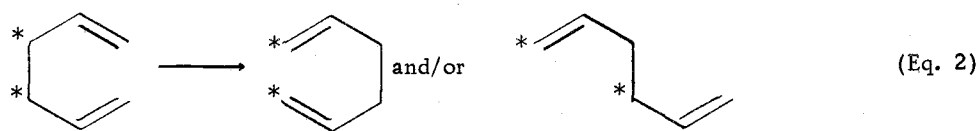
PYROLYSIS OF CIS-1-TRIMETHYLSILOXY-1-CYCLOPROPYL-3-CYCLONONENE AND REARRANGEMENT OF 2-PHENYL-1-TRIMETHYLSILOXY-1-VINYLCYCLONONANE

INTRODUCTION

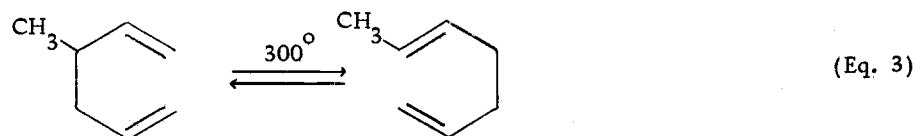
One of the best examples of a valence isomerization of the multicenter reaction type is the thermal rearrangement of bialllyl compounds to isomeric bialllyl compounds discovered by A. C. Cope and his associates. This rearrangement proceeds at temperatures as low as 165-185°, if the bialllyl system has unsaturated substituents in the 3-position.



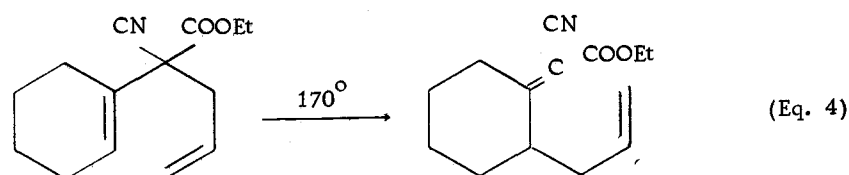
The tendency of the substituent to enter into conjugation with the double bond apparently acts as the driving force. Based on kinetic studies, a cyclic mechanism has been postulated for this valence isomerization, just as for the related Claisen rearrangement. Such reactions are first order. The process has been known as the Cope rearrangement. The term "Cope rearrangement" is used to describe all processes of the following types, irrespective of the detailed mechanisms.



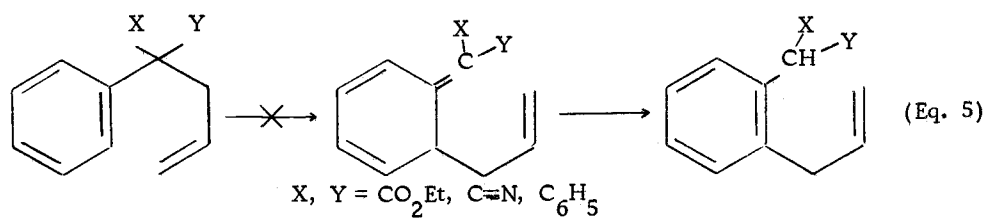
Even the simple molecule 3-methyl-1,5-hexadiene rearranged, albeit slowly and reversibly.

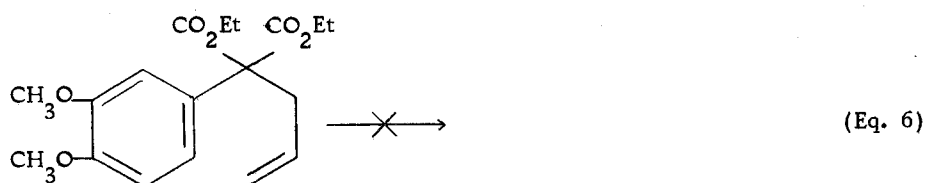


Whyte and Cope discovered that the vinyl group could be incorporated into a ring, e. g., ethyl-1-cyclohexenylallylcyanoacetate (29).



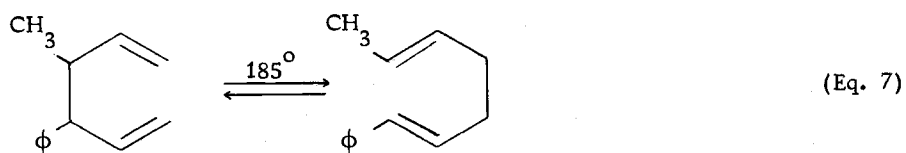
However, the reaction failed if the vinyl group was part of an aromatic system (8, 9).



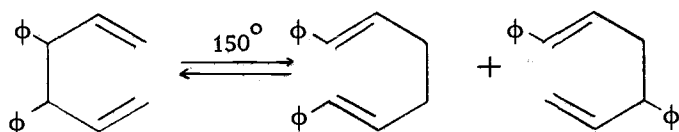


In ways completely paralleling the early work on the ortho Claisen rearrangement, the Cope rearrangement was shown to proceed with inversion of the structure of the migrating allylic group (8), to be intramolecular (9), and to follow the first-order rate expression (9). Activation energies and entropies for the rearrangement bear a strong resemblance to those found for the Claisen rearrangements (12, 1).

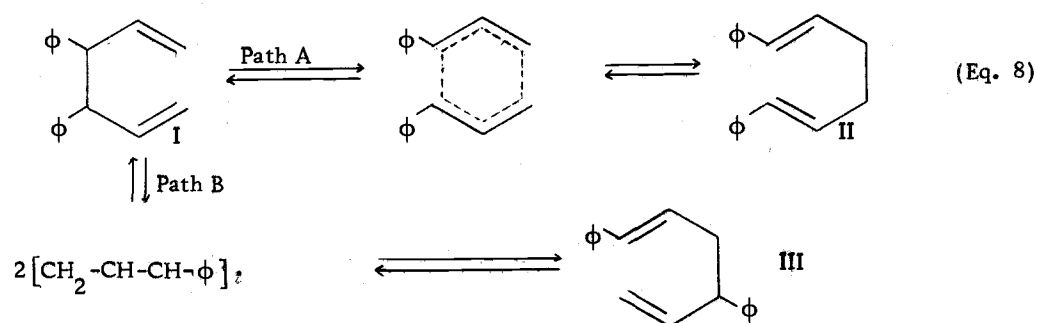
Levy and Cope examined the rearrangement of substituted 1,5-hexadienes (19). Since that time a few other such rearrangements have been reported.



The rearrangement of 3,4-diphenyl-1,5-hexadiene (17) represents an especially interesting example, since two products were observed.

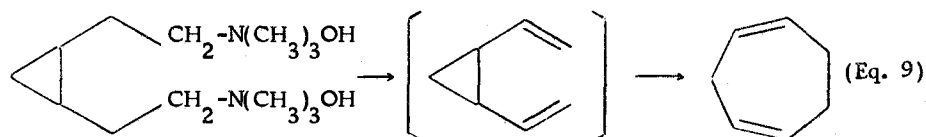


Mechanism:

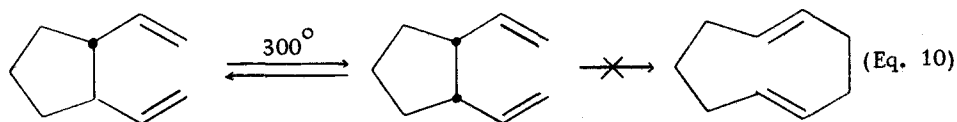


The product ratio of (II):(III) was 3:2. The co-formation could be explained in terms of two competing processes, the concerted Cope rearrangement and a homolytic cleavage of I to the mesomeric radical which could recombine to form III as well as II. Although the formation of both products could be accommodated by the operation of the single process (path B), the author argued that the observed product ratio seems to require the concurrence of the concerted process (path A), since if path B alone were used III would be expected to predominate in the product mixture. In any event, there can be no doubt that the homolytic dissociation process (path B) is contributing in some measure in the rearrangement of I, and the point of interest here is that this rearrangement appears to be a

"limiting" case of the "no mechanism" category, i. e., the entropies of activation for paths A and B lie very close together. Vogel (28) first investigated cis-1, 2-divinylcyclopropane, which, in all probability, should be unstable. In an effort to obtain the hydrocarbon by Hofmann degradation of the base at 80°, he isolated only its isomerization products, cyclohepta-1, 4-diene and cyclohepta-1, 3-diene, the latter being formed by hydride shift.



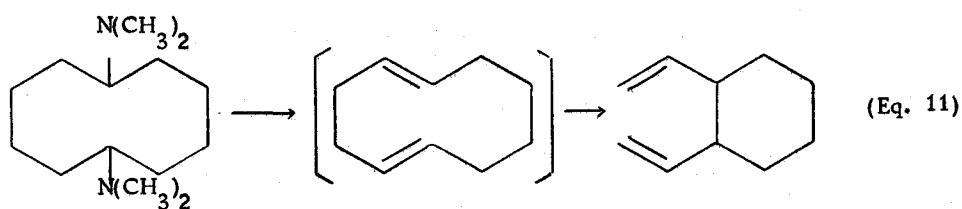
In contrast to cis-1, 2-divinylcycloalkanes with small strained rings, the homologous cis-1, 2-divinyl-cyclopentane is stable up to 250°. Even at higher temperatures, it can not be converted into the nine-membered ring compound cyclonona-1, 5-diene. Instead, the establishment of a cis-trans equilibrium is observed.



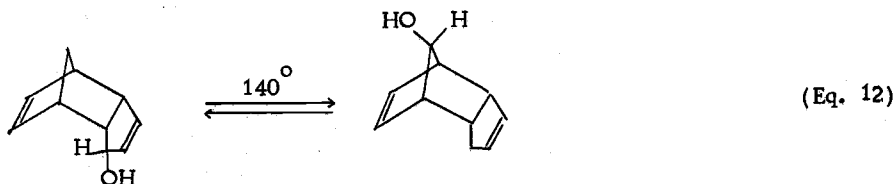
The failure of cis-1, 2-divinylcyclopentane to undergo the Cope rearrangement, even under extreme conditions, was attributed to

the fact that in the system cis-1, 2-divinylcyclopentane/cyclonona-1, 5-diene a reverse ring strain relationship obtains. It was believed that cyclonona-1, 5-diene was unstable and isomerized easily to 1, 2-divinylcyclopentane, thus reversing the desired rearrangement. This assumption was strongly supported by Grob and Schiess (15).

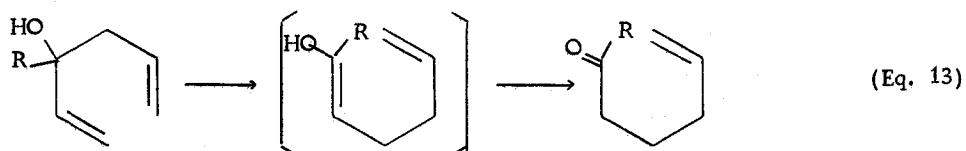
Cyclodeca-1, 5-diene, formed by N-oxide elimination and Hofmann degradation of the cis and trans forms of the diamine, undergoes rearrangement under the reaction conditions of 1, 2-divinylcyclohexane and other isomeric hydrocarbons.



Woodward and Katz (30) have provided an excellent example of a Cope rearrangement in which the bialllyl system is contained in a bicyclic structure.

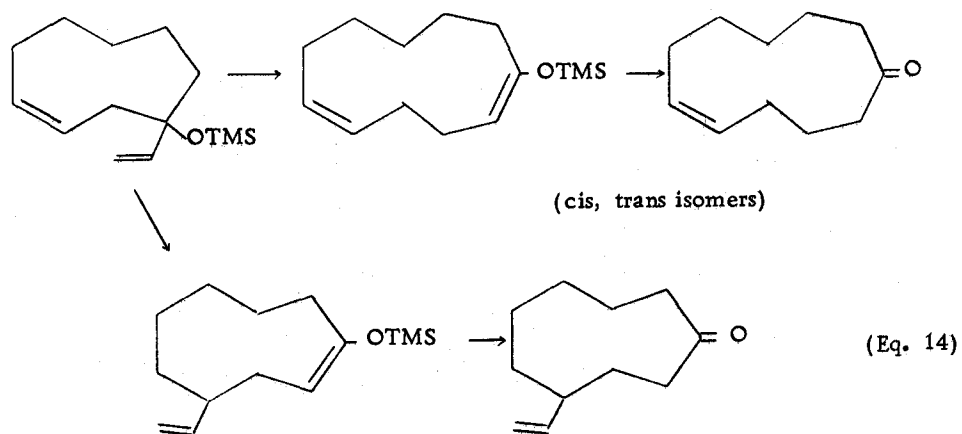


Berson and Jones (5) studied the rearrangement of a 1, 5-hexadiene system substituted with a hydroxyl group at C-3. They



found it gave the progenitor of a ketone, thus permitting the synthesis of δ, ϵ -unsaturated carbonyl compounds. For that kind of reaction, the term "oxy-Cope rearrangement" was proposed.

Thies and Wills (26) observed the rearrangement of a compound that had the vinyl group attached to a medium size ring. Their comparison between the trimethylsiloxy and hydroxy derivatives showed that the former resulted in less polymerization than the latter. The reaction yielded predominantly [1, 3] shift products and a minor amount of [3, 3] shift product.



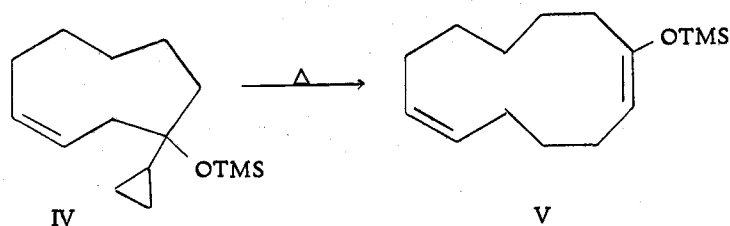
This result is somewhat different from that found for open chain systems in which the oxy-Cope rearrangement gives [3, 3] shift but not [1, 3] shift products.

Part 1

Pyrolysis of 1-Trimethylsiloxy-1-Cyclopropyl-3-Cyclononene

RESULTS AND DISCUSSION

cis-1-Trimethylsiloxy-1-cyclopropyl-3-cyclononene, IV, was synthesized by the route given in Figure 1 (6, 14). When IV was heated in evacuated ampoules at several temperatures, none of the major products obtained was the anticipated 1-trimethylsiloxy-1,6-dodecadiene, V, which would correspond to the products obtained from the analogous vinyl compound (see Eq. 14).



On pyrolyzing IV at 285° for one hour, no appreciable change was detected by glc. When the temperature was increased to 305° for one hour, two new compounds appeared. The retention times of these two peaks were unchanged by hydrolysis; this suggested that the new products contained no siloxy groups. With pyrolysis conditions of 350° for one hour, four more peaks (total: six) were detected that had shorter retention times than the previous two compounds. The mixture of the products was also hydrolyzed, and then checked by glc. No retention times were changed. Infrared revealed no distinct functional groups except double bonds, suggesting alkene formation

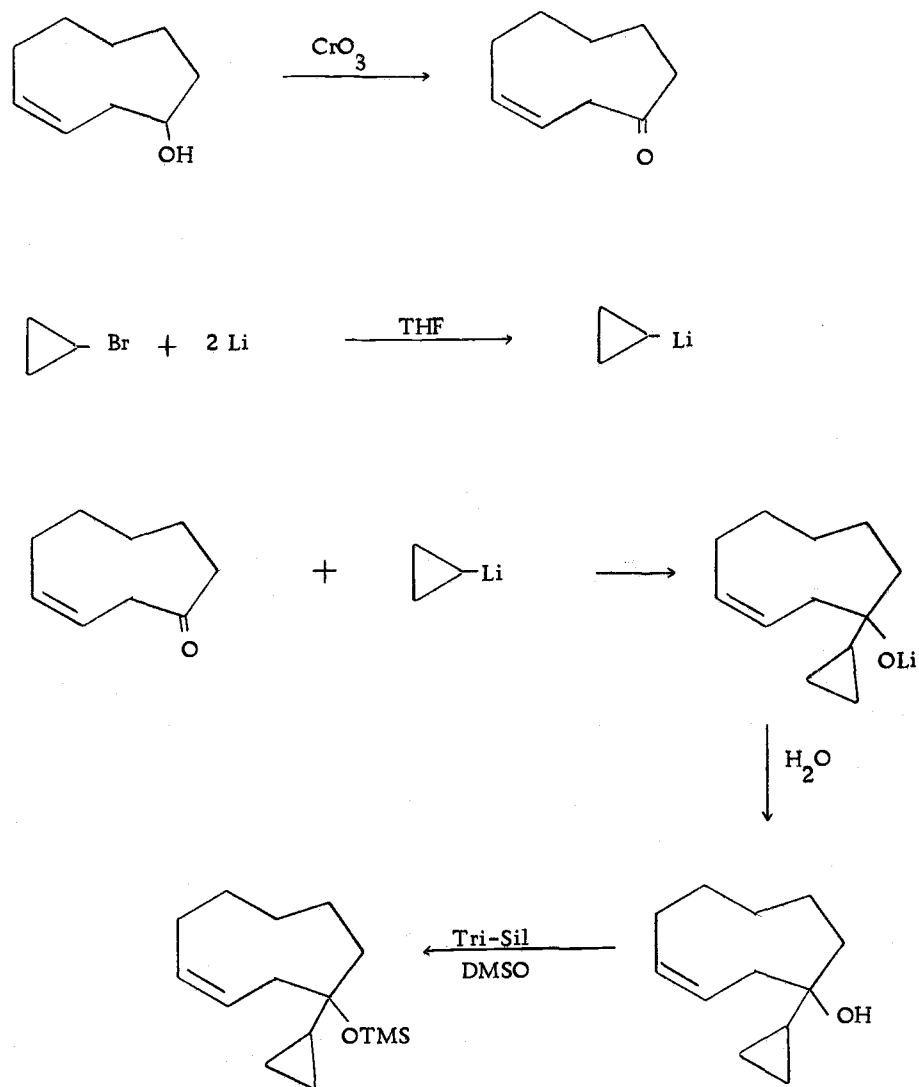
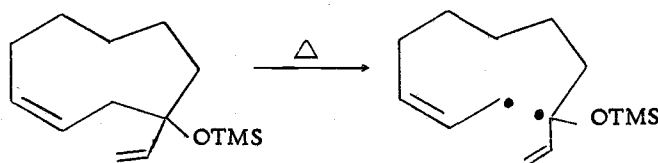


Figure 1. Synthesis of *cis*-1-trimethylsilyloxy-1-cyclopropyl-3-cyclononene (IV).

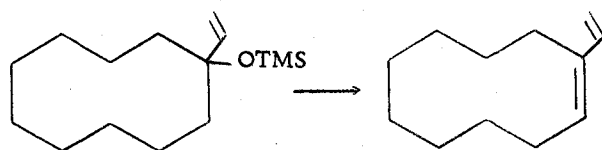
by desiloxylation. These undesired products were not investigated any further.

A diradical or a concerted mechanism could have given the siloxy-Cope rearranged [1, 3] shift product, V. Considering that the analogous compound, 1-trimethylsiloxy-1-vinyl-3-cyclononene (26), gave the rearranged products by a diradical route, the starting



compound, IV, should give the rearrangement by a diradical route rather than by a concerted mechanism. The starting material, IV, has one allyl and one cyclopropyl group that are the major factors affecting the bond dissociation energy. In comparing the rates of production of the allyl and cyclopropyl radicals at 130°, the allyl radical is produced more than 25 times faster than the n-butyl radical, while the cyclopropyl radical is produced only 3.89 times faster than the n-butyl radical. Therefore, the allyl radical is produced more than 6.4 times faster than the cyclopropyl radical based on this evidence (16). Thus, the activation barrier of anticipated rearrangement of IV must be in between those of a 1,5-hexadiene and a 1-hexene structure. An unpublished work,

thermolysis of a monovinyl case was studied by J. E. Billigmeier. When 1-trimethylsiloxy-1-vinylcyclodecane was pyrolyzed at 350°,



two olefins resulted that were desilylated products instead of the [1, 3] shift products. This is apparently due to the fact that the activation energy of the siloxy-Cope rearrangement is so high that the desilylation successfully competes.

The calculated value of the overall energy difference (Table 1) shows that the failure of IV to undergo siloxy-Cope rearrangement by diradical scheme can not be attributed to the fact that the difference of total energy between IV and V is not favorable. Therefore the main reason for the failure appears to be the lack of radical stabilization energy for IV which increases the activation barrier and allows the desilylation to compete.

Table 1. Overall energy change for conversion of IV to V.

Bond energy changes ^{a/}	+21.4 kcal/mol
Conjugation energy diff. ^{b/}	- 2.8 kcal/mol
Strain energy diff. ^{c/}	-37.4 kcal/mol
Extra "Skew butane" ^{d/}	- 1.8 kcal/mol
Total energy diff.	-20.6 kcal/mol

^{a/} Calculated by the method of Cox (10).

^{b/} Based on thermochemical data for vinyl-ethyl ether (22).

^{c/} Based on the data for cyclononene and cyclopropane (3) and the strain energy of cyclododecadiene was assumed to be negligibly small.

^{d/} Skew butane interactions, 1.8 kcal/mol, were used to approximate the extra interactions introduced by the cyclopropyl and trimethylsiloxy groups.

Entropy change was assumed to be small compared to other values.

EXPERIMENTAL

Product compositions were determined by gas chromatography utilizing an Aerograph Hy-Fi III Model 1200 equipped with a flame ionization detector. The infrared spectra were recorded with Beckman IR. 8 Infrared Spectrophotometer. Nuclear magnetic resonance spectra were measured on a Varian Model HA-100 analytical NMR Spectrometer. Medium resolution mass spectral data were obtained with the Atlas CH7 Mass Spectrometer with glc inlet. High resolution mass spectra were obtained with a CEC 110B instrument at the University of Oregon. All elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

cis-3-Cyclononenone

A solution of 1.25 g (0.009 mol) of cis-3-cyclononenol (23) in 150 ml of ether was placed in a one-liter three-necked round-bottom flask equipped with a reflux condenser. The mixture was cooled in an ice bath. While a solution of 12 g of chromium trioxide in 150 ml of water was added dropwise over a period of two hours with stirring. The reaction was continued another 12 hours at room temperature. Then, the organic layer was separated and the water layer was extracted three times with 50 ml of ether. The organic layers were combined and washed twice with 100 ml of water and

were dried over magnesium sulfate. Solvent was evaporated by a rotoevaporator.

Analysis of the crude product by glc showed over 90% conversion. The crude product was purified by means of chromatography on 50 ml of SilicAR, eluting with 500 ml of 3% ether-pentane which gave 0.94 g (0.0068 mol) of product.

ir(neat) 1700cm^{-1} .

Preparation of Cyclopropyllithium

Lithium, 0.25 g (0.035 mol), in 18 ml of ether was placed in 50 ml three necked flask equipped with magnetic stirrer. A solution of 4.0 g (0.033 mol) of cyclopropyl bromide in 10 ml of ether was added dropwise over 1.5 hours under nitrogen atmosphere while the flask was in an ice bath. One more gram of cyclopropyl bromide was added to dissolve the lithium completely. The resulting light-brown mixture was used directly for cyclopropylation of the above ketone.

cis-1-Cyclopropyl-3-Cyclononen-1-ol

A solution of 2.5 g (0.02 mol) of cis-3-cyclononenone in 10 ml of ether was added dropwise to the crude cyclopropyllithium solution, while the flask remained in an ice bath. After stirring for two hours, the reaction mixture was poured into a beaker that contained 100 ml of ether and 50 ml of 5% sulfuric acid. The organic layer was

separated and the water layer was extracted three times with 20 ml of ether. The combined organic layers were washed twice with 25 ml of 8% sodium carbonate, twice with 50 ml of water and dried over magnesium sulfate. The crude product was analyzed by glc. The broad alcohol peak was not completely resolved from a small shoulder representing an unidentified impurity, but the yield was estimated to be about 80% based on ketone.

ir(neat) 680, 1010, 1450, 3420 cm^{-1} .

cis-1-Trimethylsiloxy-1-cyclopropyl-3-cyclononene (IV)

A mixture of 200 μl of cis-1-cyclopropyl-3-cyclononen-1-ol and 600 μl of dimethylsulfoxide (DMSO) was placed in a small vial. Then 400 μl of Tri-Sil (purchased from Pierce Chemical Co.) was added little by little shaking the vial in between additions. By this time, two clear layers had separated. The upper layer was collected and the lower DMSO layer was washed with dry pentane several times. The collected pentane layers were combined with the upper layer. After evaporating the volatile solvent, the product was purified by means of preparative gas chromatography (5% C. W. 4000 on Anachome, 12 ft., 140°).

ir(neat) 745, 832, 1010, 1060, 1240, 1450 cm^{-1} .

nmr (CCl_4 , δ) 0.1(s, 9), 0.2-0.6(m, 5), 1.2-1.8(m, 8), 2.1-2.4(m, 4), 5.3-5.8(m, 2).

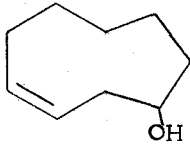
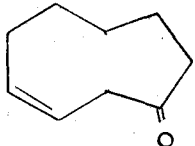
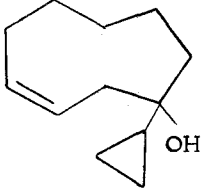
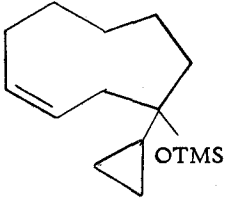
Pyrolysis and Hydrolysis of cis-1-trimethylsiloxy-1-cyclopropyl-3-cyclononene (IV)

Pyrex ampoules were prepared by washing with dilute ammonium hydroxide solution, rinsing with water and drying at 110° overnight. Three 20 ul samples of IV were added into three ampoules, and evacuated for about 20 minutes to eliminate volatile substances before sealing with a torch. The samples were pyrolyzed at 285°, 305°, and 350° for one hour, respectively. No appreciable change was shown by glc at 285°, but two new peaks that had shorter retention time than the above two peaks appeared at 350°.

The products resulting from the pyrolysis at 350° for one hour were placed in a 10 ml-test tube to which was added 1 ml of a hydrolysis mixture (18) consisting of 10 ml of pyridine, 1 ml of water and 2 drops of concentrated hydrochloric acid. After the mixture was refluxed for two hours, using a cold finger condenser, it was poured into a vial that contained 3 ml of ether and 1 drop of hydrochloric acid. The ether layer was collected and washed three times with 10% hydrochloric acid solution, then with water. The mixture was dried over magnesium sulfate. The glc showed that no hydrolysis of these products had taken place. Infrared revealed no distinct functional groups except carbon-carbon double bond.

ir(neat) 670, 2900cm⁻¹.

Table 2. Relative retention times for the compounds used for synthesis of cis-1-trimethylsiloxy-1-cyclopropyl-3-cyclononene.

Compounds	Temp. (° C)	Retention time (min)
	120	3.0
	120	1.8
	140	25.6
	120	2.8

The above compounds were run by 0.125 in. x 7 ft., 2.5% KOH-2.5% Carbowax column. The flow rate was adjusted at 25 ml/min.

SUMMARY

This work was performed to study the behavior of the cyclopropyl group on the siloxy-Cope rearrangement. Ring expansion by three carbons might have been expected, however desiloxylation occurred prior to the rearrangement. This appears to be due to the fact that the cyclopropyl group does not provide sufficient stabilization to the radical center.

Part 2

The Thermal Isomerization of 2-Phenyl-1-
Trimethylsiloxy-1-Vinylcyclononane

RESULTS AND DISCUSSION

The starting material, 2-phenyl-1-trimethylsiloxy-1-vinylcyclononane (VI) was prepared by a ring expansion process from an eight-membered ring ketone after several different routes had failed. The most difficult step throughout the process was phenylation at the α -position of the medium size ring ketones. Addition of the 10-membered ring ketone to the benzyne system (25) was attempted by both the one-pot and two-pot methods with no success (Figure 2). A second attempt involved a Grignard reaction, dehydration and hydroboration (2, 7, 11). However, the last step failed; this might be attributed to steric hindrance by the phenyl group (Figure 3). An alternate procedure of epoxidation followed by hydride reduction was tried without success. Ring expansion attempts with phenyldiazomethane (6, 20, 21) to give an α -phenyl group failed (Figure 4). The successful reaction sequence began with a Grignard reaction on cyclooctanone followed by bromination with N-bromosuccinimide. Treatment of this bromohydrin with isopropylmagnesiumbromide resulted in the ring-expanded α -phenyl ketone (6, 13) (Figure 5). Subsequent reaction with vinyl lithium followed by trimethylsilylation with Tri-Sil resulted in the desired compound VI.

Pyrolysis of VI in the gas phase gave the desired rearrangement (VI \rightarrow VII+VIII) smoothly in the temperature range 213-330°.

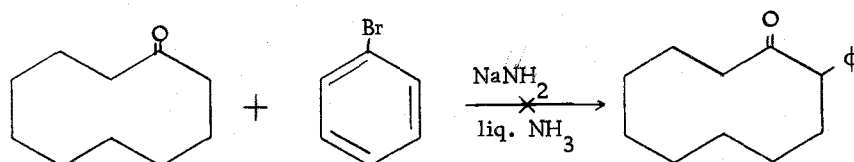


Figure 2. Attempted synthesis of α -phenyl ketone using benzyne.

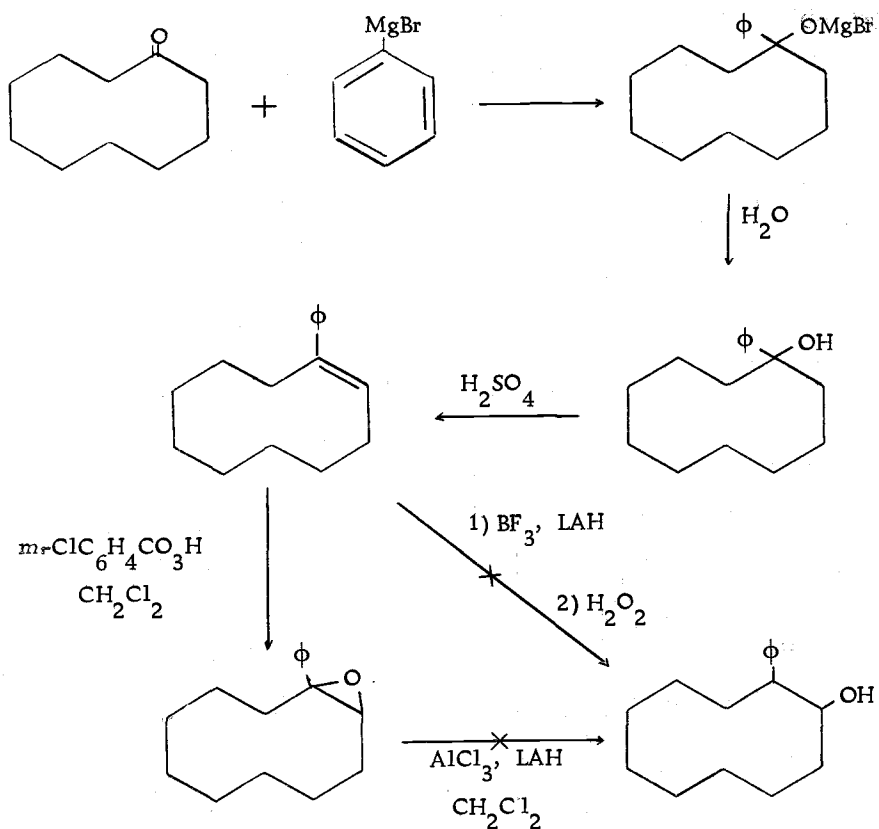


Figure 3. Attempted synthesis of α -phenyl ketone by a Grignard reaction and hydroboration.

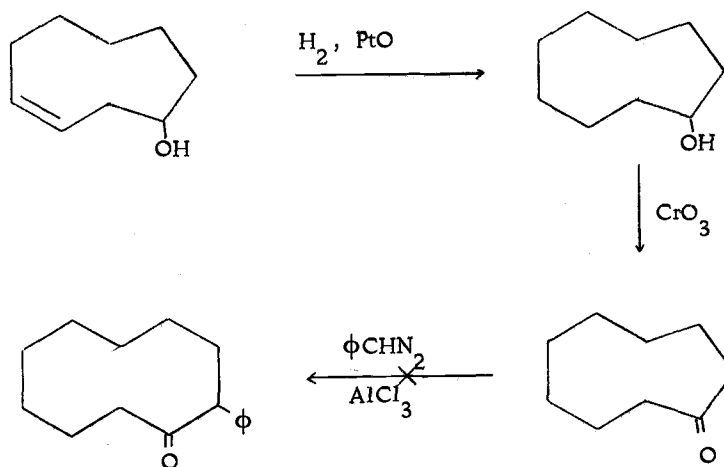


Figure 4. Attempted synthesis of α -phenyl ketone using phenyl diazomethane.

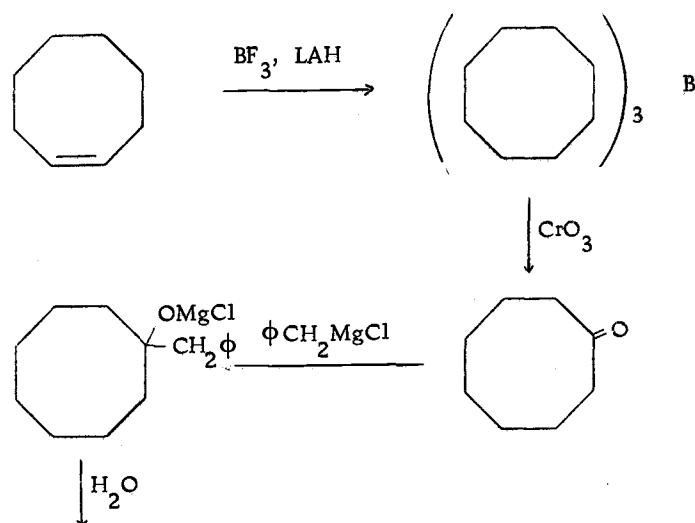


Figure 5. Synthesis of 2-phenyl-1-trimethylsiloxy-1-vinylcyclononane.

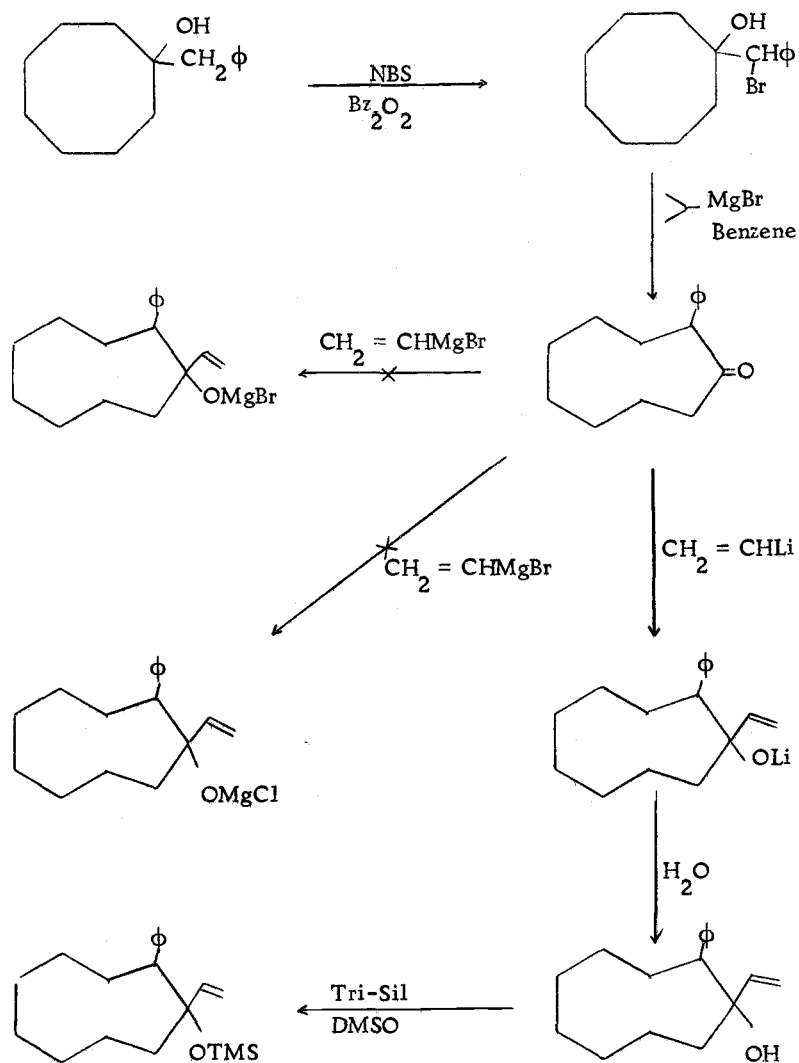
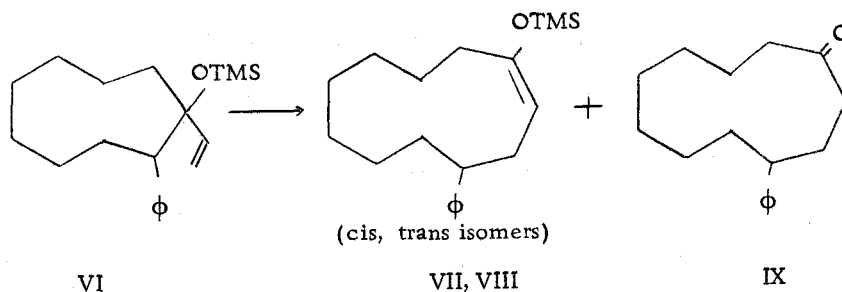
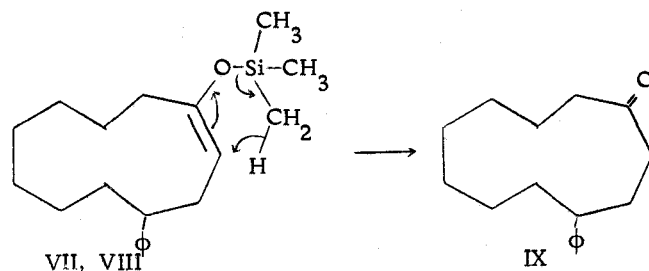


Figure 5. (Cont.)



This result is analogous to the case of pyrolysis of cis-1-trimethylsiloxy-1-vinyl-3-cyclononene (see Eq. 14) except that appreciable ketone formed during the pyrolysis. This ketone could be produced by means of a six-centered rearrangement on the siloxy-Cope rearranged products, VII and VIII. Alternatively if there were moisture in ampoule, the rearranged products, VII and VIII, could



have hydrolyzed to give ketone IX during the pyrolysis. However, when carefully dried ampoules were used, IX still appeared as a major product. Of course, VII and VIII gave IX when the pyrolysis products were hydrolyzed with pyridine-water-hydrochloric acid.

The amount of polymerization was not significant at the lower temperatures but increased with increasing temperature. A

reasonably low rate of polymerization could be obtained that did not appreciably affect the kinetic study below 280°.

The structures of the rearranged products VII, VIII and IX were based on the following evidence. When the mixture of products was hydrolyzed, VII and VIII gave only one product which was identified as ketone, IX. Mass spectroscopy indicated a molecular weight of 316 for VII and VIII respectively and 244 for IX (Figure 6). The nmr spectra (Figure 7 and 8) for IX were recorded using the shift reagent, $\text{Eu}(\text{fod})_3$ (24). This paramagnetic reagent forms a complex with compounds, causing shifts in the nmr spectra due to paramagnetic anisotropy. The protons near the oxygen move faster than those far from it; the α protons shift downfield fastest, followed by β protons, and so on. Before adding shift reagent, the nmr spectrum of IX showed a five proton multiplet at 7.5 δ , a five proton multiplet at 2.4-2.9 δ and a fourteen proton multiplet at 1.3-2.1 δ . The expected regions for the benzylic proton and the four α protons are 2.7-2.9 δ and 2.2-2.6 δ respectively. Therefore, the five protons at 2.4-2.9 δ could be reasonably assigned as one benzylic proton and four α protons which was later confirmed by adding shift reagent. When the amount of shift reagent is gradually increased, the α protons shift downfield fastest and separate from the benzylic γ proton. The β protons separate from the large multiplet and gradually overtake the γ proton as more shift reagent is added.

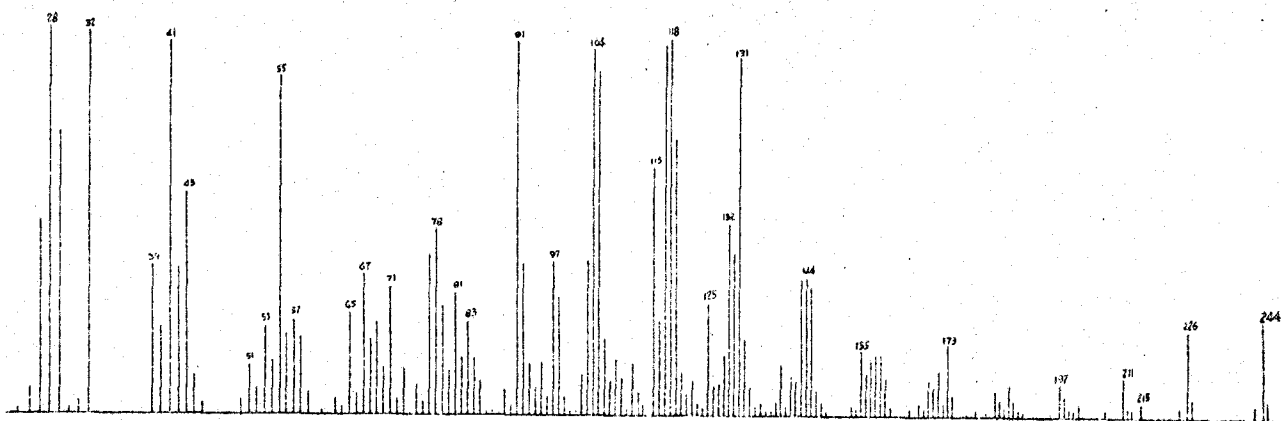


Figure 6. Mass Spectrum of 4-phenylcyclodecanone.

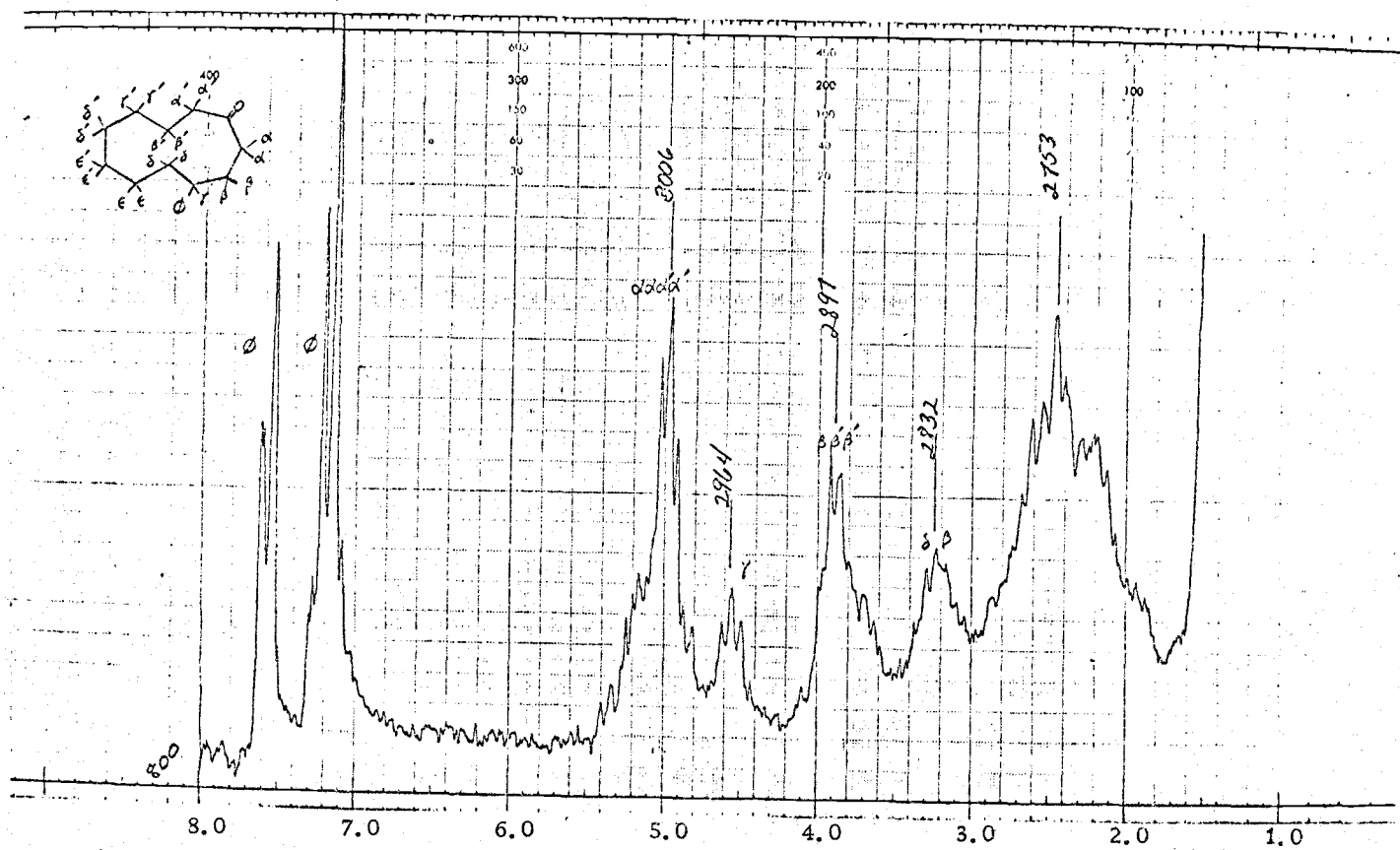


Figure 7. NMR spectrum of 4-phenylcycloundecanone with shift reagent, $\text{Eu}(\text{fod})_3$.

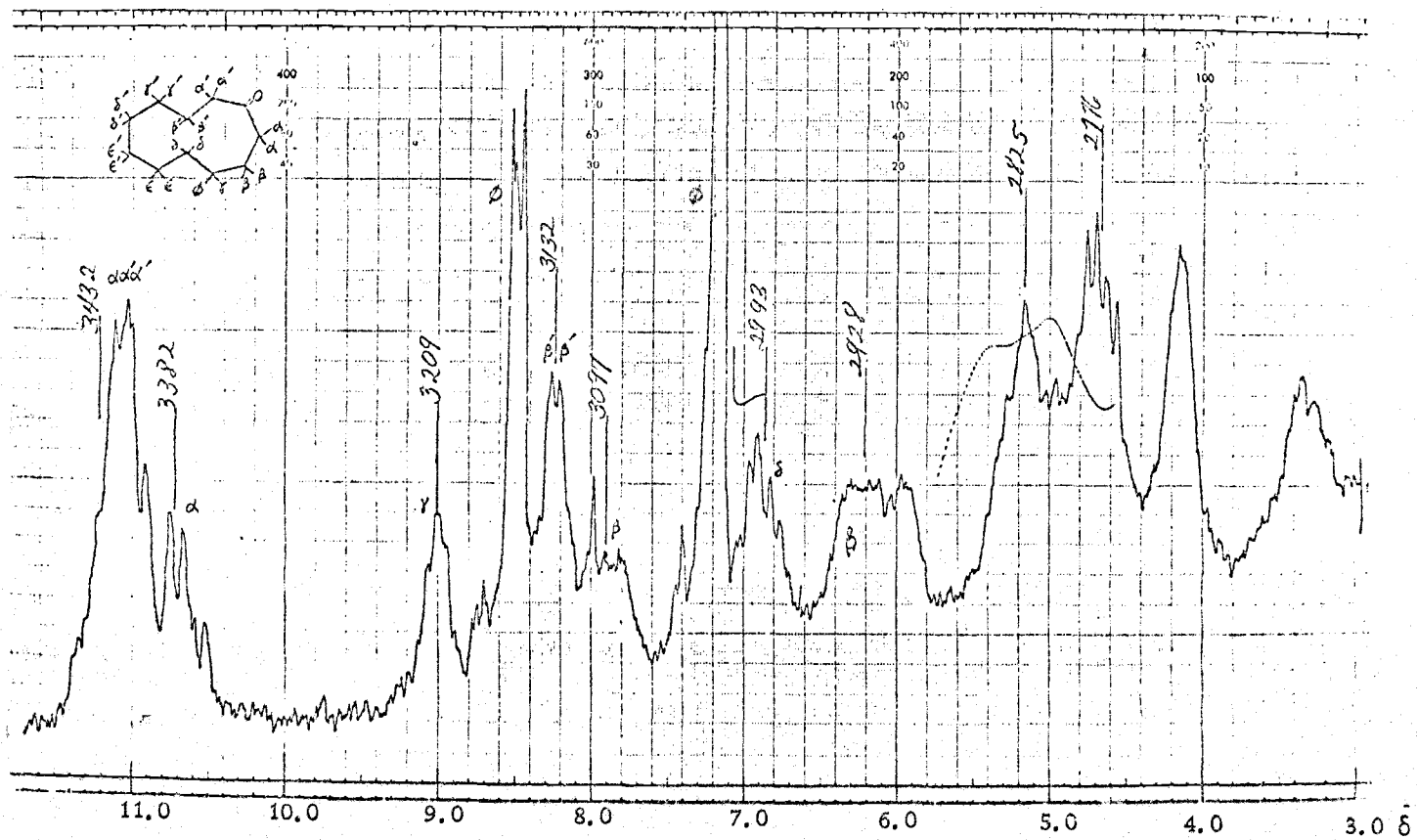
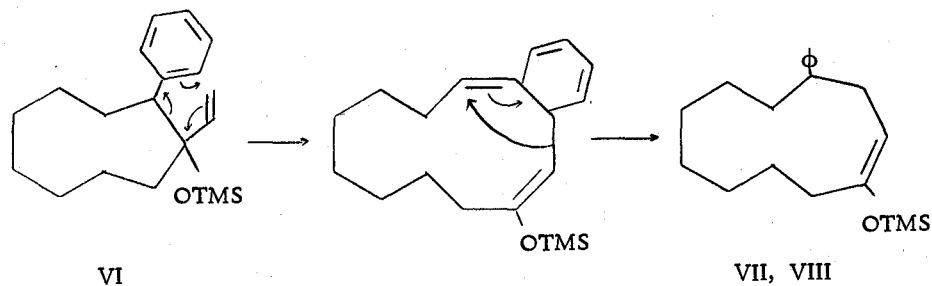


Figure 8. NMR spectrum of 4-phenylcycloundecanone with more shift reagent, $\text{Eu}(\text{fod})_3$.

One set of decoupling studies was performed on the sample shown in Figure 7. When the signal at 3.9 δ was irradiated, the α protons and the γ proton were partially decoupled, which indicates that at least one of the β protons must be contained in the 3.9 δ pattern. The irradiation at 3.9 δ also sharpened the pattern at 3.2 δ , which suggests that the other β proton is contained in that pattern; however, the 3.2 δ and 3.9 δ patterns are too close to be certain of the decoupling. When the γ proton was irradiated, the 3.9 δ pattern collapsed as did the pattern at 3.2 δ . To further confirm the above assignments a second set of decoupling studies was performed after adding more shift reagent (see Figure 8) to further separate the patterns. Irradiation of the α proton at 10.7 δ resulted in the sharpening of the β protons at 7.8 δ and 6.2 δ . Irradiation of the β proton at 7.8 δ sharpened the 6.2 δ pattern assigned to the other β proton. These studies show that the phenyl ring is in fact in the γ position. The decoupling study revealed an unexpected result, viz, one of the δ protons moved downfield faster than one of the β protons. The 6.9 δ pattern in Figure 8 was assigned as a δ proton, because irradiation of the δ proton caused the partial decoupling of γ proton. When the proton was irradiated, part of the 4.7 δ pattern, that should contain the another δ and the ϵ protons, showed a definite sharpening.

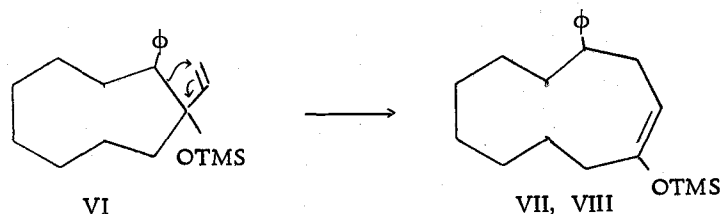
For the reaction mechanism, three different routes could be considered to give the rearranged products. One possible mechanism

is a concerted [3, 3] shift pathway followed by a [1, 3] shift. A concerted [3, 3] shift on 4-phenyl-1-butene structure attempted by Whyte and Cope (see Eq. 5 and 6) was unsuccessful,



possibly because the anticipated rearrangement would require that the aromatic ring give up its resonance. The compound (VI) that has 4-phenyl-1-butene structure would also give the same kind of high energy intermediate.

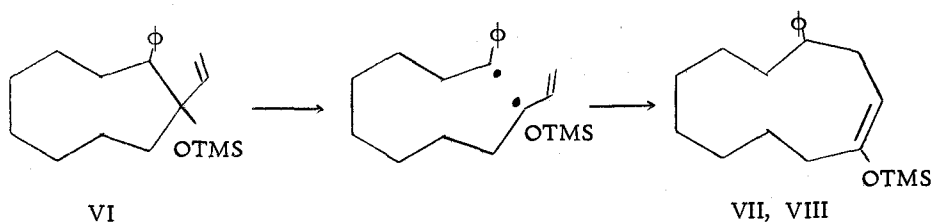
Another possible mechanism giving the rearranged products is a concerted [1, 3] sigmatropic shift by the symmetry allowed process $[\sigma 2a + \pi 2s]$, which would result in inversion at the C-2 center (31).



The analogous compound, cis-1-trimethylsiloxy-1-vinyl-3-cyclononene (see Eq. 14) did not give any evidence for such a concerted [1, 3] shift. However a phenyl group on the migrating carbon

of VI could favor the concerted [1, 3] shift, possibly as a result of conjugation between the phenyl group and the p-orbital of the migrating carbon. It is interesting that 3, 4-diphenyl-1, 5-hexadiene (see Eq. 8) gave [1, 3] shift product. For that system, the author argued in favor of a diradical reaction however a [1, 3] concerted rearrangement was not considered. Such a concerted [1, 3] shift would not be ruled out by that author's data.

An alternative mechanism for the rearrangement of VI is bond cleavage and recombination. The possibility of this mechanism was evaluated by comparing bond dissociation energies with the experimental value. The activation energy for the cleavage of ethane into two methyl radicals is 85 kcal/mol (3). The conjugative effect of a



vinyl group and phenyl group lowers the barrier by 26-28 kcal/mol (4). Also the activation energy value would be expected to be lower than that for biallylic (1, 5-hexadiene) by an amount equal to the bond-weakening effect of two additional alkyl groups (6 kcal/mol) (3) and ring strain energy (3-4 kcal/mol) (4). Another effect is that of the α -oxygen which lowers the barrier by about 2.4 kcal/mol (4). By

using the above data, the calculated activation energy for VI reacting by the biradical mechanism should be about 45 kcal/mol $[85 - (28 + 6 + 3.5 + 2.4)]$. If VI goes by either a concerted or a diradical mechanism, the total rearrangement process should be first order. The approximate first-order rate constants were determined at 280°, 260°, 225° and 213°. Two or three values of reaction constants were averaged for each temperature. The Arrhenius plot from which the indicated activation parameter was derived was close to linear (Table 3) (Figure 9). The experimental value of the activation energy was 25.8 kcal/mol which is not consistent with the value, 45.1 kcal/mol. This leaves some question as to whether the concerted mechanism may be possible for this particular compound or possibly that there is a competition between the above two mechanisms. Further work should be carried out to determine the activation parameters more accurately and to definitely establish that the process is first order.

Table 3. First order rate of disappearance of 2-Phenyl-1-trimethylsiloxy-1-vinylcyclohexane.

Temp. ($^{\circ}\text{C}$)	$10^4 k \text{ sec}^{-1}$
280	3.1 ± 0.05
260	1.2 ± 0.28
225	0.25 ± 0.02
213	0.12 ± 0.02

$$E_a = 25.8 \pm 0.5$$

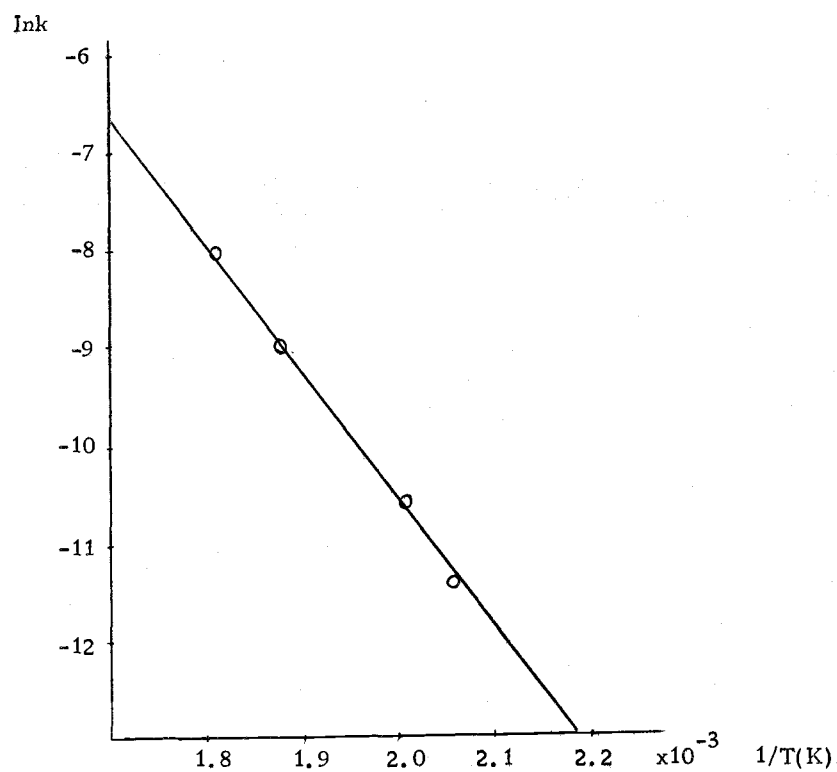


Figure 9. Arrhenius plot.

EXPERIMENTAL

Cyclooctanone

Cyclooctene, 12 g (0.11 mol), and 2.08 g (0.005 mol) of lithium aluminium hydride in 60 ml of ether were placed in 500 ml flask fitted with a stirrer, condenser, additional funnel and thermometer. To the reaction mixture was added 2.28 ml (0.018 mol) of boron trifluoride etherate in 8 ml of ether, dropwise over a period of one hour at 25-30°. After two hours, excess hydride was destroyed with 10 ml water. The chromic acid solution, prepared from 20 g (0.2 mol) of chromium trioxide and 150 ml of water, was added dropwise over a period of two hours, maintaining the temperature at 25-30°, while it was stirred. After the reaction was stirred overnight, the upper layer was separated, and the aqueous layer was extracted with two 40 ml portions of ether. Gas chromatographic examination indicated more than 90% conversion. After evaporating solvent, the crude ketone was used directly in next Grignard reaction.

ir(neat) 1450, 1680, 2940 cm^{-1} .

Preparation of Benzyl Magnesium Chloride

Magnesium, 1.25 g (0.152 mol), in 43 ml of ether and a small crystal of iodine were placed in a three-necked round-bottom flask

fitted with a dropping funnel. One-third of 7.6 g (0.06 mol) of benzyl chloride was added to the flask at once under a nitrogen atmosphere and the flask was partially immersed in a bath containing water heated to about 40°. As soon as the ether began to boil, and reaction set in, the bath was removed and stirring was begun. The remainder of the benzyl chloride was added during the course of 10 minutes. The reaction was continued for about five more minutes after all the benzyl chloride had been added, and then the mixture was refluxed gently for about 30 minutes. By this time the magnesium was completely dissolved.

1-Benzyl-1-cyclooctanol

To the stirred benzylmagnesium chloride solution was added 6.3 g (0.05 mol) of cyclooctanone dropwise while the flask was kept in an ice bath. After addition, the stirring was continued for three hours at room temperature, and then the reaction was quenched with saturated ammonium chloride solution. The separated organic portion was washed with water and dried over magnesium sulfate.

After removal of the solvent under vacuum, the alcohol was distilled under vacuum, bp 120-130°/0.5 torr., yielding 5.7 g (0.026 mol) of 1-benzyl-1-cyclooctanol.

ir(neat) 695, 730, 1100, 1450, 2900, 3010, 3450 cm^{-1} .

nmr (CCl_4 , δ) 1.2(OH, 1), 1.5(m, 14), 2.6(s, 2), 7.1(m, 5).

1-(α -bromobenzyl)-1-cyclooctanol

Freshly distilled 1-benzyl-1-cyclooctanol, 16 g (0.073 mol), in 80 ml of carbon tetrachloride was placed in 1000 ml three-necked round bottom flask with magnetic stirrer. To this mixture, 14 g (0.079 mol) of N-bromosuccinimide and 0.4 g of benzoyl peroxide was added to the flask, and the mixture was brought to reflux with the aid of an oil bath under a nitrogen atmosphere. As soon as the orange color appeared, the heat was removed. The mixture refluxed by itself and a spontaneous reaction began in 5 minutes after removing the heat. The mixture turned to clear yellow as a lot of succinimide crystals appeared. Then the mixture was refluxed an additional hour and the succinimide was filtered off. The carbon tetrachloride was removed under vacuum. The residual light yellow oil was used directly in the ring enlargement reaction. The nmr spectra in CCl_4 showed one benzyl hydrogen at 3.56 δ as a singlet.

2-Phenylcyclononanone

The crude bromohydrin was dissolved in 150 ml of dry benzene in 500 ml three-necked round bottom flask. A solution of 0.074 mol of isopropylmagnesiumbromide (1.8 g of magnesium, 9 g of isopropyl bromide in 25 ml of ether) was added dropwise under a nitrogen atmosphere while the reaction was cooled with an ice bath. After

complete addition, the ice bath was removed and the reaction mixture was refluxed for an hour. Then the brown solution was cooled and the reaction was quenched by adding saturated ammonium chloride solution. After separation of the benzene layer, the layer was washed with 10% sodium carbonate solution followed by water. The separated benzene layer was then dried over magnesium sulfate and the solvent was subsequently removed under vacuum. The glc indicated approximately 80% purity. This crude product was purified by vacuum distillation, bp 110-116°/0.3 torr. which gave 2.3 g (0.0106 mol) of product.

mass spec.: M.W. = 216

ir(neat) 695, 1020, 1100, 1260, 1450, 1540, 2950, 3020 cm^{-1} .

nmr (CCl_4 , δ) 1.6(m, 12), 2.4(m, 2), 3.9-4.1(m, 1), 7.4(m, 5).

2-Phenyl-1-vinyl-1-cyclononanol

A mixture of 15 ml (0.015 mol) of 1 M vinyl lithium solution in THF (purchased from Alfa Inorganic, Inc.) and 1 g (0.0047 mol) of 2-phenyl-1-cyclononone in 5 ml of THF was stirred for about 5 minutes under the nitrogen atmosphere. Then the reaction was quenched by adding 5 ml of water. After separation of the organic layer, it was dried over magnesium sulfate. The glc indicated about 40% conversion. This was purified by chromatography on 50 ml of SilicAR. Distilled pentane was used until olefin began to elute,

followed by 3% ether-pentane.

ir(neat) 3450cm^{-1} .

2-Phenyl-1-trimethylsiloxy-1-vinylcyclononane

The trimethylsiloxy derivative was prepared by the same method as in Part 1. The product was purified by means of preparative gas chromatography (10% SF 96 AC 80/90A, 17 ft., 240°). The ir revealed neither hydroxyl nor carbonyl absorption.

nmr (CCl_4 , δ) 0.1(m, 9), 1.5(m, 14), 2.6(m, 1), 4.6-5.5(m, 3), 6.9(m, 5).

mass spec.: Calculated m/e for $\text{C}_{20}\text{H}_{32}\text{OSi}$: 316.222

Found m/e: 316.221

Pyrolysis and Hydrolysis of 2-phenyl-1-trimethylsiloxy-1-vinylcyclononane

The pyrolysis and hydrolysis procedures used were the same as in Part 1. The conditions for the pyrolysis and the yields resulting from hydrolysis are shown in Table 4. The product after pyrolysis and hydrolysis was separated by means of preparative gas chromatography (5% KOH, 5% C.W. 4000, 10 ft., 180°) and analyzed.

nmr (CCl_4 , δ) 1.3-2.1(m, 14) 2.4-2.9(m, 5), 7.5(m, 5).

mass spec.: M.W. = 224

Anal. calcd. for $\text{C}_{17}\text{H}_{24}\text{O}$: C, 83.55; H, 9.89

Found: C, 83.23; H, 9.67

Table 4. The yields resulting from the pyrolysis of 2-phenyl-1-trimethylsiloxy-1-vinylcyclononane.

Temp. (° C)	Period (min.)	Apparent conversion (%)	Actual yield of product (%)	Polymer (%)
213	705	42.1		
	1440	58.2		
225	360	43.8		
	720	63.0		
260	360	29.9		
	720	65.7		
	1080	74.2		
280	360	67.9	59.3	12.4
	720	88.7	73.8	16.7
310	40	98.0	58.3	41.2
330	40	100.0	52.4	47.6

* 2-Phenyl cyclononane was used as an internal glc standard to evaluate the actual yield of of total products.

Table 5. Relative retention times for the compounds, used for synthesis of 4-phenylcycloundecanone.

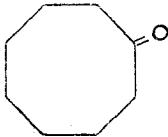
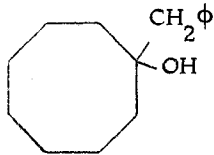
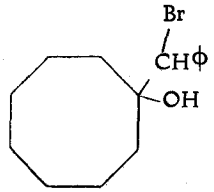
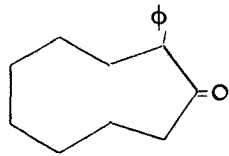
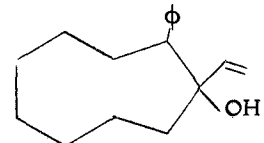
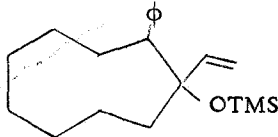
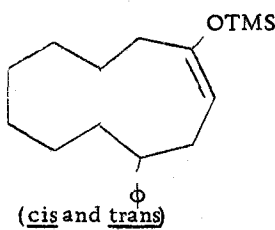
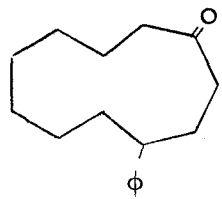
Compounds	Temp. (°C)	Retentive time (min)
	120	2.2
	120	27.8
	120	21.6
	120	22.0
	140	10.2

Table 5. Continued

Compounds	Temp. (° C)	Retentive time (min)
	130	4.6
 (cis and trans)	140	6.0 7.6
	140	20.2

The above compounds were run by 0.125 in. x 7 ft., 2.5% KOH-2.5% Carbowax column. The flow rate was adjusted at 25 ml/min.

SUMMARY

The object of this work was to observe the rearrangement of a compound that had an aromatic group and an allyl group instead of a 1,5-hexadiene structure. The siloxy-Cope rearrangement of 2-phenyl-1-trimethylsiloxy-1-vinylcyclononane gave rearranged products, cis and trans-4-phenyl-1-trimethylsiloxy-1-cycloundecene and the rearranged-hydrolyzed product, 4-phenylcycloundecanone. The structure of the compound resulting from the hydrolysis of the rearranged products was shown to be 4-phenylcycloundecanone by nmr, mass spectroscopy and microanalysis. The reaction mechanism was not thoroughly studied. An appreciable amount of polymerization took place at high temperature.

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APPENDIX I

One of the rearranged products of 3, 4-diphenyl-1, 5-hexadiene by Koch's work was misassigned as a [1, 3] shift product. According to the latest work by Lutz, the rearranged products were both [3, 3] shift products; trans-trans-1, 6-diphenyl-1, 5-hexadiene and cis-trans-1, 6-diphenyl-1, 5-hexadiene. Thus there is no precedent for a phenyl at 3-position favoring the [1, 3] shift.

Lutz, R. P., S. Bernal, R. J. Boggio, and M. W. McNicholas.
Dual reaction pathways in an open-chain Cope. Journal of
American Chemical Society 93:3985-3990. 1971.