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Thermal rearrangements of unsaturated and strained organosilanes and their hydrocarbon counterparts

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Iowa State University

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Thermal rearrangements of unsaturated and strained
organosilanes and their hydrocarbon counterparts

Power, Martin Dale, Ph.D.

Iowa State University, 1989

Thermal rearrangements of unsaturated and strained

organosilanes and their hydrocarbon counterparts

by

Martin Dale Power

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INTRODUCTION

The potential energy surface for the almost isothermal rearrangement of propyne to allene has been calculated by Honjou et al. These calculations show that cyclopropene is an intermediate on this surface lying approximately 22 kcal/mol above propyne and allene (1). The propyne to allene rearrangement has recently been shown experimentally (2) to have a transition energy identical to the above calculations.

This work will study the thermal isomerization of a hydridosilylacetylene to discover if its thermal chemistry resembles that of the analogous propyne. We will also study the thermal chemistry of ^{13}C-labeled-1-phenylpropyne to see if evidence can be gained for the proposed vinylcarbene or methylvinylidene intermediates proposed in the theoretical calculations mentioned above.

Conlin et al. (3) reported the thermal isomerization of 2-methylene-1,1-dimethylsilacyclobutane to 1,1-dimethyl-silacyclopent-2-ene and 1,1-dimethylsilacyclopent-3-ene. This ring expansion via a 1,2-silyl migration across an isolated π-system has the advantage of releasing the strain energy of a four-membered silacyclobutane ring (4).

This work will attempt to thermally generate methylene-cyclopropanes and isomerize them to silacyclobutenes. Also,

the mechanistic aspects of the thermal isomerization of trimethylsilylcyclopropane will be explored with regard to the generation of carbenes via 1,2-silyl migrations.

LITERATURE SURVEY

Thermal Rearrangements of Silylacetylenes and Acetylenes

In 1960, Wiberg and Bartley (5) reported the thermal isomerization of cyclopropene to propyne. In this simple helium flow experiment, no kinetics were reported nor was a mechanism proposed.

$$\triangle \xrightarrow[\text{Helium flow}]{325°C \text{ to } 425°C} CH_3-C\equiv C-H$$

1   2
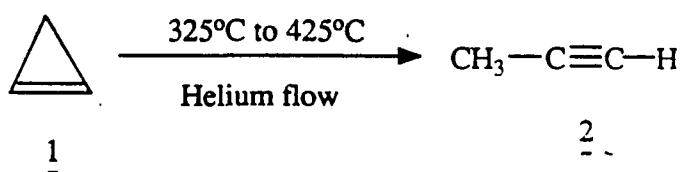
York et al. (6) synthesized optically active 1,3-diethylcyclopropene 3 in a long and tedious synthesis. Its thermal kinetics were carried out in a static reactor and the starting material was found to racemize significantly (nine times) faster than its conversion to acyclic products 4-7.

Also reported by York were Arrhenius parameters for loss of optical activity, product formation, and racemization. While identical activation energies were obtained for these three processes, the log A for product formation was somewhat lower than for loss of optical activity and racemization.

Table 1. Arrhenius parameters for the thermal racemization and structural isomerization of optically active 1,3-diethylcyclopropene

	log A	E_a (kcal/mol)
loss of optical activity	11.8	32.6
product formation	10.4	32.2
racemization	11.5	32.7
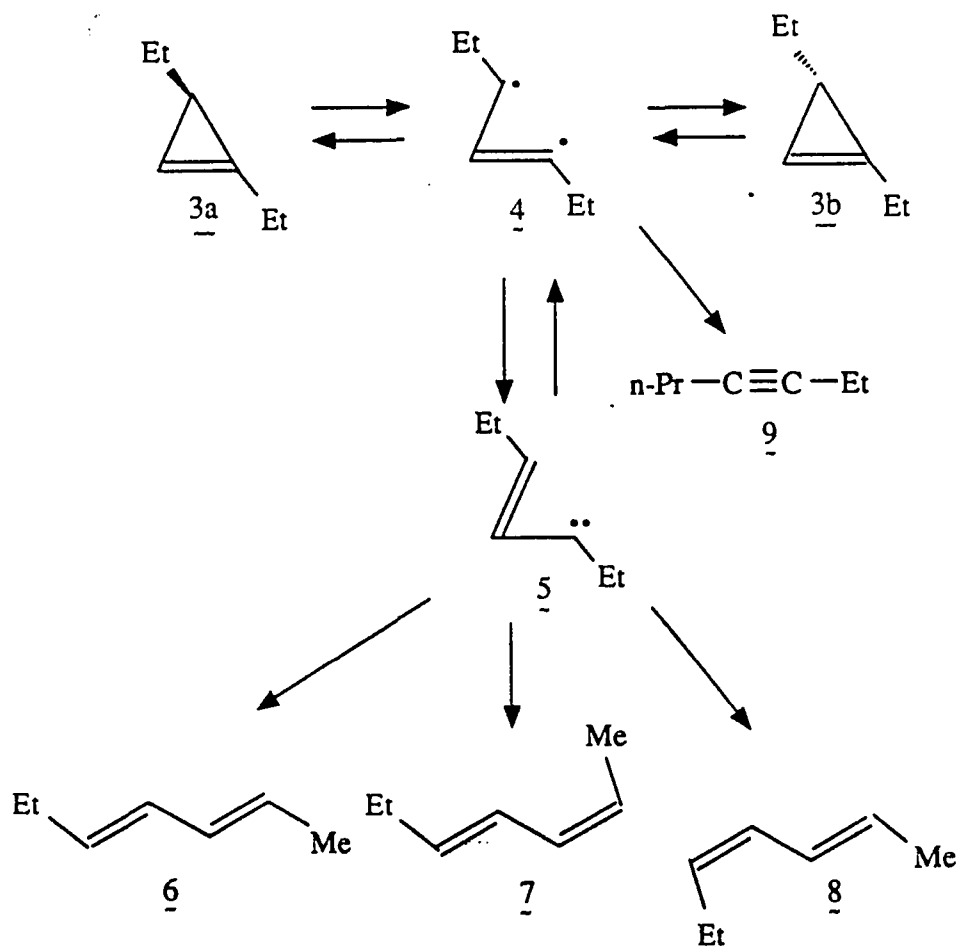
In 1975, two separate research groups reported very different sets of Arrhenius parameters in the shock tube isomerization of allene to propyne. While Lifshitz et al. (7) obtained log k = 13.17 - 60.4 kcal mol^{-1}/RT, the research of Bradley and West (8) yielded log k = 14.43 - 92.8 kcal mol^{-1}/RT. The former group also performed crossover experiments to demonstrate unimolecularity of the isomerization. Although the activation energies vari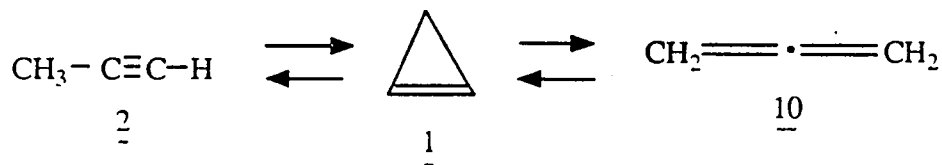ed by over 30 kcal/mol, both sets of authors favored a direct 1,3-hydrogen migration mechanism through transition state 11.

$$CH_2=C=CH_2 \rightleftarrows HC \overset{H}{\underset{C}{\diagup\!\!\diagdown}} CH_2 \rightleftarrows CH_3-C\equiv C-H$$

10   11   2
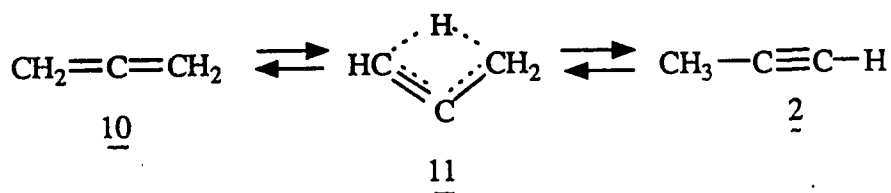
In 1976, Walsh (9) tied all of this research together by proposing cyclopropene to be an intermediate on the pathway from allene to propyne. Repeating earlier work by Srinivassan (10), Walsh found allene to be present in the isomerization mixture of cyclopropene to propyne. Walsh performed his own calculations using thermochemical data and obtained an activation energy of 64.3 kcal/mol for the allene to propyne isomerization. A new mechanism was proposed for this reaction: two 1,2-hydrogen shifts instead of a concerted 1,3-migration. Walsh also obtained log k =

13.25 - 37.5 kcal mol^{-1}/RT for the decomposition of cyclopropene.

$$CH_3 - C\equiv C-H \quad \rightleftarrows \quad \triangle \quad \rightleftarrows \quad CH_2 =\!\!\cdot\!\!= CH_2$$

$$\underset{\underset{\sim}{2}}{} \qquad\qquad \underset{1}{} \qquad\qquad \underset{\underline{10}}{}$$

In 1980, Hopf et al. (11) discovered that 1-^{2}H-propyne $\underline{12}$ formed 3-^{2}H-propyne $\underline{14}$ approximately 3.5 times faster than it formed 1-^{2}H-allene $\underline{15}$. They suggested this as evidence of an intermediate on this pathway other than allene. They proposed this intermediate to be 1-^{2}H-cyclopropene $\underline{13}$.

$$CH_3 - C\equiv C-D$$
$$\underline{12}$$

$$\left[\triangleleft^D \right] \quad \rightleftarrows \quad CH_2 = C = CHD$$
$$\underline{13} \qquad\qquad \underline{15}$$

$$DCH_2 - C\equiv C-H$$
$$\underline{14}$$
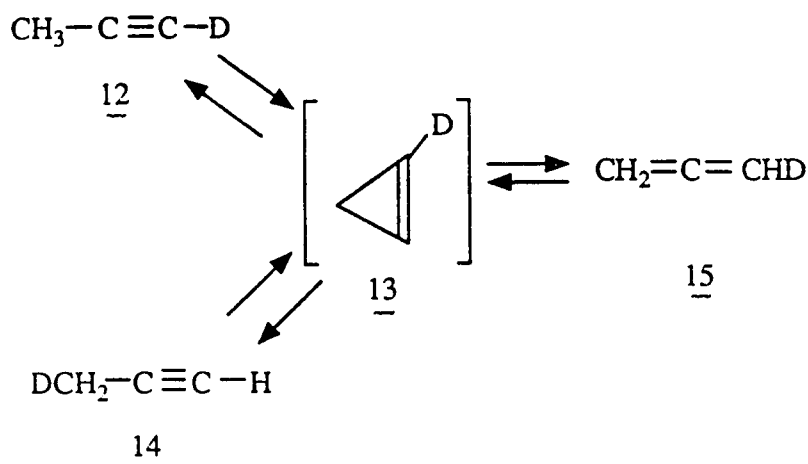
In 1985, Honjou et al. (1) calculated the lowest energy pathway for the interconversion of allene, cyclopropene, and propyne on the C_3H_4 singlet surface. They found that vinyl methylene and propylidene are also minima on this surface.

The activation energy for the isomerization of allene to propyne was calculated to be 68.4 kcal/mol and for cyclopropene to propyne is 41.5 kcal/mol. They proposed two 1,2-hydrogen shifts and calculated a direct 1,3-hydrogen migration to have an activation energy of 94.9 kcal/mol.
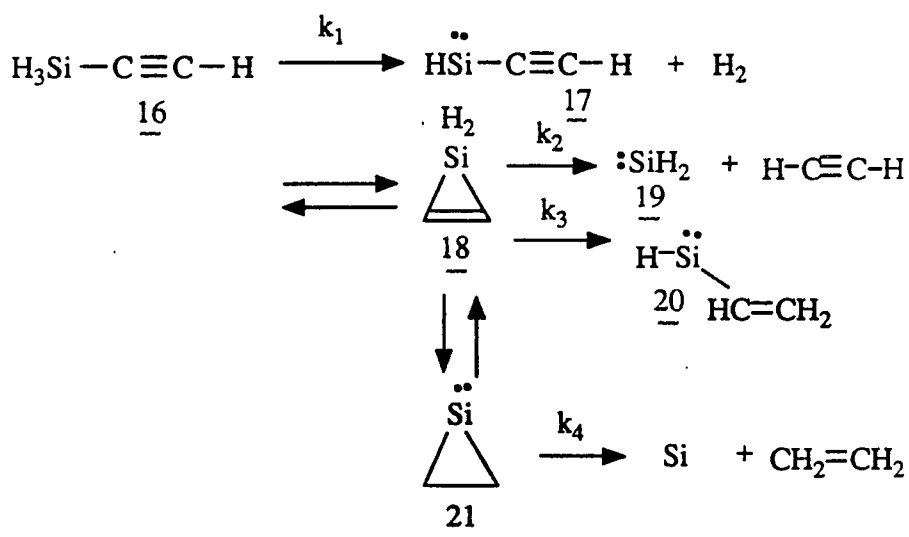
69

63

67

58 kcal

H

H_3C

44 kcal

22.5 kcal

$H_2C=C=CH_2$
0.7 kcal

1,3-H >90 kcal/mol

$H_3C-C\equiv CH$
0 kcal
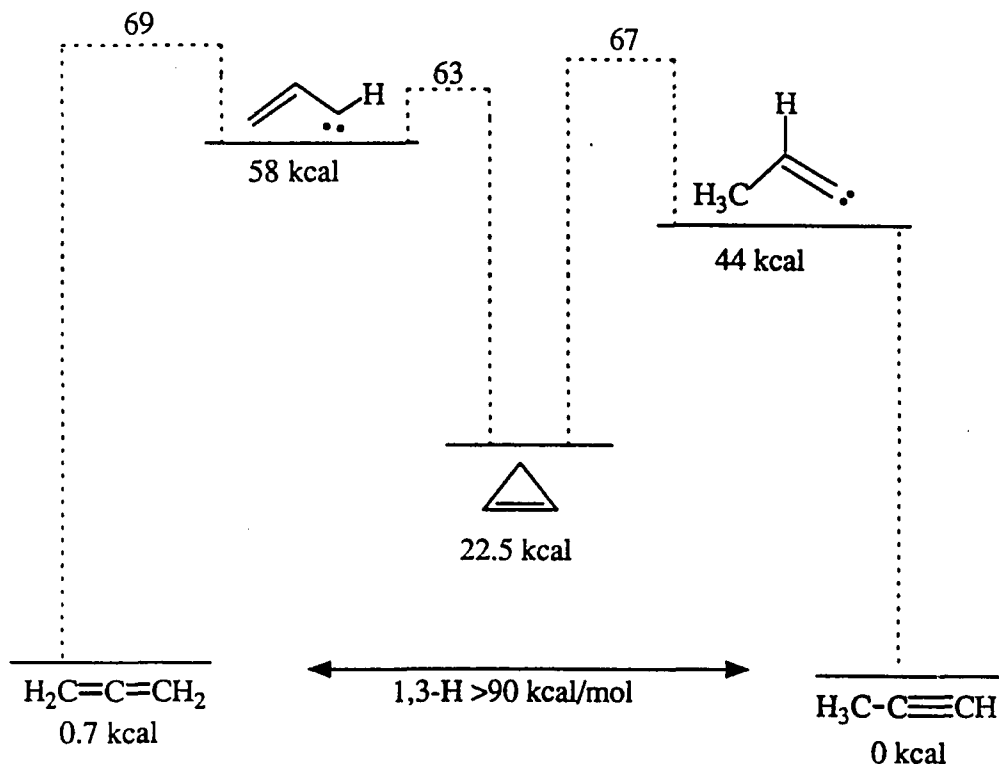
While several papers (12-14) and a review (15) have been published since Honjou's calculations, the most recent experimental work by Kakumoto et al. (2) are in full agreement with these calculations. In shock tube experiments, this research group obtained log k = 14.34 - 68.1 kcal mol^{-1}/RT and found the rearrangement to be exothermic by 1.6 kcal/mol.

Rogers et al. (16) reported the shock tube kinetics for the decomposition of ethynylsilane $\underset{\sim}{16}$, the silicon analog of propyne. They assumed the decomposition to proceed by four major pathways: [1] 1,1-elimination of hydrogen to form ethynylsilylene $\underset{\sim}{17}$, [2] rearrangement to silacyclopropene $\underset{\sim}{18}$ and extrusion of silylene $\underset{\sim}{19}$ to form acetylene, [3] rearrangement to silacyclopropene $\underset{\sim}{18}$ and ring opening to form vinylsilylene $\underset{\sim}{20}$, and [4] rearrangement of the silacyclopropene $\underset{\sim}{18}$ to unknown 1-silacyclopropylidene $\underset{\sim}{21}$ which extrudes elemental silicon to form ethylene.

$$H_3Si-C\equiv C-H \xrightarrow{k_1} HSi-C\equiv C-H + H_2$$

$$\underset{16}{} \qquad \underset{17}{}$$

18 $\xrightarrow{k_2}$:SiH$_2$ + H-C≡C-H (19)

18 $\xrightarrow{k_3}$ H-Si̤ 20 HC=CH$_2$

21 $\xrightarrow{k_4}$ Si + CH$_2$=CH$_2$

Rogers measured the rate constant for the total decomposition of ethynylsilane and found a value of 1985 s^{-1}. He also measured ethylene yield in the presence of added acetylene (k_4 = 337 s^{-1} and 17% of reaction pathway) and measured silylene $\underset{\sim}{19}$ by trapping it with an excess of

added 1,3-butadiene (k_2 = 278 s^{-1} and 14% of reaction).

Rogers later increased k_2 to 615 s^{-1} based on observations

that silylene trapping with 1,3-butadiene is usually only

45% efficient (k_2 = 615 s^{-1} or 31% of the decomposition

reaction of ethynylsilane). The value for k_1 was taken from

other 1,1-H_2 eliminations to be 932 s^{-1}. K_1 was adjusted to

595 s^{-1} due to the pressure difference between his system

and the system in which the 932 s^{-1} value is determined. K_3

was determined by subtraction to be 437 s^{-1}.

Brown and co-workers (17-19) have demonstrated the

isomerization of acetylenes utilizing isotopic carbon

labelling. Pyrolyses of ^{13}C- and ^{14}C-labelled acetylenes

showed that scrambling had occurred in the alkyne carbons.

The proposed explanation is sequential 1,2 shifts via

substituted vinylidenes 23 or 24.
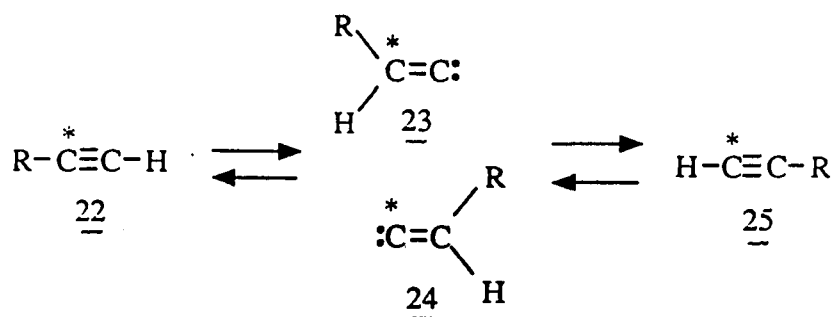
R = phenyl, adamantyl, D

* denotes ^{13}C or ^{14}C label

Other evidence which supports the intermediacy of
vinylidenes was found in the pyrolyses of (methylaryl)-
acetylenes such as o-tolylacetylene 26, 8-methyl-1-
naphthylacetylene 28, o-tolylphenylacetylene 30, and Barton
and Groh's work with o-dimethylsilylphenylacetylene 33 (20).
All of these acetylenes underwent closure upon pyrolysis to
form five- and six-membered rings. These products were all
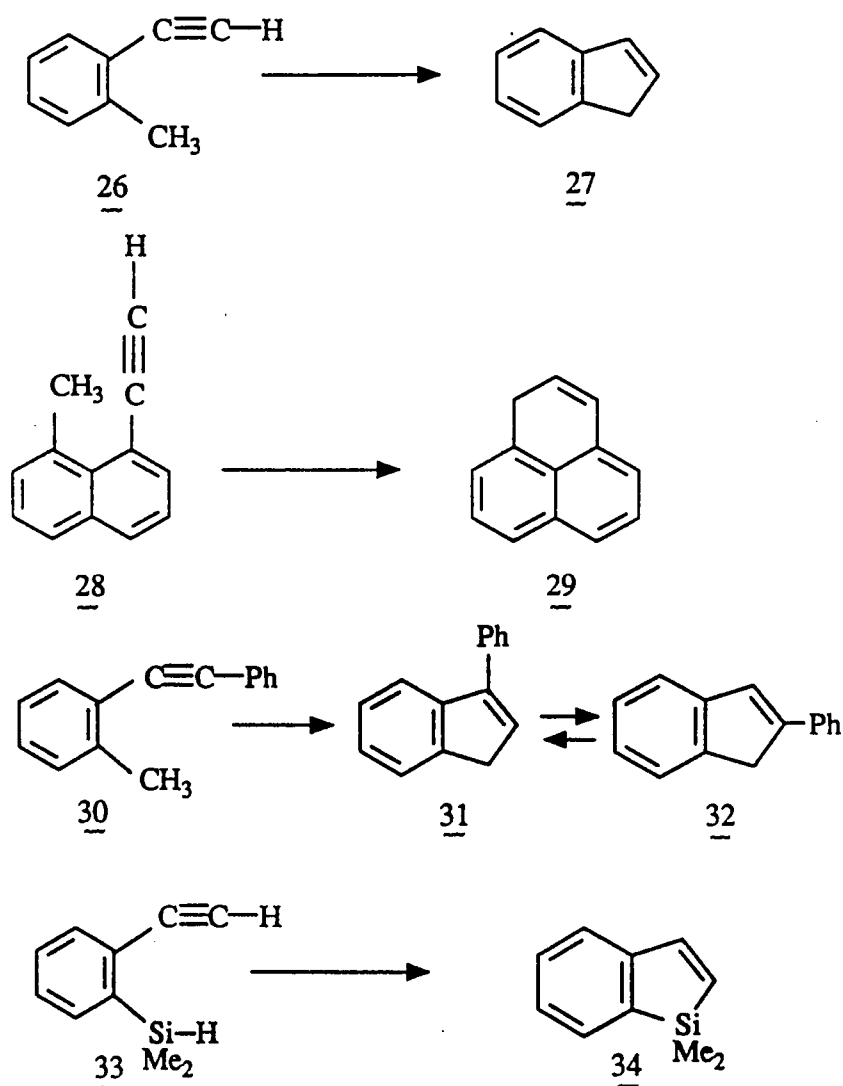
explained by the vinylidene intermediate being intramolecularly trapped by a C-H or a Si-H bond.

Brown et al. (17) have studied the thermal isomerization of methylenebenzocyclobutene 35 to indene 27. He proposes ring opening to o-quinoid allene 36 and rearrangement to indene 27 through o-tolylacetylene 26.
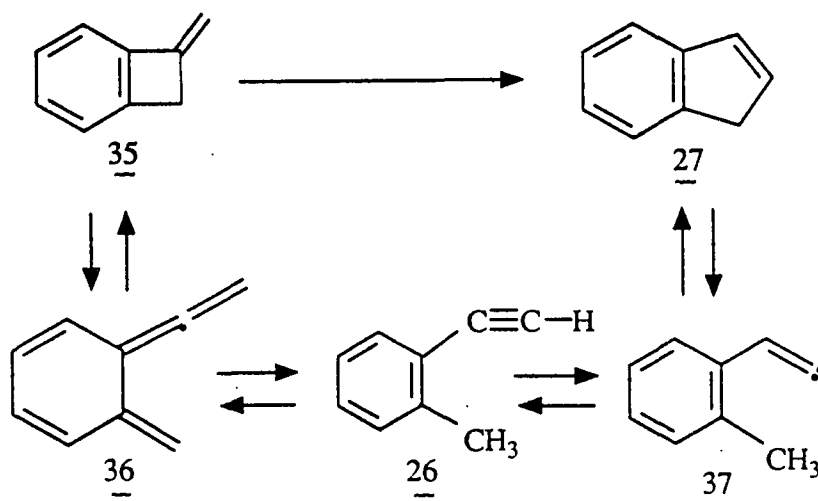
Formation of acenaphthylene 42 in 80% yield from the pyrolysis of 1-naphthylacetylene 38 yielded further evidence for vinylidene intermediates. Formation of 42 can be envisioned by either direct C-H insertion of the vinylidene or by addition to a π-bond followed by cleavage of the internal housene bond of 40 and 1,2-hydrogen shift.

Brown found that when he pyrolyzed o-tolyl-1-^{13}C-acetylene 43, he recovered indene with the carbon label in positions 1, 2, and 3. The initial acetylene isomerization
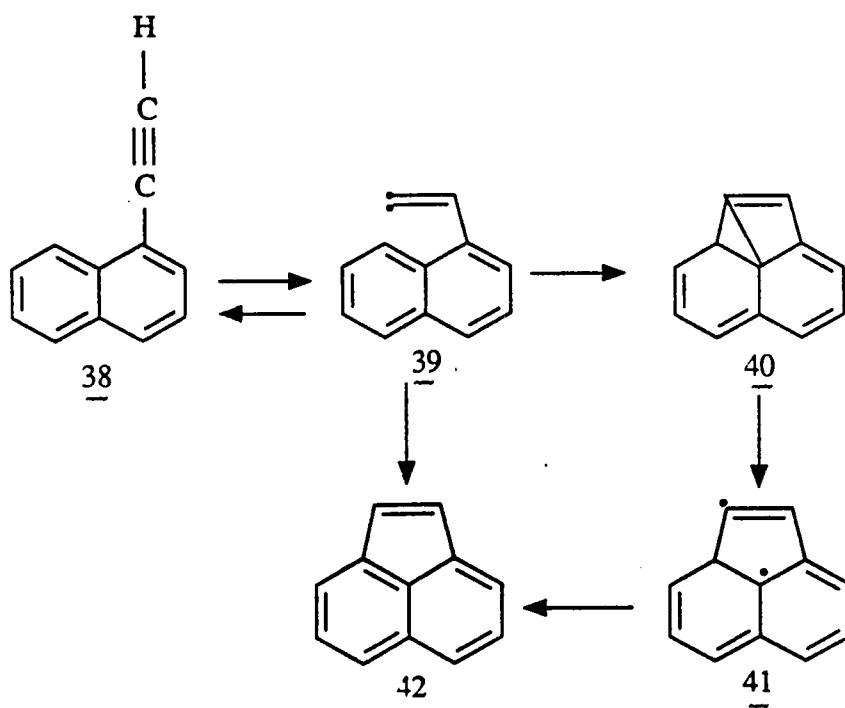
scrambles the label between the 2 and 3 position of indene.
The 1 and 3 positions are known to scramble by two
sequential 1,5-hydrogen migrations.
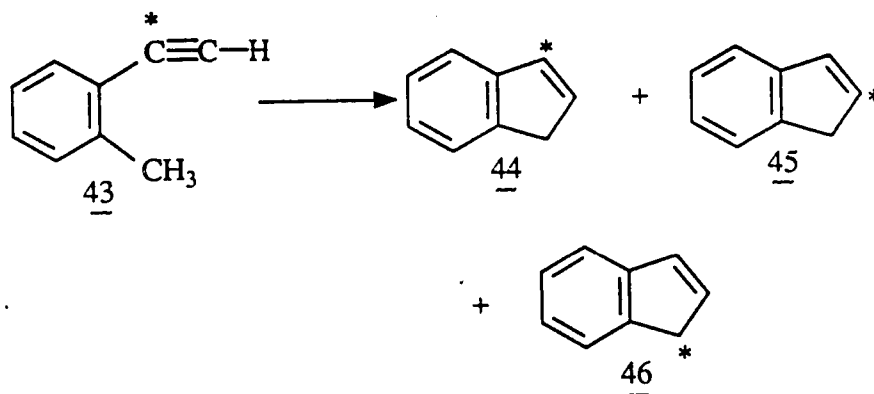
In 1942, Alder et al. (21) first reported an adduct
formed by the pyrolysis of indene and maleic anhydride.

He proposed several structures and mechanisms for these
adducts. Nineteen years later, he independently generated
isoindene 50 from 49 and trapped it with dienophiles to give
2,3-benzobicyclo[2.2.1]heptane adducts.
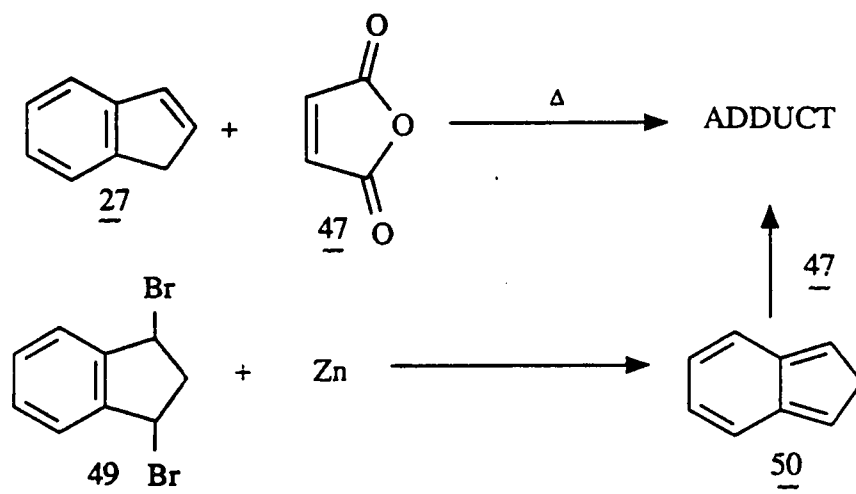
Berson and Aspelin (22) determined that the mechanism of
the adduct formed in the pyrolysis of indene and maleic
anhydride formation did not result from reaction of indene
with the dienophile followed by rearrangement. In their
deuterium labeled indene experiment, it was shown that the
indene underwent isomerization to isoindene and this
reactive diene was trapped with maleic anhydride.
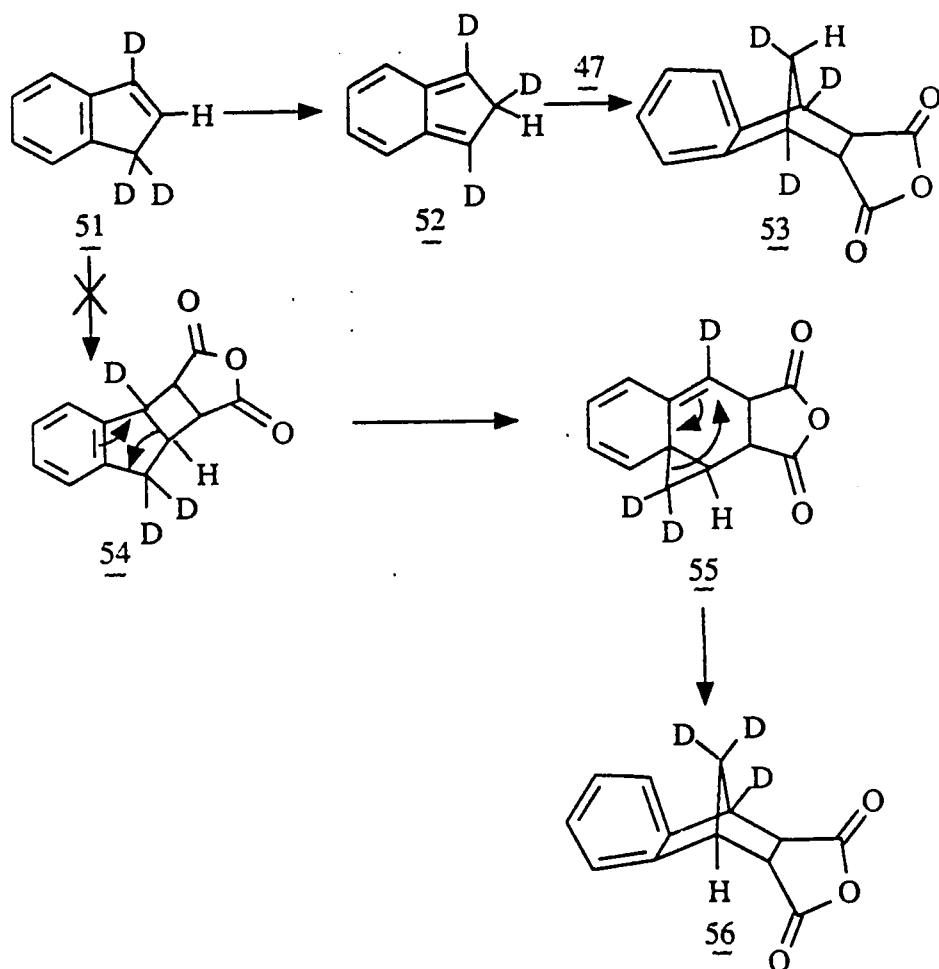
Roth (23) demonstrated the 1,5 hydrogen migration of indene in a deuterium labeling experiment. He used ^{1}H NMR integration to watch the non-aromatic protons equilibrate.
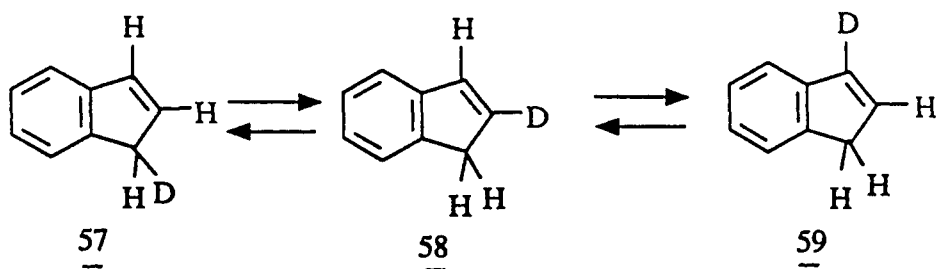
In 1966, Isaacs (24) studied the kinetics of the
indene-maleic anhydride adduct formation. He found the
disappearance of indene to be dependent on the concentration
of maleic anhydride in the solution. He further stated that
while this supports the isoindene intermediacy, it is not
demanding of it.

Koelsch and Johnson (25) and Miller and Boyer (26)
separately studied the rearrangement of di- and tri-phenyl
indenes. In every case studied, the compounds equilibrate
to mixtures of di- or triphenyl indenes independent of the
regiochemistry of the starting material.
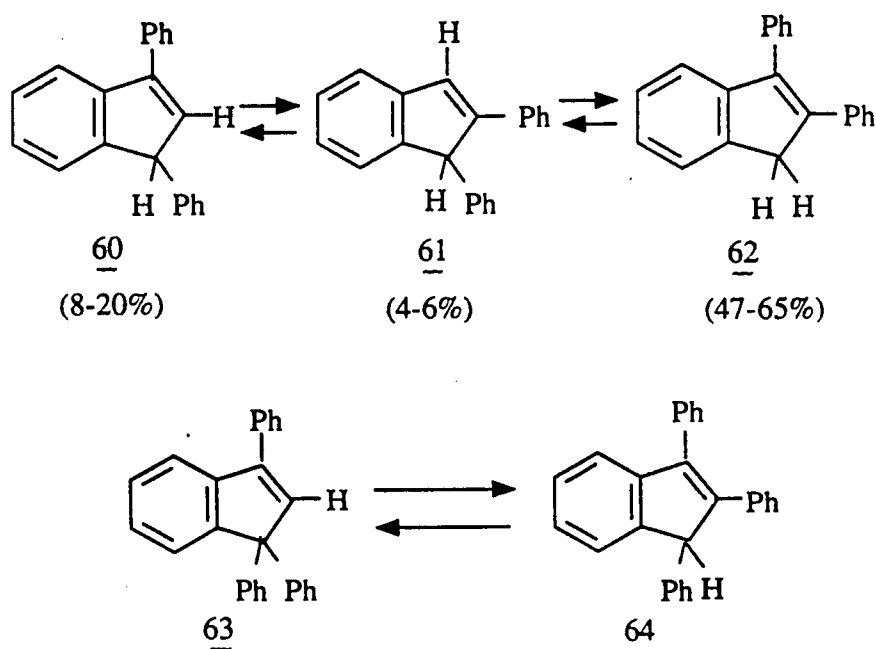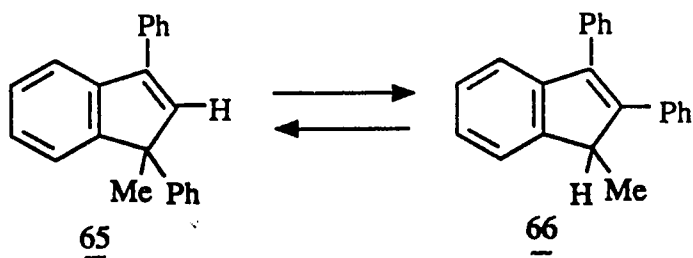
Rakita and Davison (27) synthesized and studied the variable temperature ^{1}H NMR of group IV trimethylindenyl compounds of silicon, germanium, and tin. Over the temperature range which he explored, Rakita found totally fluxional behavior only for the tin derivative. Cotton and Marks (28) later performed similar experiments with bis(indenyl)mercury which were inconclusive.
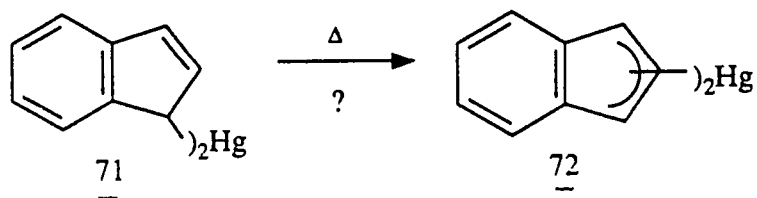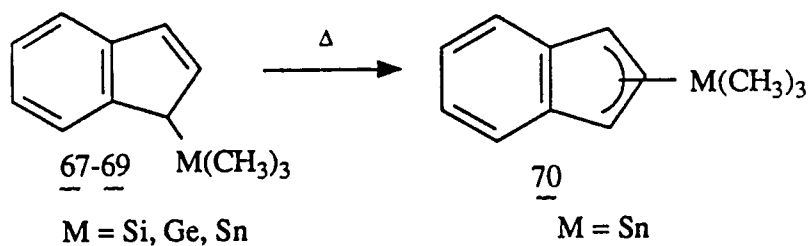
Thermal Rearrangements of Strained Organosilanes

and Their Hydrocarbon Counterparts

The rearrangement of an olefin to a carbene is a very rare reaction, in agreement with a usually large endothermic gap. Numerous calculations have been carried out to determine the activation energy for the rearrangement of ethylene 73 to methylcarbene 74 via a 1,2-hydrogen shift.

$$CH_2\!\!=\!\!CH_2 \longrightarrow CH_3\!\!-\!\!\overset{\bullet\bullet}{C}H$$

$$\underset{\underline{73}}{} \qquad\qquad \underset{\underline{74}}{}$$

As shown in Table 1, the relative energies and activation energies vary widely from one calculation to another. The first calculation shows a 51.6 kcal/mol activation energy (29), the middle calculations rise to reach a maximum value of 99.1 kcal/mol (30), and the most recent calculations estimate activation energies between 74.2 and 82.1 kcal/mol (31,32). Although the actual values vary widely, it is the consensus of these calculations that a 1,2-hydrogen migration of ethylene 73 to form methylcarbene 74 is a process of respectable activation energy, based largely if not totally on the relative energy gap. The first two calculations probably should not be given serious consideration since the minimum activation energy should be 60-65 kcal/mol, the value of a carbon-carbon π-bond (33).

Table 2. Summary of calculations on singlet C_2H_4 isomers

| Basis Set or Level | Relative Energies (kcal/mol) | | | |
	$CH_2=CH_2$	CH_3-CH	TS	Ref.
MINDO/2	0.0	51.6	51.6	(29)
MINDO/3	0.0	52.0	52.7	(34)
MNDO	0.0	73.3	95.2	(34)
ab initio double zeta	0.0	72.3	93.2	(35)
double zeta	0.0	72.1	99.1	(30)
4-31G//4-31G	0.0	74.0	93.9	(32)
6-31G*//6-31G*	0.0	68.0	82.1	(31)
6-31G*//4-31G	0.0	68.0	79.4	(32)
MP2/6-31G**//4-31G	0.0	81.5	79.7	(32)
MP3/6-31G**//4-31G	0.0	77.3	79.4	(32)
MP4SDQ/6-31G**//4-31G*	0.0	78.1	80.7	(31)
MP4SDTQ/6-31G**//4-31G*	0.0	75.3	74.2	(31)

Several entries in the table show methylcarbene to be higher in energy than the transition state and deserve further comment. Nobes et al. (32) show the transition state to be 1.8 kcal/mol lower than methylcarbene in their MP2/6-31G**//4-31G calculations. They attribute this to overestimation of the electron correlation correction in this calculation and point out that their best calculation,

MP3/6-31G**//4-31G, does yield a 1.9 kcal/mol barrier for the methylcarbene to ethylene.

Raghavachari et al. (31) also had a transition state 1.1 kcal/mol below the relative energy of methylcarbene in their MP4SDTQ/6-31G**//4-31G calculations. The authors conclude from their calculations that singlet methylcarbene does not exist as an intermediate on this surface. Instead, it is a transition state for the degenerate 1,2-hydrogen shift in ethylene.

An example of an olefin to carbene isomerization via a 1,2-carbon migration has recently been demonstrated by Eaton and Hoffmann (36) in the photolysis of cubylphenyldiazomethane 75. The initially formed cubylphenylcarbene 76 undergoes a 1,2-alkyl shift to produce the very strained, twisted olefin 9-phenyl-1(9)-homocubene 77 which was trapped with ethanol to form 79, the Markovnikov addition product. Also formed was an isomer of 79, which was originally assigned structure 81, the anti-Markovnikov addition product of ethanol and 77. However, homonuclear coupled ^{13}C NMR methodology showed that the ipso-carbon of the phenyl ring was not coupled to an aliphatic carbon bearing a hydrogen (37). The structure of the isomer of 79 was corrected to 80, which is the expected adduct of ethanol and 1-phenyl-9-homocubylidene 78. Further trapping experiments with

2,5-diphenylisobenzofuran, cis-2-butene, and trans-2-butene
yielded cyclopropanohomocubane products 82, 83, and 84.
These results not only enhance the belief that 9-phenylhomo-
cubylidene 78 is the trapped species, but the retention of
stereochemistry of adducts 83 and 84 show that carbene 78
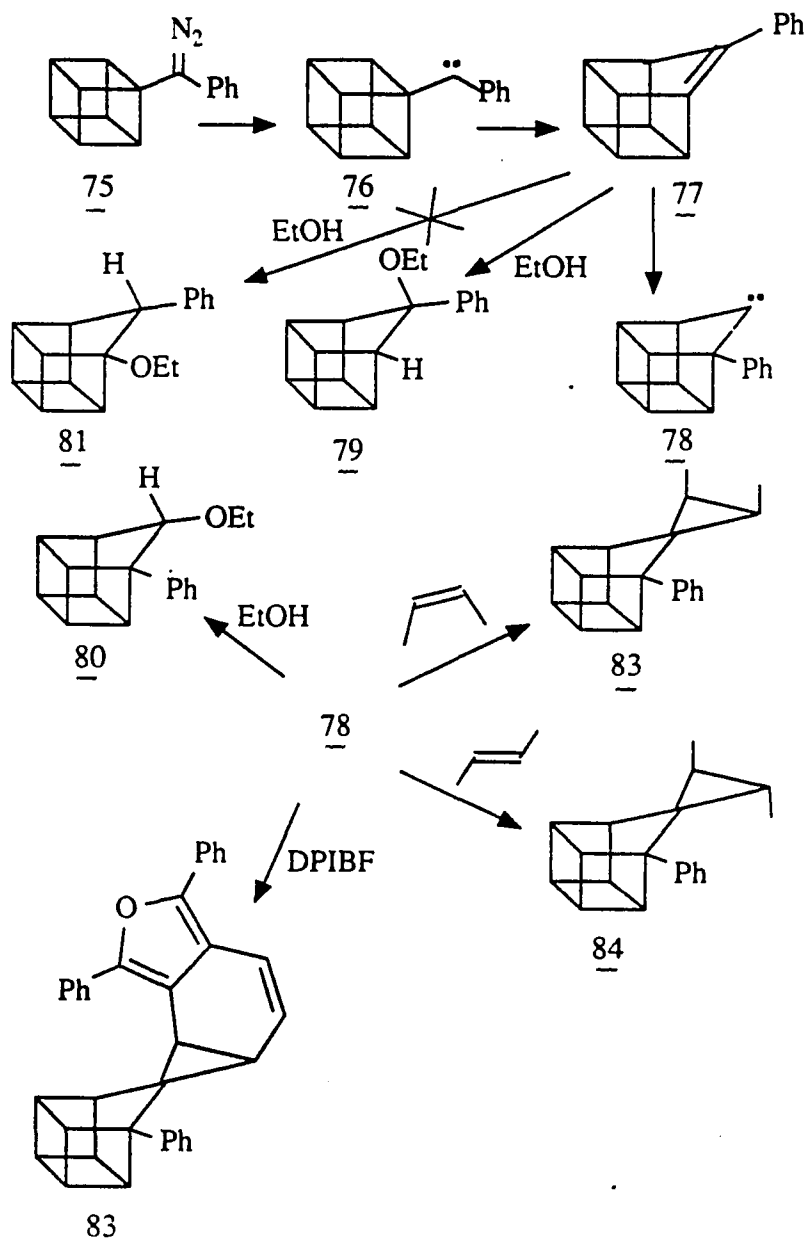
reacts in stereospecific, singlet carbene addition reactions (38).

The heat of formation of olefin 77 has been calculated to be 201 kcal/mol, very near the calculated value of carbene 78 (199 kcal/mol) (39). This thermochemical neutrality explains why the olefin to carbene rearrangement can occur so readily in this system.

Barton and Yeh (40) propose a 1,2-carbon migration across a bridgehead double bond in the thermal generation and rearrangement of 1-norbornene. The high strain energy of the anti-Bredt olefin 1-norbornene reduces the activation energy in this olefin to carbene rearrangement.
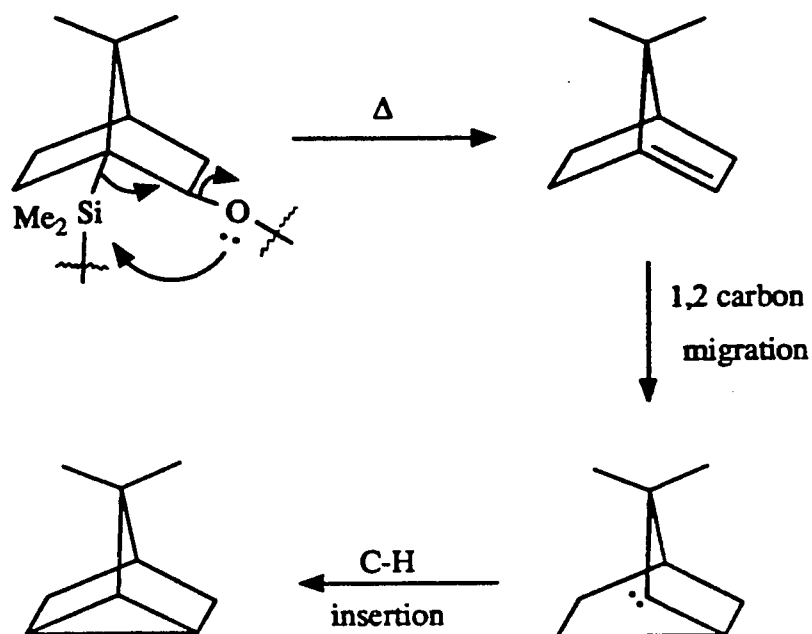
Trimethylsilyl groups migrate much more readily than
does hydrogen (41). The trimethylsilyl group of $5-^{2}H-5-$
trimethylsilylcyclopentadiene undergoes a 1,5-sigmatropic
migration approximately one million times faster than does
the deuterium (42).

$$\underset{\underset{86}{Si(CH_3)_3}}{} \quad \xrightarrow[\;]{1} \quad \underset{\underset{85}{D \;\; Si(CH_3)_3}}{} \quad \xrightarrow[\;]{1 \times 10^6} \quad \underset{\underset{87}{D}}{Si(CH_3)_3}$$
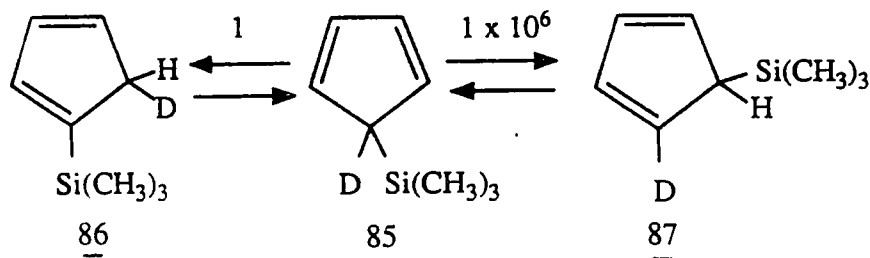
There also exists evidence that suggests 1,2-silyl
migrations are more facile than similar 1,2-hydrogen
migrations in a possible allene to vinylcarbene
rearrangement. Barton and Hussman found that
trimethylsilyl-3-(trimethylsilyl)allenyl ketone 88 readily
cyclizes to 2,4-bis(trimethylsilyl)furan 90 at 150°C (43).
Allenylmethyl ketone 91 requires 530°C in a He flow
pyrolysis (44). Both cyclizations were proposed to proceed
by initial 1,2-shifts as shown in Scheme I. If this is the
initial step in the mechanism, it seems logical that this
1,2-shift is the rate determining step since the cyclization
does not appear to be very energetically demanding.
Therefore, by virtue of the much higher temperature required
for the cyclization of allenyl methyl ketone 91, the

1,2-hydrogen migration would have a higher activation energy than the 1,2-silyl migration.
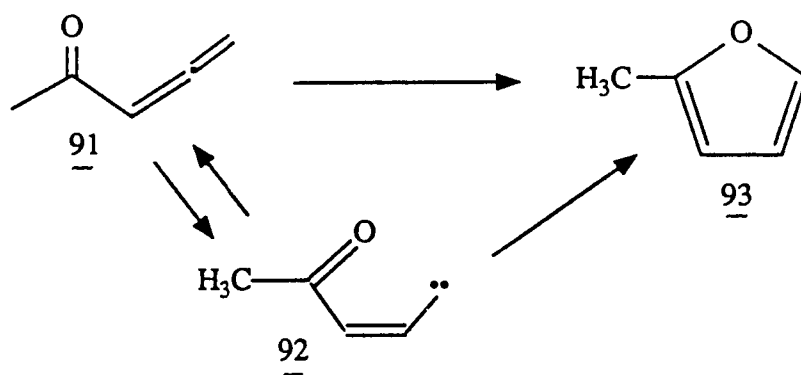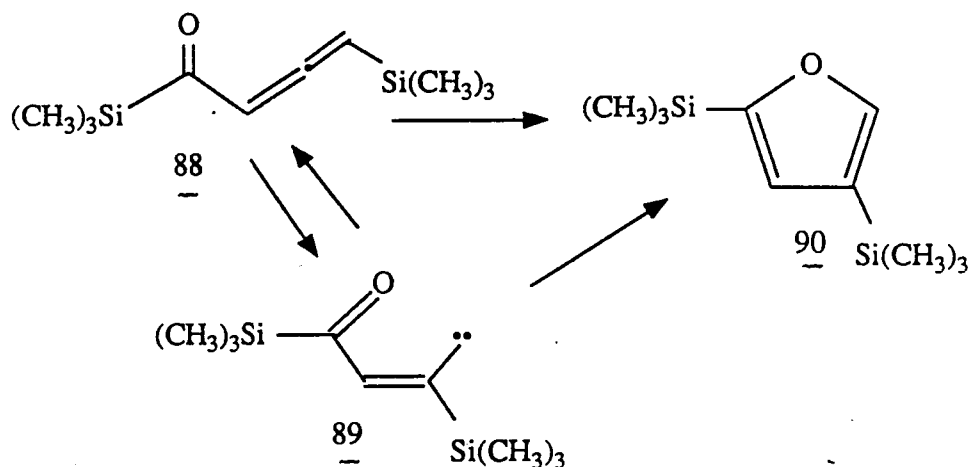
Ashe (45) has also reported that 1,2-silyl shifts are more facile than 1,2-hydrogen shifts. In the pyrolysis of endo- or exo-5-trimethylsilylbicyclo[2.1.0]pentanes 94 and 95, Ashe observed only 3-trimethylsilylcyclopentene 97, the product of a 1,2-silyl shift after initial C1-C4 homolytic bond cleavage. None of the corresponding 1,2-hydrogen shift product 98 was formed. Within his limits of detection, he estimates that the 1,2-silyl shift is at

least 10^3 times faster than the corresponding 1,2-hydrogen shift.
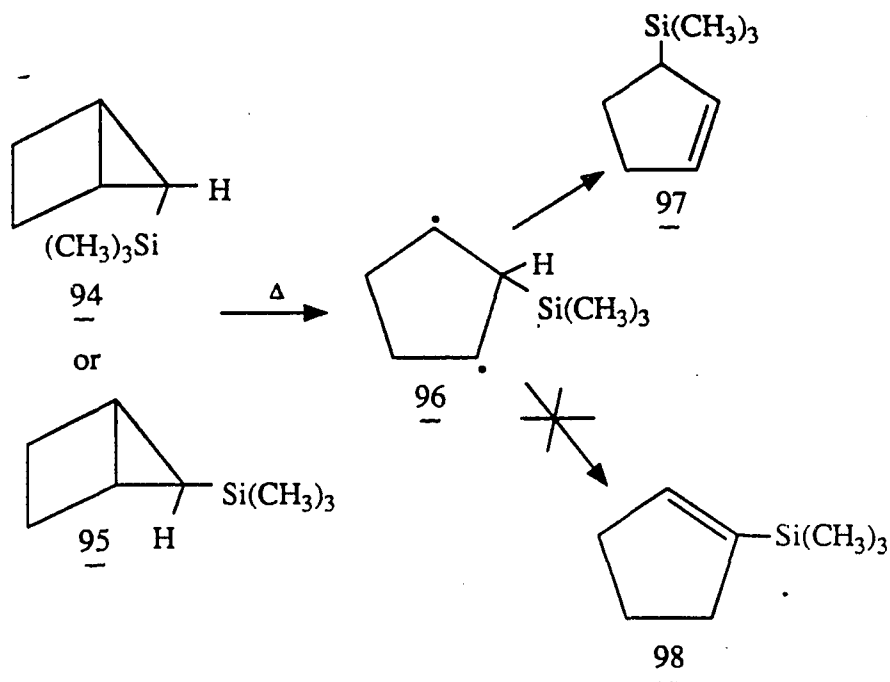
The thermal ring expansion of 2-methylene-1,1-dimethyl-silacyclobutane 99 to 1,1-dimethylsilacyclopent-2-ene 101 and 1,1-dimethylsilacyclopent-3-ene 102 represents the first claim of an olefin to carbene isomerization via a 1,2-silyl shift (3). Conlin proposes two mechanisms for this vinylsilane to β-silyl carbene rearrangement.
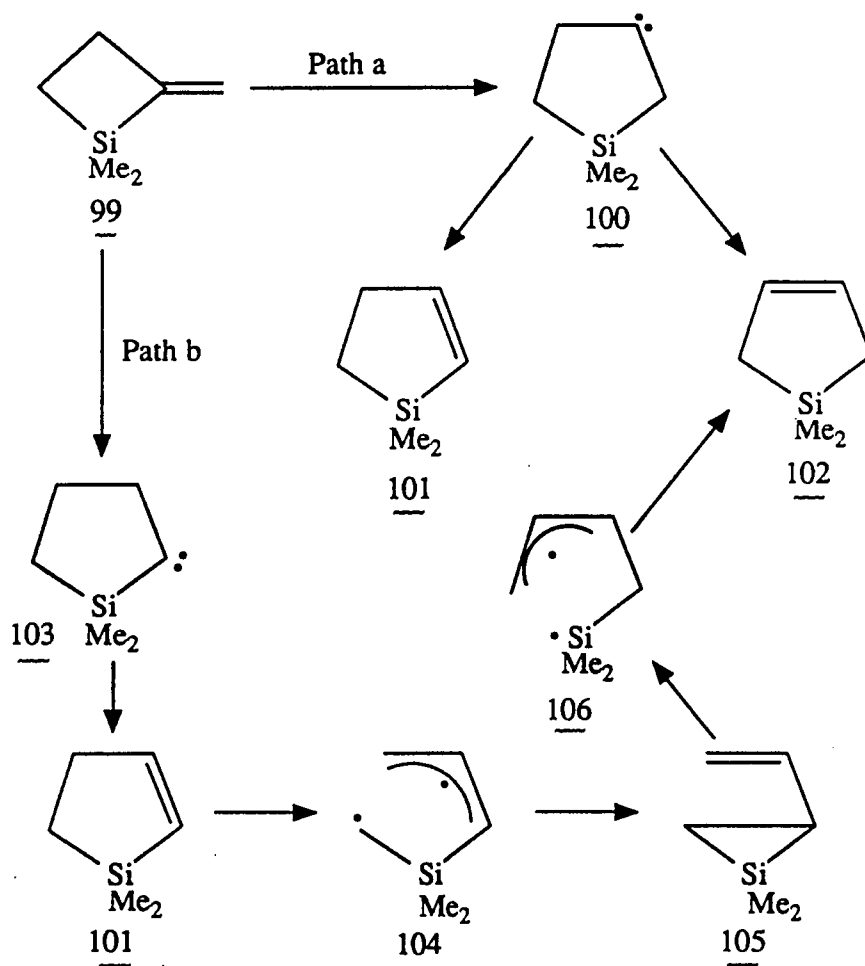
Path a involves a 1,2-silyl migration to form β-silyl carbene 100. Insertion of this carbene into a C-H bond at carbons 2 or 4 form silacyclopentenes 101 and 102, respectively. Path b involves initial 1,2-carbon migration to form β-silyl carbene 103. Insertion of this carbene into the only available α-C-H bond at C3 yields isomer 101 which can subsequently rearrange to isomer 102. Conlin then rules out mechanism b footnoting that "No isomerization occurs of [101 and 102] under these conditions."

One bothersome aspect of this ring expansion involves the energetics of the decomposition. Silacyclobutanes are known to decompose by initial heterolytic cleavage of one of the carbon-carbon bonds (46). Silacyclobutane 107 decomposes to silene 109a and ethylene 73 with an activation energy of 63.8 kcal/mol and a log A of 15.8. 1-methyl-1-vinylsilacyclobutane reportedly yields identical kinetic parameters (47). Given that radicals are usually stabilized 12-16 kcal/mol by the presence of an α-olefin (48), this should bring the activation energy for heterolytic decomposition of the C2-C3 bond of 1,1-dimethyl-2-methylene-silacyclobutane down to 48-52 kcal/mol. The minimum activation energy for the ring expansion is the strength of the π-bond which is approximately 60-65 kcal/mol (33). Given the activation energies of these two processes, it is interesting that no products are observed from such a heterolytic cleavage. One explanation is that this cleavage could be occurring, but the diradical 110 simply recloses to starting material.

$$E_{act} = 63.8 \text{ kcal/mol}$$

a. R = Me

b. R = CH =CH$_2$

Eact = 50 kcal/mol ?
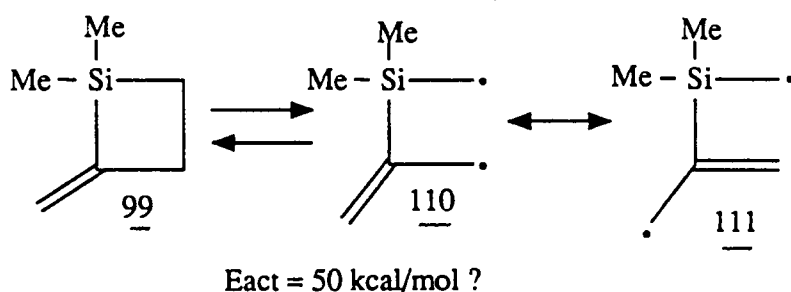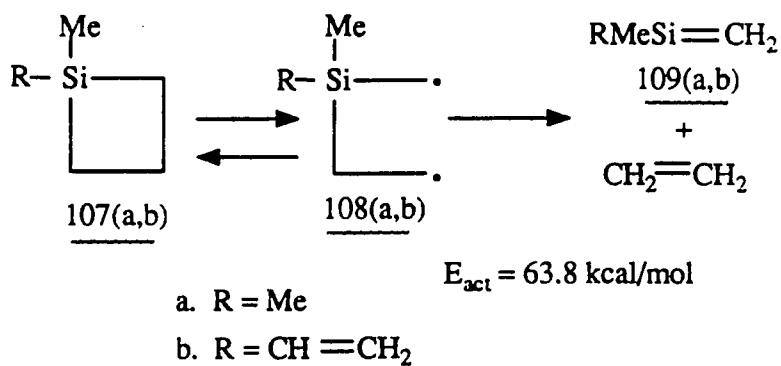
The thermal chemistry of the analogous methylenecyclo-
butane revealed another bothersome feature. Doering and
Gilbert (49) examined the interconversion of 2,2-dideutero-
and α,α-dideuteromethylenecyclobutane 112 and 113.
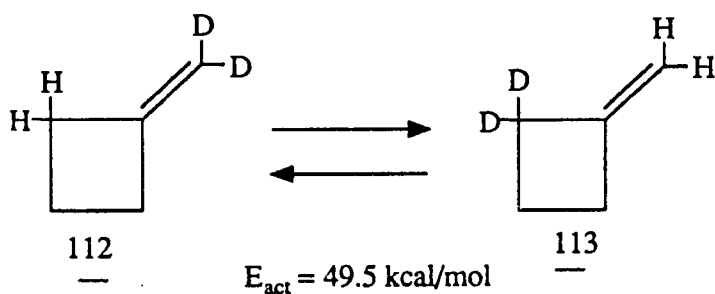
$$E_{act} = 49.5 \text{ kcal/mol}$$

Their activation energy of 49.5 kcal/mol did not agree
well with Chelsick's activation energy for the thermal

cleavage of methylenecyclobutane to ethylene and allene 114 and 115 (log A = 15.68, E_{act} = 63.3 kcal/mol) (50a,b). Doering made the suggestion that cleavage to 114 and 115 required additional twisting of the intermediate allyl radical with concomitant loss of resonance energy.
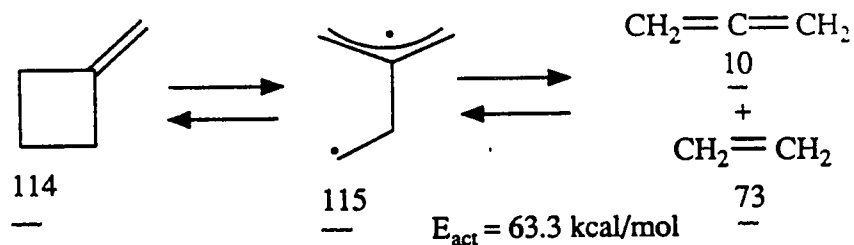
1,2-Silyl migrations to form carbenes was also proposed in the thermolysis of silyl substituted allenes (51), ketenes (52), and thioketenes (53). The rearrangements of these cummulenes is unique because the π-system to which the silicon is migrating is coplanar with the cummulene-silicon bond in the ground state molecule.
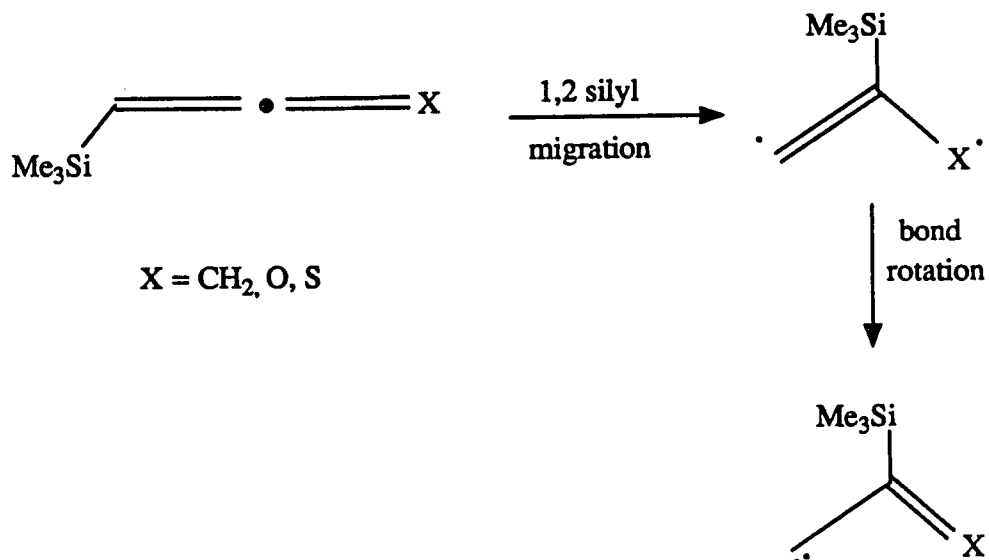
Sakurai et al. explored the thermal chemistry of
trimethylsilylcyclopropane 116 and 1,2-cyclopropyl-
1,1,2,2-tetramethyldisilane 119 (54). Compound 116
isomerized mainly (95%) to allyltrimethylsilane 117 and 119
isomerized by sequential ring openings to 1,2-diallyl-
1,1,2,2-tetramethyldisilane 121. These products lead one to
assume that the C2-C3 bond is breaking in either a homolytic
or a concerted fashion.

Anchimeric Assistance
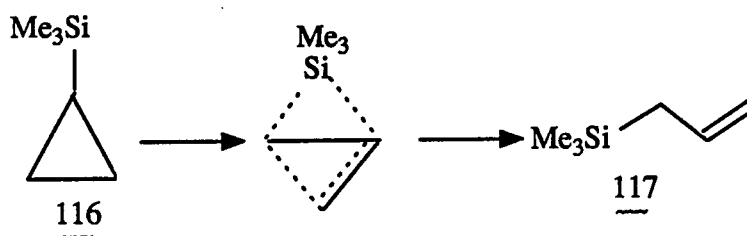
Homolytic Cleavage
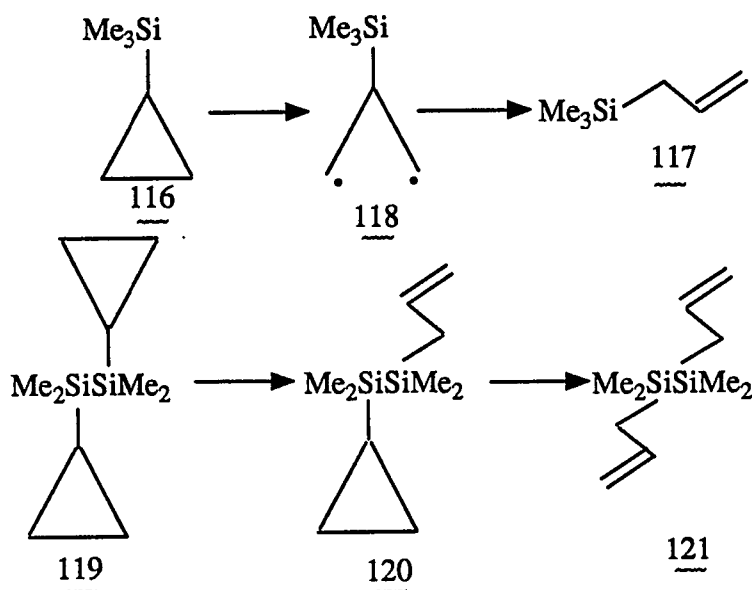
Some years later, theoretical (55) and spectroscopic (56) research concluded that the C2-C3 bond of silylsubstituted cyclopropanes is significantly shorter than the C1-C2 bonds.

SiH$_3$

1.520 Å

1.508 Å
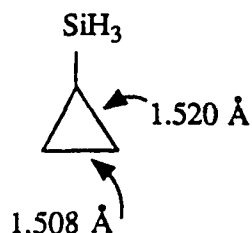
Conlin and Kwak (57) probed deeper into the thermal decomposition of trimethylsilylcyclopropane 116 in which the major pathway to decomposition is breaking the shorter and most likely stronger bond. Upon pyrolysis of 116, Conlin found a 92% yield of 117 and an 8% yield of (E)- and (Z)-1-propenyltrimethylsilane, 123a and 123b. He proposed the following mechanistic scheme adding that these results do not rule out the possibility of the silicon atom anchimerically assisting the C2-C3 bond cleavage.

$E_{act} = 56.5$ kcal/mol

$\log A = 14.3$

$Si(CH_3)_3$

118

?

$(CH_3)_3Si$ ⌁⌁ 92%

117

$Si(CH_3)_3$

116

$Si(CH_3)_3$

122

$(CH_3)_3Si$

123a

$(CH_3)_3Si$

123b

8%

$k_{overall}$:

$E_{act} = 59.1$ kcal/mol

$\log a = 14.8$

$E_{act} = 61.9$ kcal/mol

$\log a = 14.9$
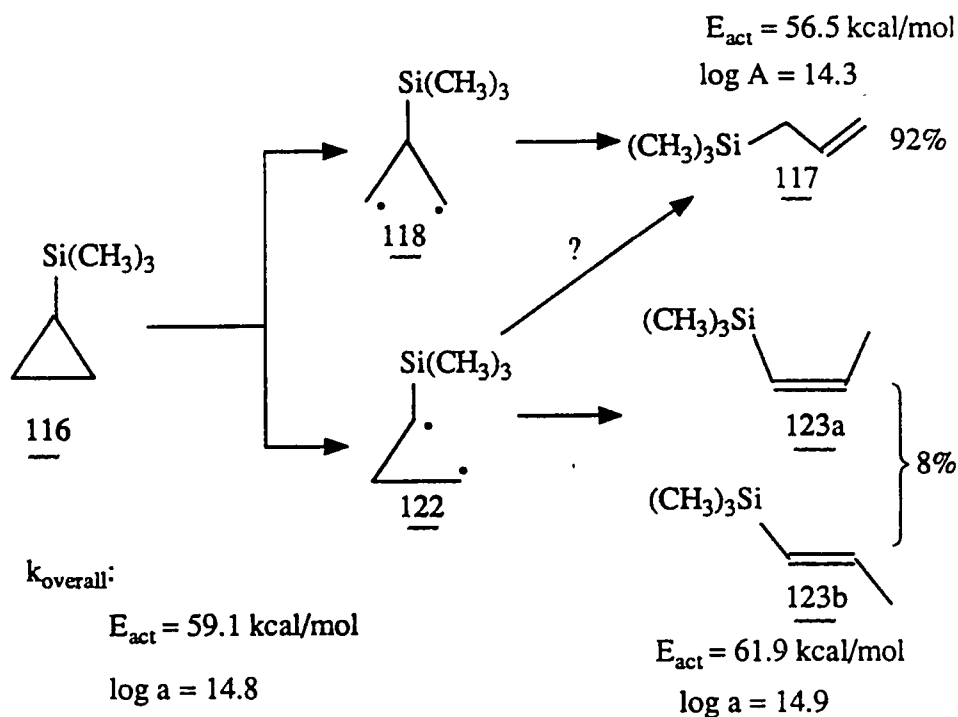
Although a direct comparison with the hydrocarbon analog t-butylcyclopropane is not available, it is of interest that trimethylsilylcyclopropane isomerizes approximately 30 times faster than cyclopropane 124 (58,59) and approximately 10 times faster than methylcyclopropane 126 and ethylcyclopropane 131 (60,61). From the products of the pyrolyses of 126 and 131, it is clear that the major decomposition pathway involves initial cleavage of the C1-C2 cyclopropane bond.

$E_{act} = 65.2$ kcal/mol

log A = 15.1

124 → 125

Me

$E_{act} = 65.0$ kcal/mol

log A = 15.4

126

127   50%

128   30%

129   15%

130   5%

Et

$E_{act} = 61.6$ kcal/mol

log A = 14.4

131

132   35%

133   20%

134   16%

135   5%
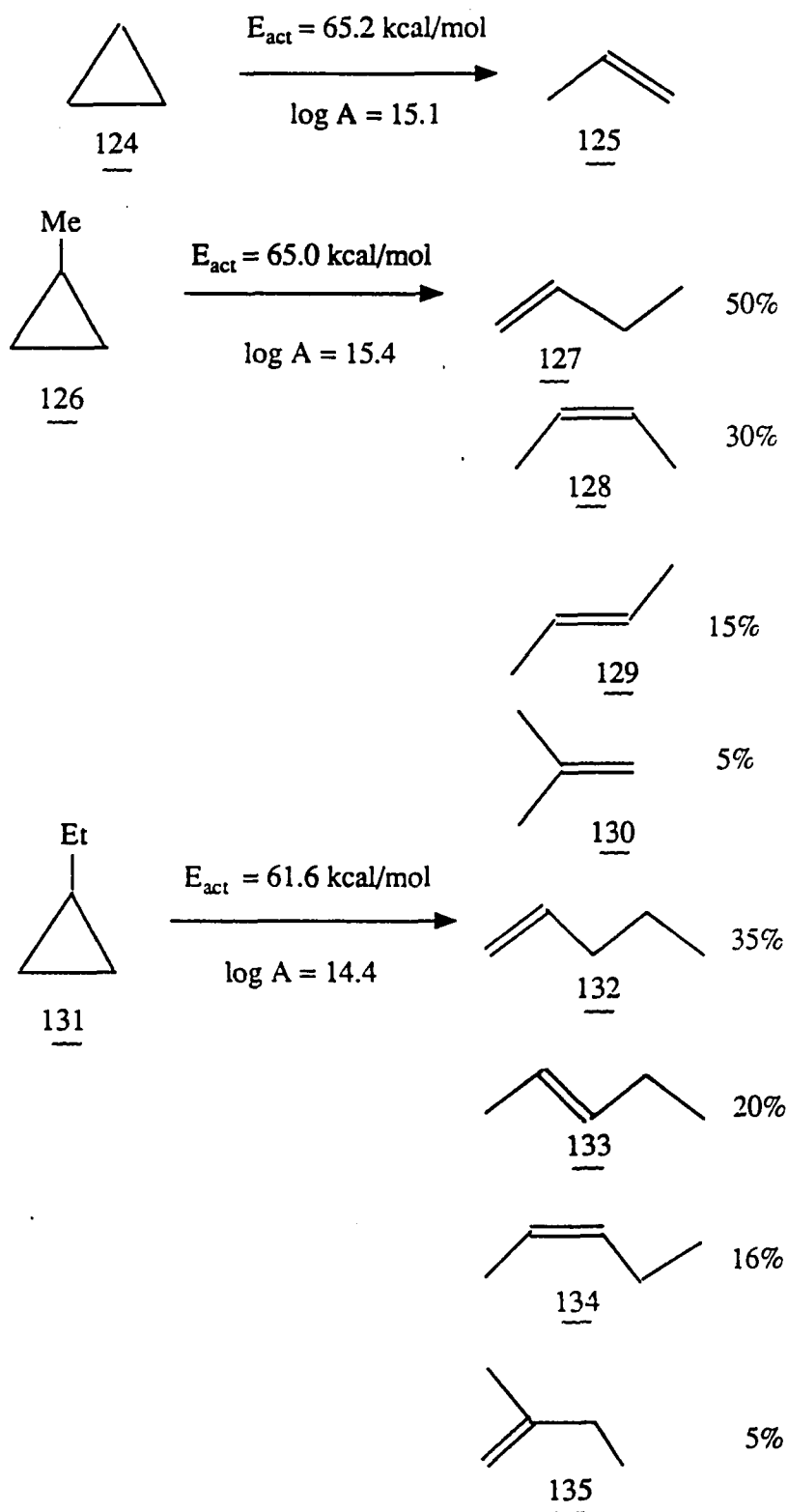
RESULTS AND DISCUSSION

Rearrangements of Silylacetylenes and Acetylenes

Honjou et al. have calculated the potential energy surface for the isomerization of methylacetylene to allene (1). They find propenylidene, cyclopropene, and vinylcarbene to be stable intermediates on this surface. Other calculations and experimental work have supported these results (2,5,6,9,11).
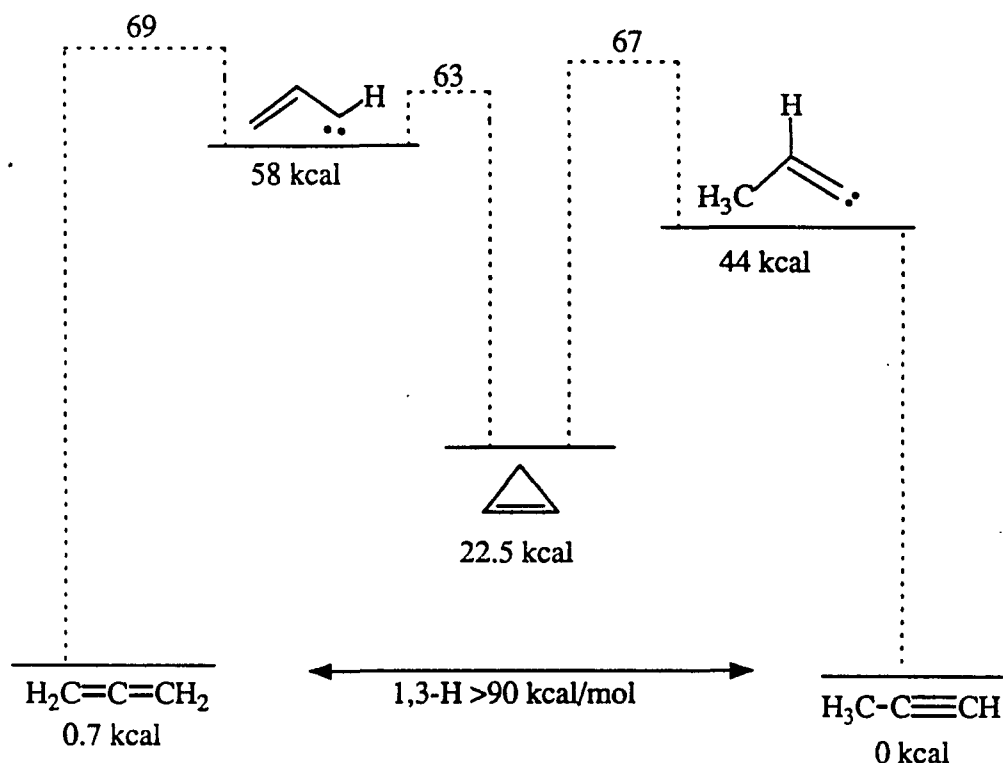
Extending this idea to organosilanes, we were curious as to the behavior of the analogous hydridosilylacetylenes. Will they undergo rearrangement to silacyclopropenes and

silaallenes? Or will, perhaps, a more energetically
favorable pathway be found?

$$\underset{\underset{136}{}}{R_2Si-C\equiv C-H}^{H} \rightleftharpoons \underset{137}{\overset{R_2}{\underset{}{Si}}\triangle} \rightleftharpoons \underset{138}{R_2Si=\cdot=CH_2}$$
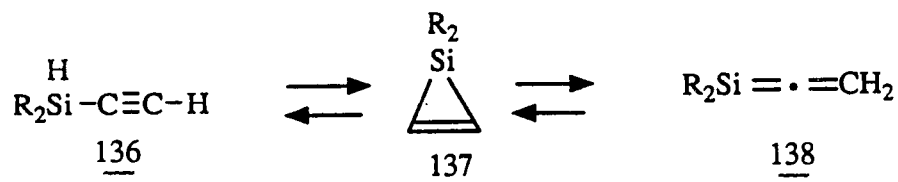
Rogers et al. have studied the shock tube reaction of
silylacetylene and extracted kinetic data for their four
assumed decomposition pathways (16). However, their only
apparent rationale for the formation of silacyclopropanyli-
dene 21 is the presence of ethylene from the decomposition
of 16. They determined the rate constant for this pathway
by subtracting the rate constant of the other processes from

$$H_3Si-C\equiv C-H \xrightarrow{k_1} \overset{\cdot\cdot}{H}Si-C\equiv C-H + H_2$$

$$\underset{18}{\overset{H_2}{\underset{}{Si}}\triangle} \xrightarrow{k_2} :SiH_2 + H-C\equiv C-H \quad 19$$

$$\xrightarrow{k_3} H-\overset{\cdot\cdot}{Si} \underset{20 \ HC=CH_2}{}$$

$$\underset{21}{\overset{\cdot\cdot}{\underset{}{Si}}\triangle} \xrightarrow{k_4} Si + CH_2=CH_2$$
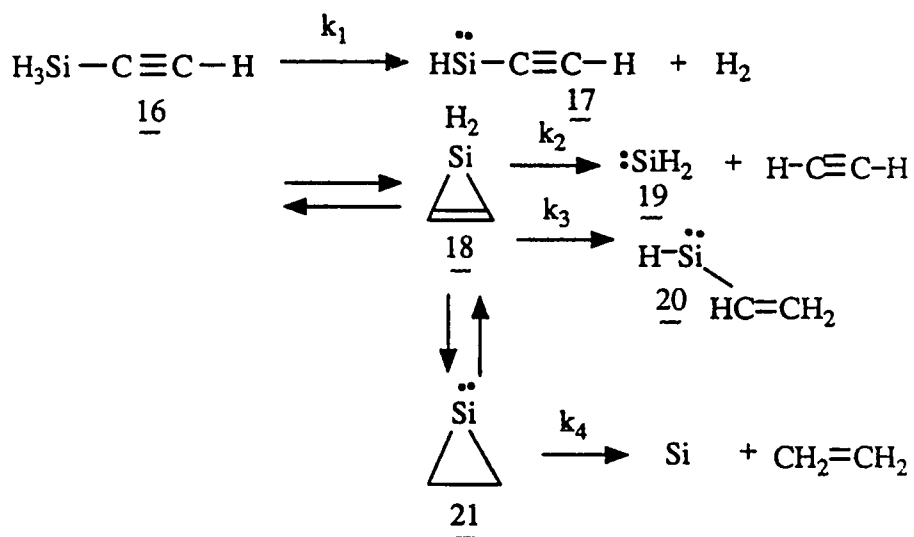
the total decomposition rate constant of silylacetylene.
One of the other processes, a 1,1-elimination of hydrogen

from silane 16 to form silylene 17, is very well documented and only complicates the picture of the total decomposition.

We chose to study the termal decomposition of dimethylsilylacetylene. Of Rogers' four decomposition pathways, only the pathway for silacyclopropene formation and subsequent silylene extrusion would be possible since there is only one silyl hydrogen in the starting material. The other three pathways require a.minimum of two silyl hydrogens. We hypothesized that if a rearrangement were to occur to a silacyclopropene or a silaallene, these species would be of much higher energy species than a silaacetylene based on strain energy calculations of Boatz et al. (4) and the reactivity of silicon-carbon pπ -pπ bonded species (62). The reverse reaction would, therefore, occur much more readily than the forward and we would have a very slim chance of observing a silacyclopropene or a silaallene. However, since both silacyclopropene and silaalene are symmetric with respect to the position of the olefinic hydrogens, a monolabelled acetylene such as 139 should scramble the non-methyl hydrogens.

Synthesis of 138 was begun by reacting calcium carbide with deuterium oxide to generate dideuteroacetylene. Dideuteroacetylene was bubbled into a tetrahydrofuran

$$D-C\equiv C-Si\overset{Me_2}{\underset{139}{H}} \rightleftarrows \overset{Me_2}{\underset{\underset{D\ 140\ H}{}}{Si}} \rightleftarrows H-C\equiv C-Si\overset{Me_2}{\underset{141}{D}}$$

$$Me_2Si\!=\!C\!=\!CH_2$$
$$142$$
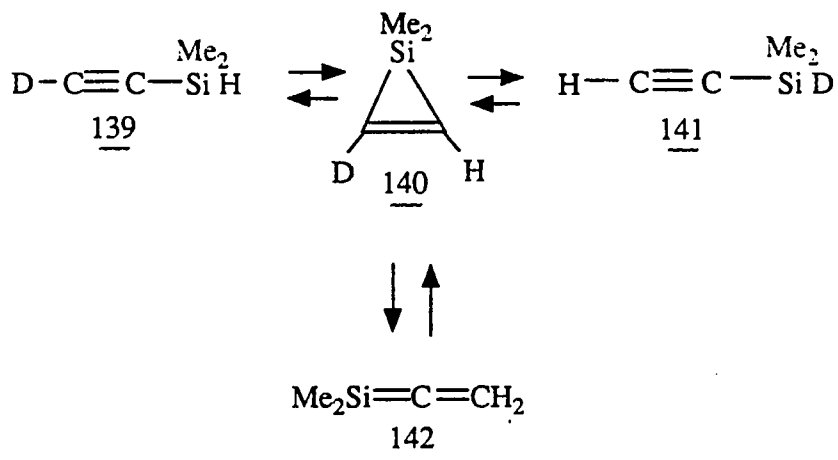
solution of methylmagnesium chloride to form 1-deutero-2-chloromagnesioacetylene and quenched with dimethylchlorosilane to yield 1-deutero-2-dimethylsilylacetylene in 21% yield. FVP of 1-deutero-2-dimethylsilylacetylene at increasing temperatures yielded increasing yields of (deuterodimethylsilyl)acetylene 141.

Temperature (°C)	H Me_2Si-C≡C-D	D Me_2Si-C≡C-H
510	97%	3%
700	89%	11%
750	81%	19%
800	57%	43%

Stirred-flow reactor pyrolysis of dimethylsilyl-acetylene 143 showed formation of acetylene and bis(dimethylsilyl)acetylene 144. These products presumably

arise from extrusion of dimethylsilylene from starting
material or from a dimethylsilacyclopropene intermediate.

$$\underset{143}{Me_2\overset{\overset{\displaystyle H}{|}}{Si}-C\equiv C-H} \xrightarrow[650°C]{SFR} H-C\equiv C-H + \underset{144}{Me_2\overset{\overset{\displaystyle H}{|}}{Si}-C\equiv C-\overset{\overset{\displaystyle H}{|}}{Si}Me_2}$$
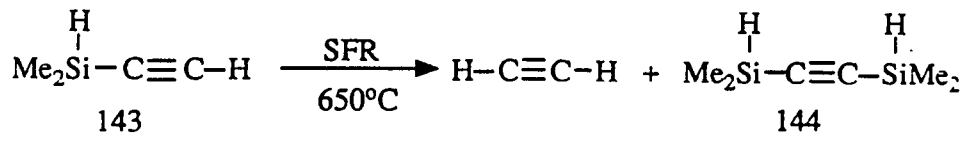
Also pyrolyzed was dimethylsilylphenylacetylene 145.
Under FVP conditions, 145 yielded mainly phenylacetylene 146
with small amounts of phenyldimethylsilylacetylene 147,
indene 27, and styrene 148. The presence of 146 and 147
supports the intermediacy of silacyclopropene 149.
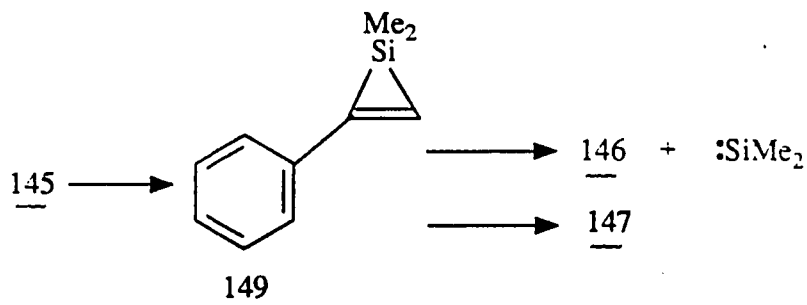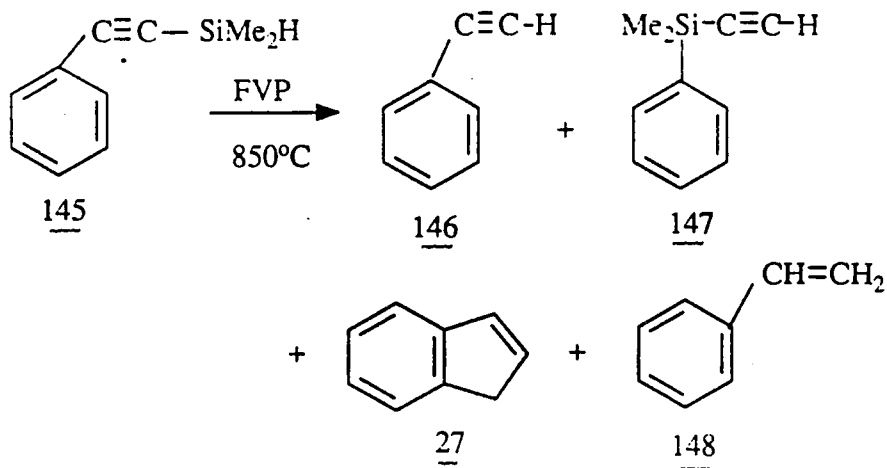
Since pyrolysis of the analogous carbon system, 1-phenylpropyne 150, had not been reported previously, we studied its thermal chemistry under flash vacuum conditions. Between the temperatures of 650°C and 1000°C, 150 yielded phenylallene 151, indene 27, and phenylacetylene 146. The indene to phenylallene ratio increased with temperature.

$$Ph\text{—}C\equiv C\text{—}CH_3 \xrightarrow{FVP} Ph\text{—}C\text{=}C\text{=}CH_2 + 27 + Ph\text{—}C\equiv C\text{—}H$$

150		151		146
100%	700°C	0%	0%	0%
>95%	800°C	<5%	<1%	<1%
50%	900°C	28%	38%	34%
38%	925°C	15%	51%	34%
0%	1000°C	0%	50%	50%
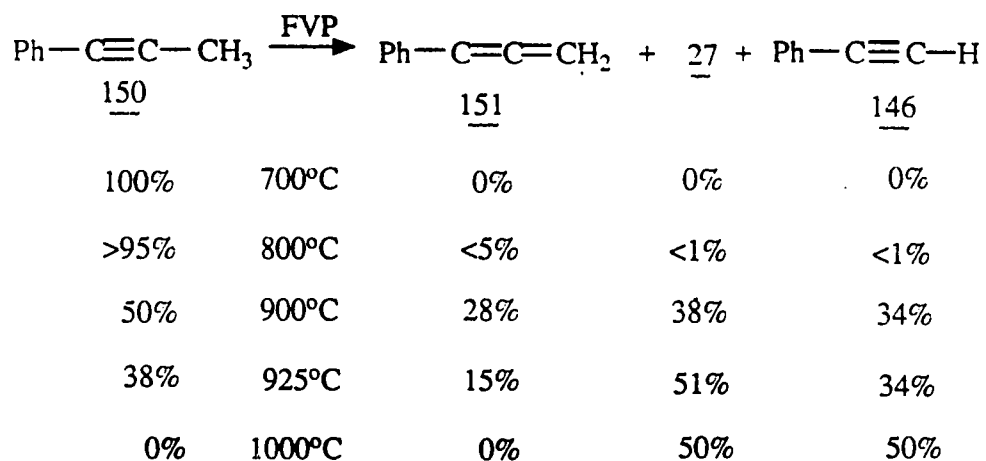
Although the reversible thermal isomerization of alkynes and allenes is very well documented (1,2,7-9, 11-15), very little is known about the formation of indene from the thermolysis of either alkynes or allenes. R. F. C. Brown and co-workers observed indene 27 and substituted indenes from the pyrolysis of monoarylhydridoarylacetylenes and diarylacetylenes (17-19). In their work, evidence was also presented for the degenerate thermal rearrangement of acetylenes by synthesizing and pyrolyzing [13]C- and ^{14}C-labelled alkynes.

$$R-C\overset{*}{\equiv}C-H \;\rightleftharpoons\; \underset{23}{\overset{R}{\underset{H}{\diagdown}}} \overset{*}{C}=C: \qquad \underset{24}{\overset{*}{:}}C=\overset{R}{\underset{H}{C\diagdown}} \;\rightleftharpoons\; H-\overset{*}{C}\equiv C-R$$

22   25
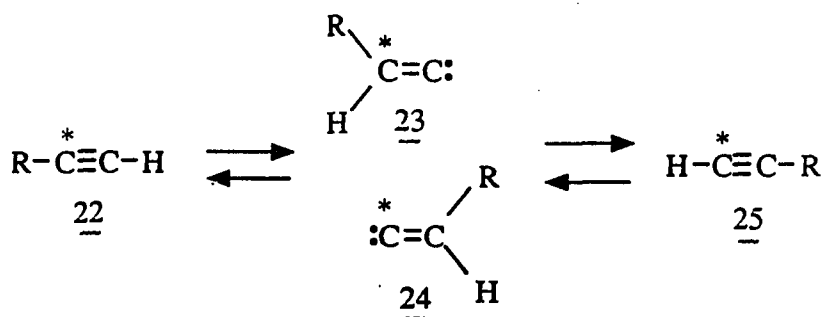
R = phenyl, adamantyl, D

* denotes ^{13}C or ^{14}C label

The indene products arose from the pyrolysis of o-tolylacetylenes. The ortho-methyl group provided an efficient intramolecular C-H trap for the proposed vinylidene intermediate.

152   153   154
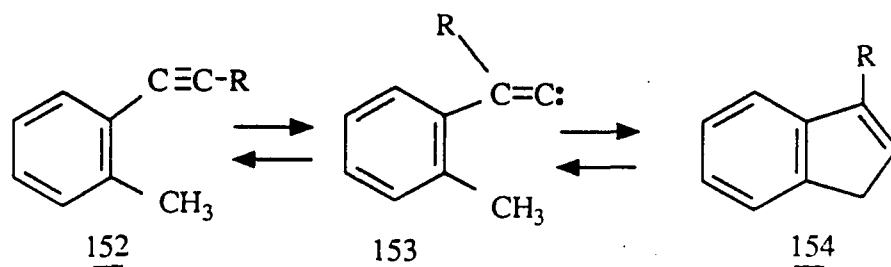
R = H, Ph

Since our starting alkyne, 150, contained no ortho-methyl trap and rearrangement to an intermediate species which did contain one was not obvious, we proposed a mechanism in which phenylallene 151 underwent a 1,2-hydrogen migration to form vinylcarbene 158. This vinylcarbene could add to a π-bond of the phenyl ring and rearrange to yield

indene $\underset{\sim\sim}{27}$. Alternatively, vinylcarbene $\underset{\sim\sim\sim}{158}$ could insert into an ortho C-H bond to form indene directly.
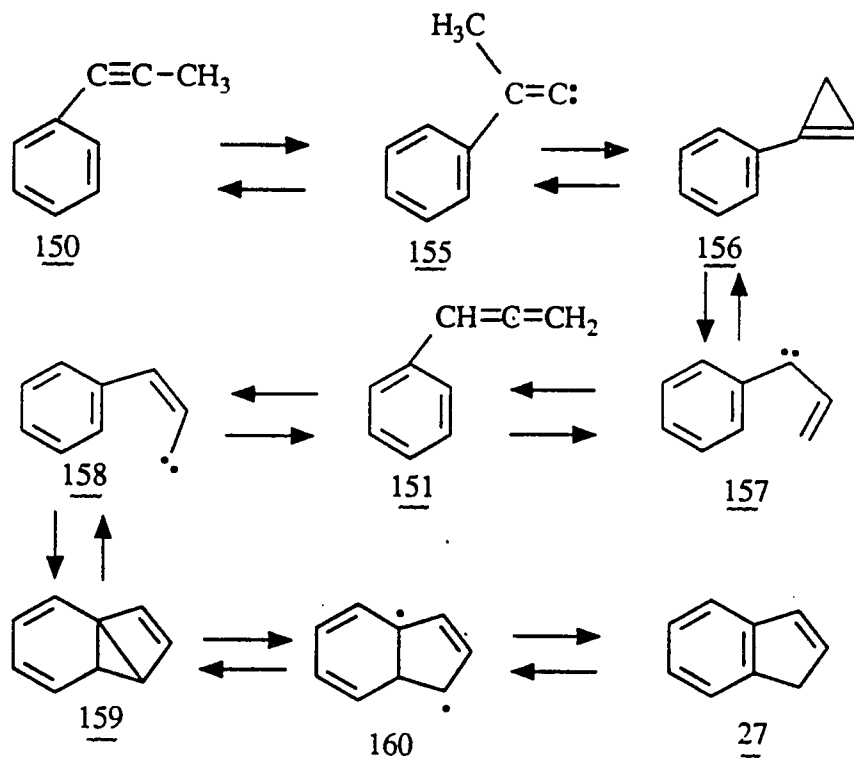
To test this mechanism, $3\text{-}^{13}\text{C-1-phenylpropyne}$ $\underset{\sim\sim\sim}{161}$ was synthesized in 55% isolated yield from the reaction of 2-lithiophenylacetylene and $^{13}\text{C-methyl}$ iodide. Pyrolysis of this compound should yield $1\text{-}^{13}\text{C-indene}$ and possibly $3\text{-}^{13}\text{C-indene}$. This latter product arises if we are at temperatures which the 1- and 3- positions interchange by two successive 1,5-hydrogen migrations (21-24). Labeled acetylene $\underset{\sim\sim\sim}{161}$ was flash vacuum pyrolyzed at 900°C and the pyrolysate was examined utilizing $^{13}\text{C-NMR}$ integration using

1,4-dioxane as an internal standard. Unexpectedly, the indene carbon label was observed at all carbons in the following amounts.
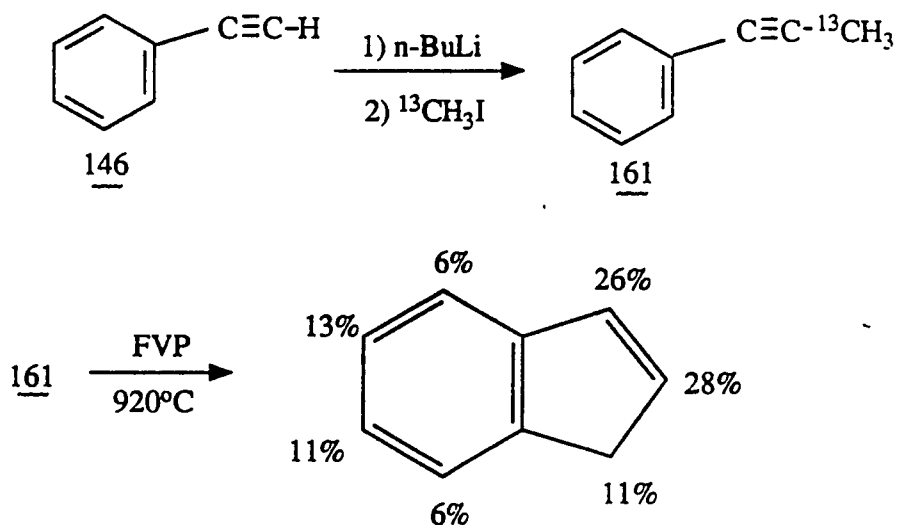
Carbons 1 and 3 of indene $\underset{\sim\sim}{27}$ are known to interchange via two 1,5-hydrogen migrations through isoindene $\underset{\sim\sim\sim}{159}$ (21-24). Intermediate $\underset{\sim\sim\sim}{159}$ has been trapped with maleic anhydride $\underset{\sim\sim\sim}{163}$ in research done by several research groups (21,22).

There is no report of scrambling the indene carbons of positions other than C1 and C3. To test if the other indene carbons do scramble, we synthesized and pyrolyzed
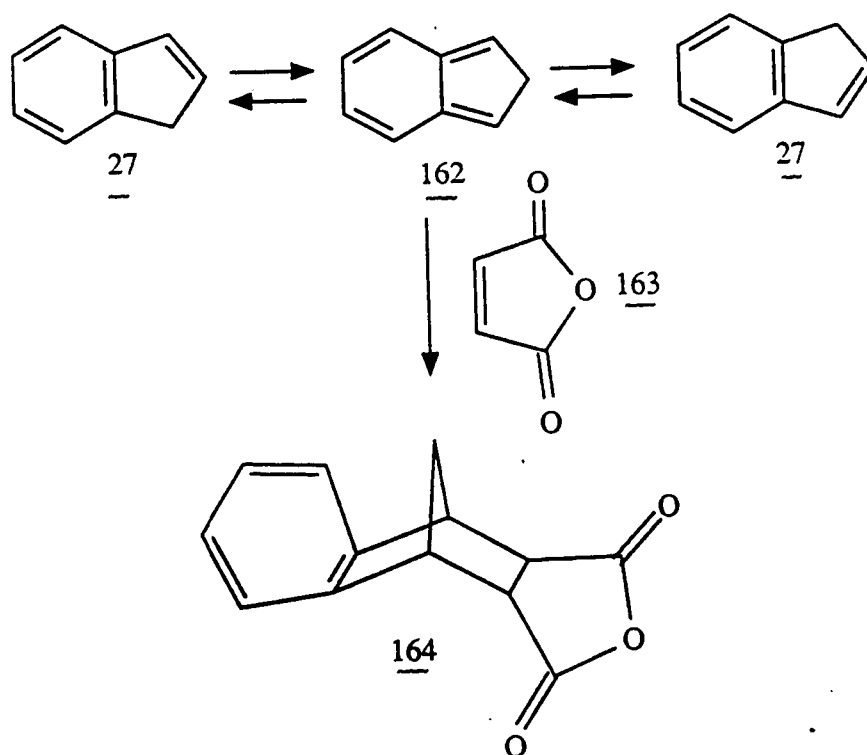
3-^{13}C-indene **168**. 2-Phenylethylmagnesium bromide was

converted into 3-phenyl-1-^{13}C-propionic acid **166** by reacting

it with ^{13}C-carbon dioxide generated from ^{13}C-barium

carbonate and excess 10% hydrochloric acid. The
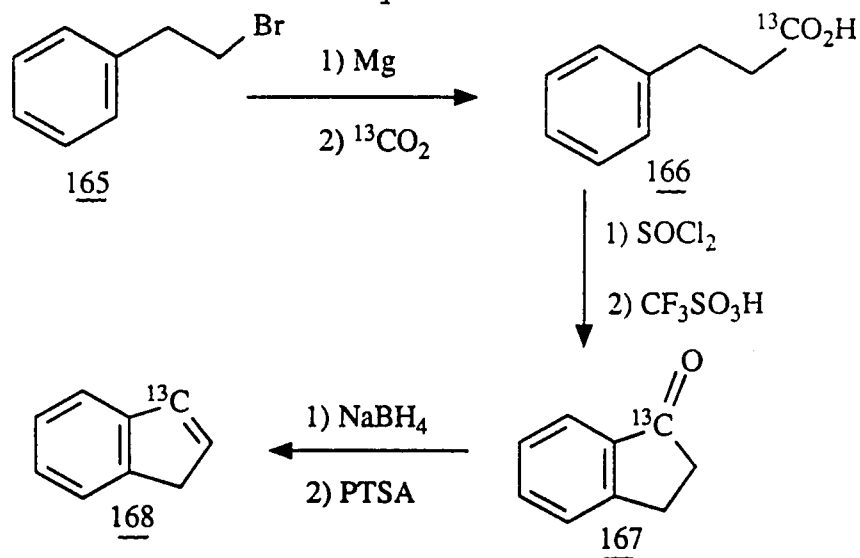
organic acid 166 was cyclized to ketone 167 by the method of Hulin and Koreeda (63) and converted to 168 by the method of Braun and Bernard (64).

At 800°C, approximately 4% of the ^{13}C label occurs at positions C4 through C7. At 900°C, 22% of the ^{13}C label was found at positions other than C1 and C3. We propose two possible mechanisms by which this rearrangement could occur. The first mechanism employs dyatropic rearrangements (65) which have been suggested in the isomerization of other polycyclic aromatic compounds (66). The second mechanism scrambles the carbon label via phenylcarbene isomerizations (67).
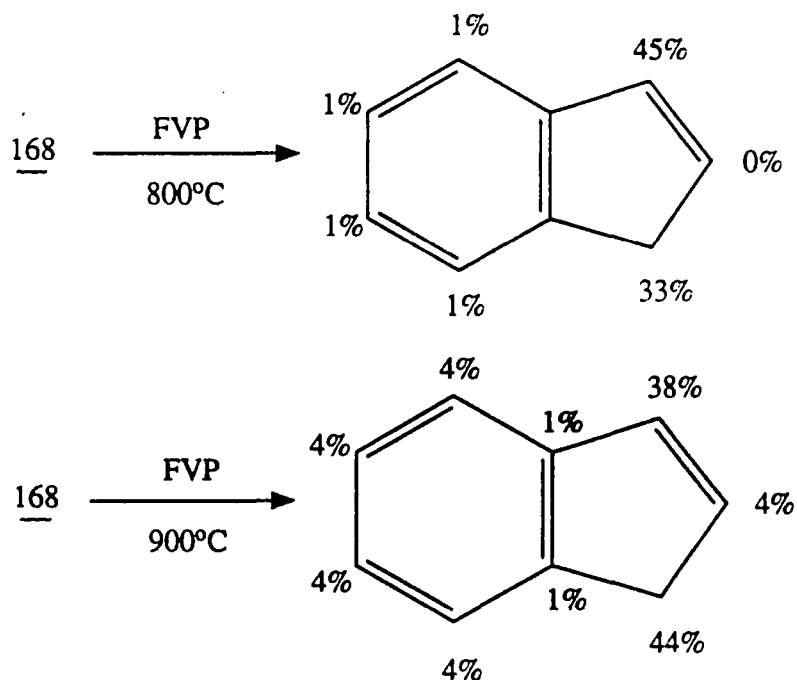
Mechanism A
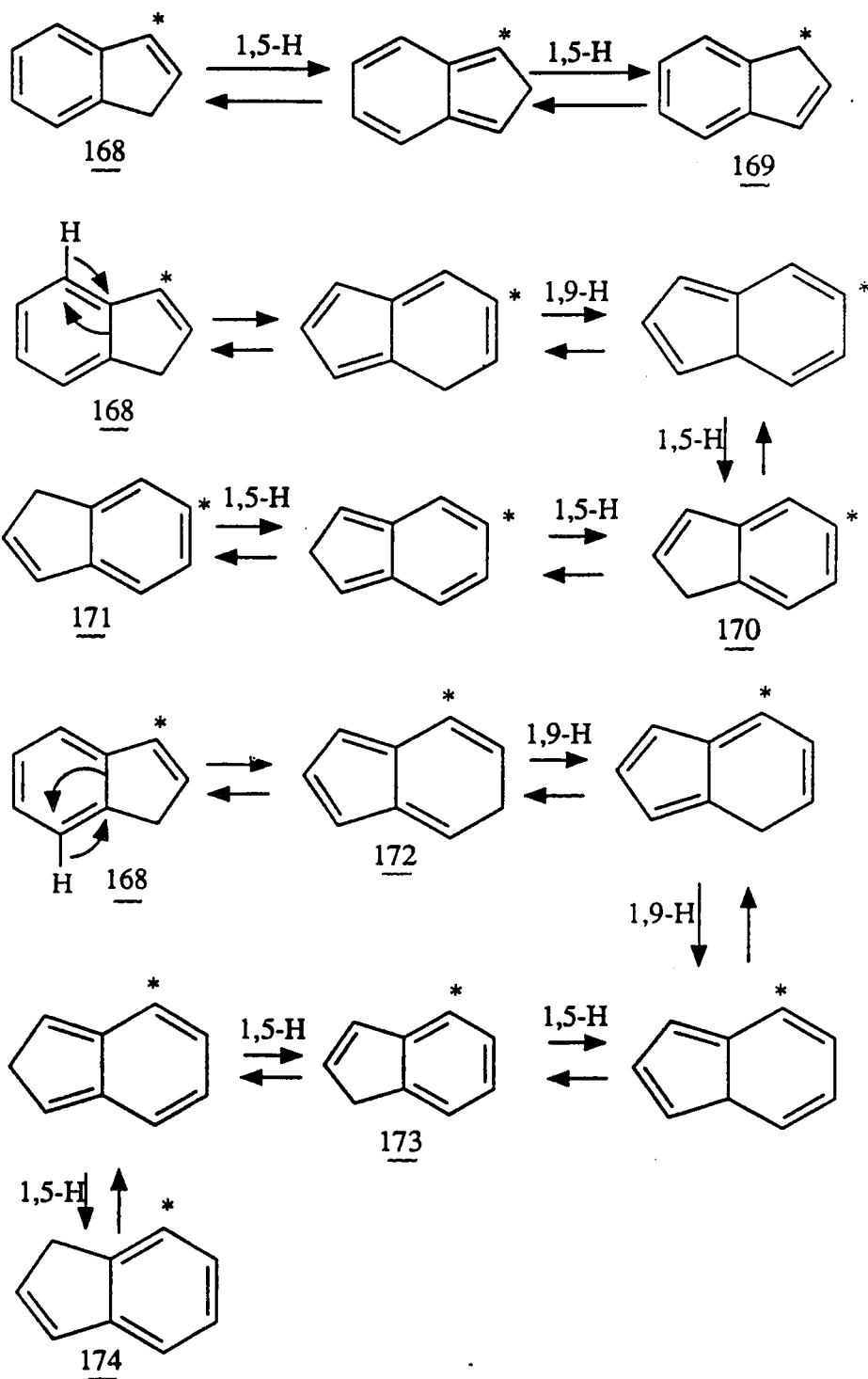
Mechanism A (continued)

$$2 \rightleftarrows 2$$

$$\uparrow\downarrow \quad \uparrow\downarrow$$

$$5 \rightleftarrows 6$$

$$\uparrow\downarrow \quad \uparrow\downarrow$$

$$3 \rightleftarrows 1$$

$$\uparrow\downarrow \quad \uparrow\downarrow$$

$$4 \rightleftarrows 7$$

$$\uparrow\downarrow \quad \uparrow\downarrow$$

$$9 \rightleftarrows 8$$
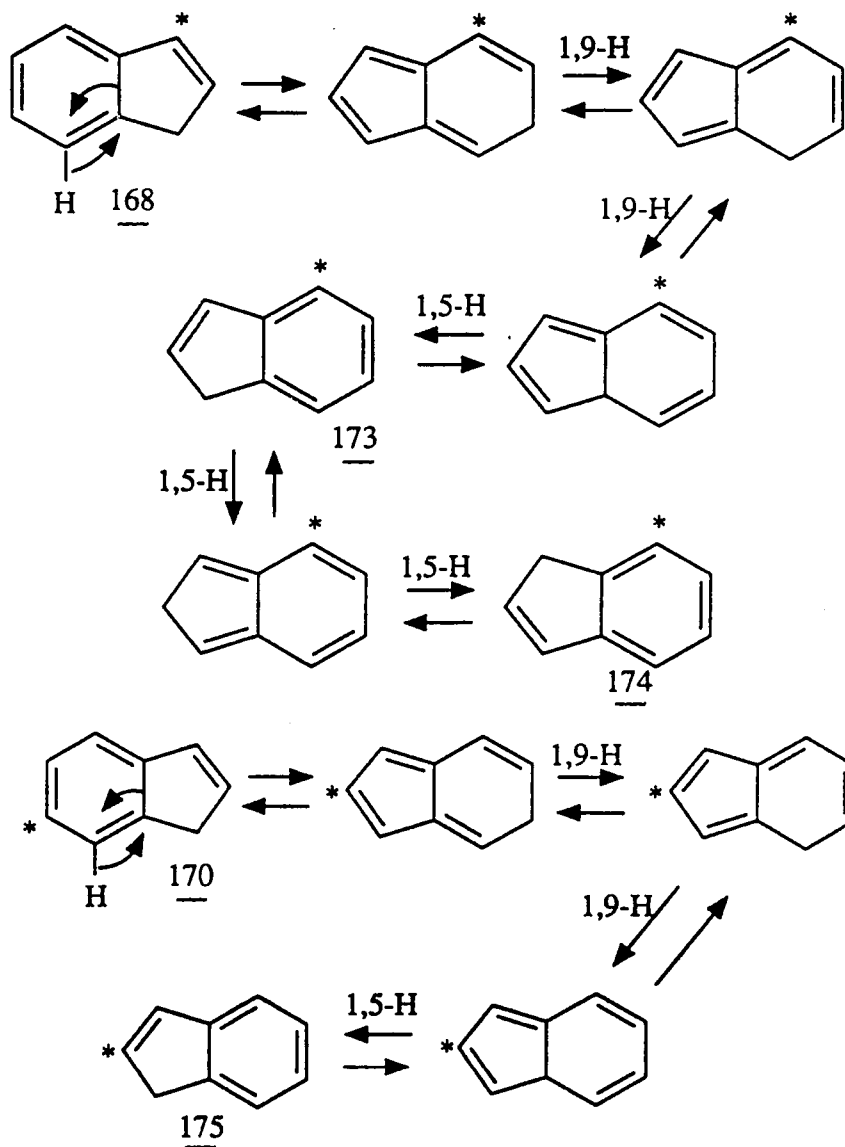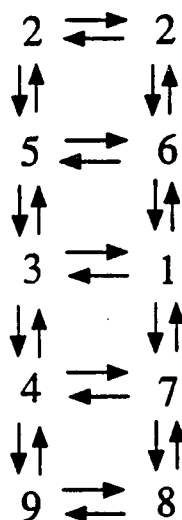
All of the labelled indenes can be accounted for by dyatropic rearrangement mentioned in Mechanism A.

The scheme to the left shows the position of the carbon label in this interconversion.

The horizontal arrows represent 1,5-hydrogen migrations while the vertical arrows represent 1,2-dyatropic shifts followed by hydrogen migrations.

Mechanism B

168

phenylcarbene rearrangement

1,5-H   1,5-H

170   171
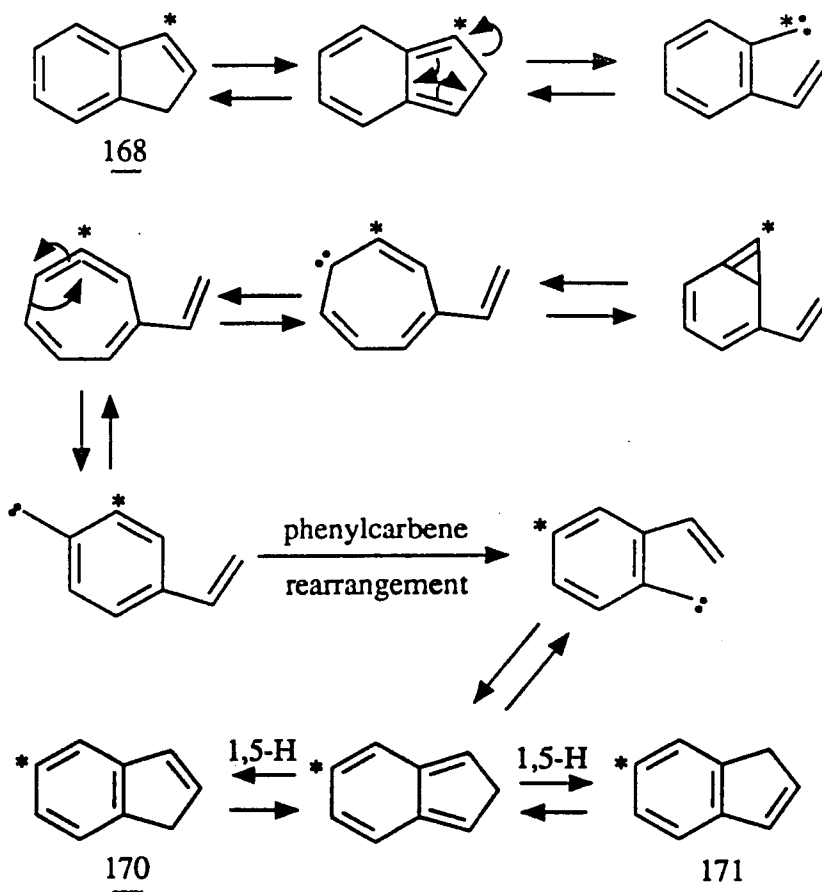
Mechanism B (continued)
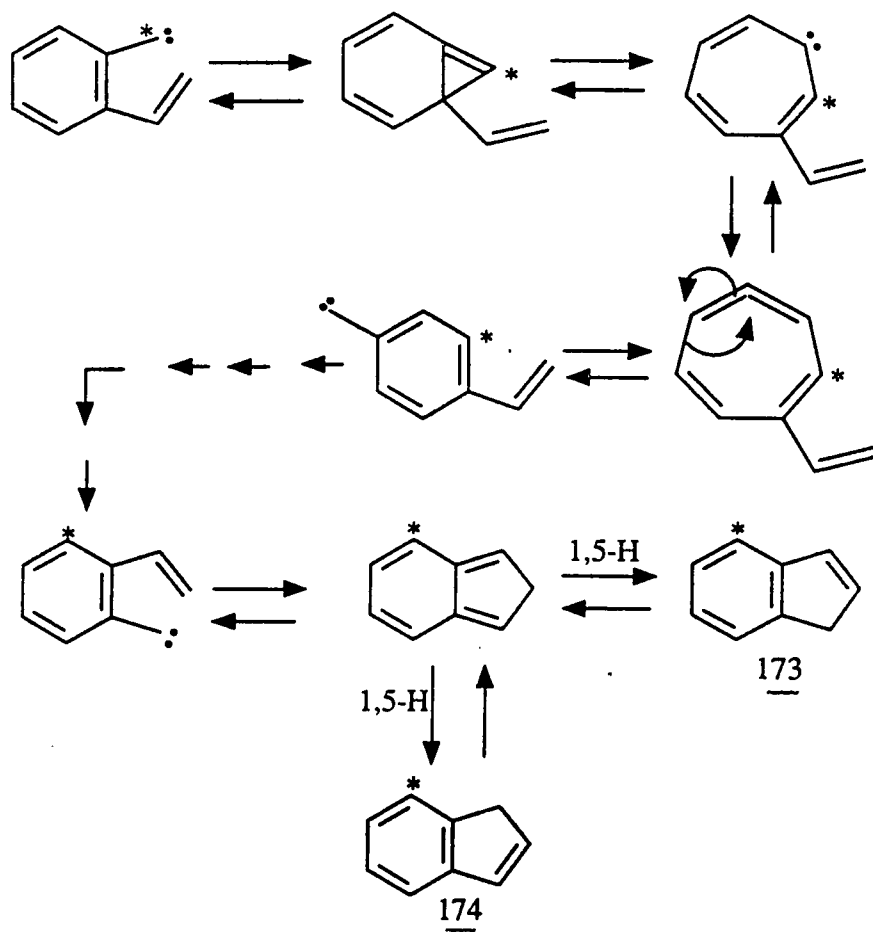
The amount of carbon label at C2 of the $3\text{-}^{13}\text{C}\text{-}1\text{-phenyl-}$
propyne pyrolysis leads us to believe that some scrambling
may occur before the formation of indene. The following
mechanism, which takes advantage of the o-tolylacetylene
rearrangement demonstrated by Brown, offers a channel by
which the carbon label can scramble to C2 of indene.
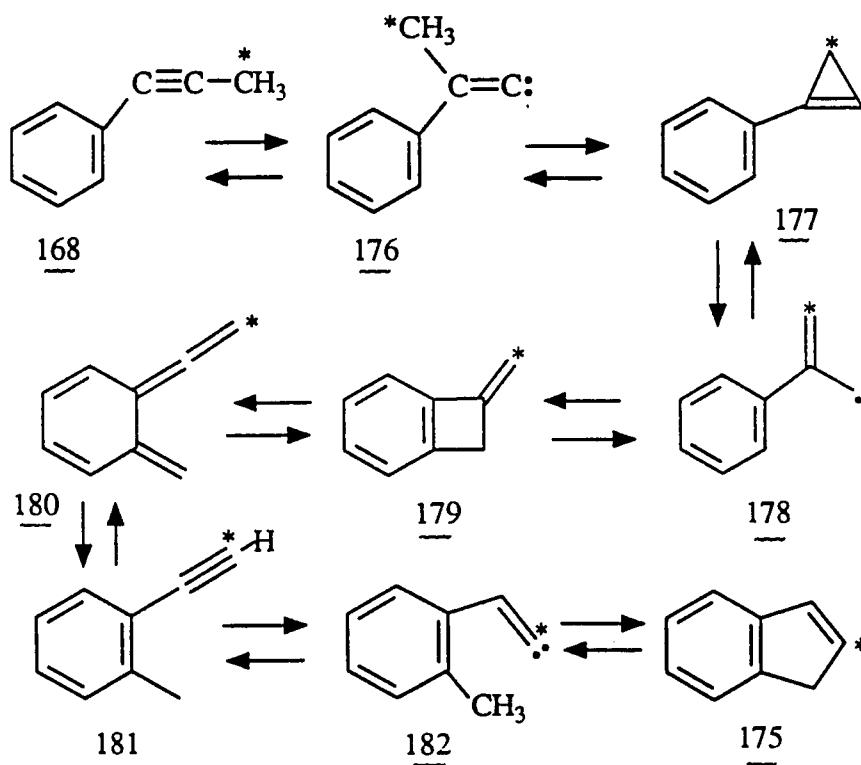
To ensure that the [1,5] hydrogen migrations were
operative under our conditions, $1\text{-}^{2}\text{H}\text{-indene}$ 206 was prepared
in 42% yield by quenching 1-indenyllithium (27) with D_2O and
pyrolyzed at 700°C, 800°C, and 900°C. The pyrolysates were
examined by $^{2}\text{H-NMR}$. At 700°C, 48.3% of the deuteria were
observed at C1, 47.1% were equally distributed between the

two olefinic positions and 4.6% were equally scrambled between the four aromatic positions. At 800°C, 33.3% of the deuteria were at C1, 17.4% each at C2 and C3, and 9.1% were at each of the positions C4-C7. At 900°C, the deuteria were totally scrambled throughout all of the positions; 23.8% were located at C1, 12.8% were located at each of the two olefinic positions, C2 and C3, and 12.6% at each of the four aromatic positions, C4-C7. Totally scrambled deuterium would show 25.0% at C1, 12.5% at C2 and C3, and 12.5% at C4, C5, C6, and C7. Above 700°C the two olefinic singlets were inseparable from one another as were the aromatic peaks. Since the peak heights were approximately equal, the relative amounts at each carbon were considered to be equal.
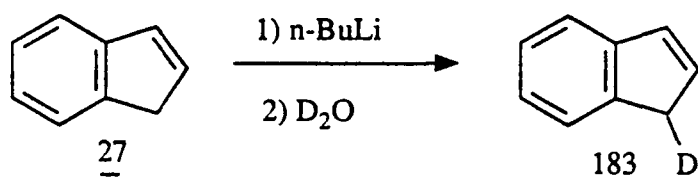
Location of deuterium upon pyrolysis of 183

°C	C_1	$C_2 + C_3$	$C_4 + C_5 + C_6 + C_7$
700	48.3%	47.1%	4.6%
800	32.0%	33.3%	34.7%
900	23.8%	25.6%	50.6%
total scrambling	25.0%	25.0%	50.0%

At first, we believed that a radical process was responsible for the deuterium incorporation into the

aromatic ring. This radical process would lead to a
significant amount of non-deutero (d_0) and dideutero (d_2)
products by the following mechanism.
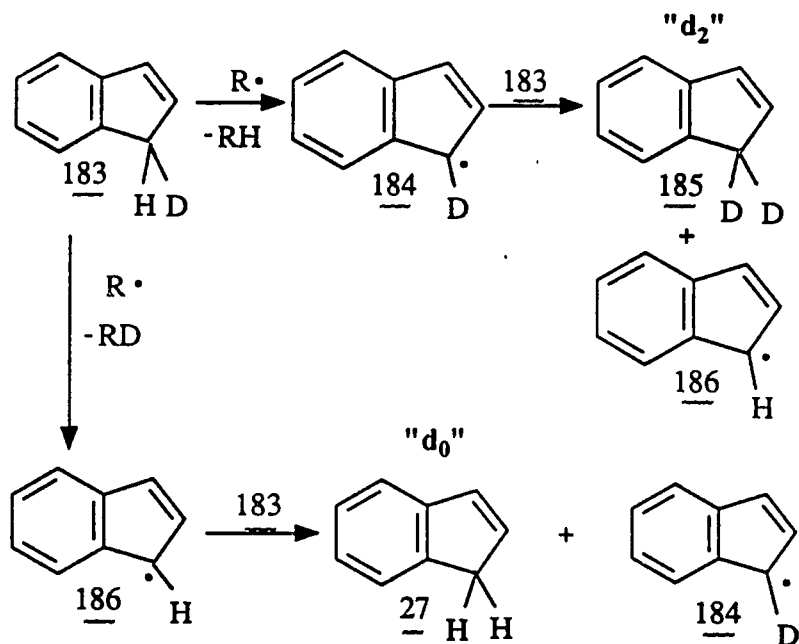
However, examination of the M-2 : M-1 : M : M+1 : M+2
ratios of the unpyrolyzed material and the three pyrolysates
showed that very little d_0 and d_2 were present. The 800°C
pyrolysate showed 0.2% d_0 and d_2 and the 900°C pyrolysate
contained 2.3% non- and dideuteroindene.

Thermal migration of a deuterium from a non-aromatic
carbon to an aromatic carbon by a unimolecular rearrangement
has not been previously reported. To explore the generality
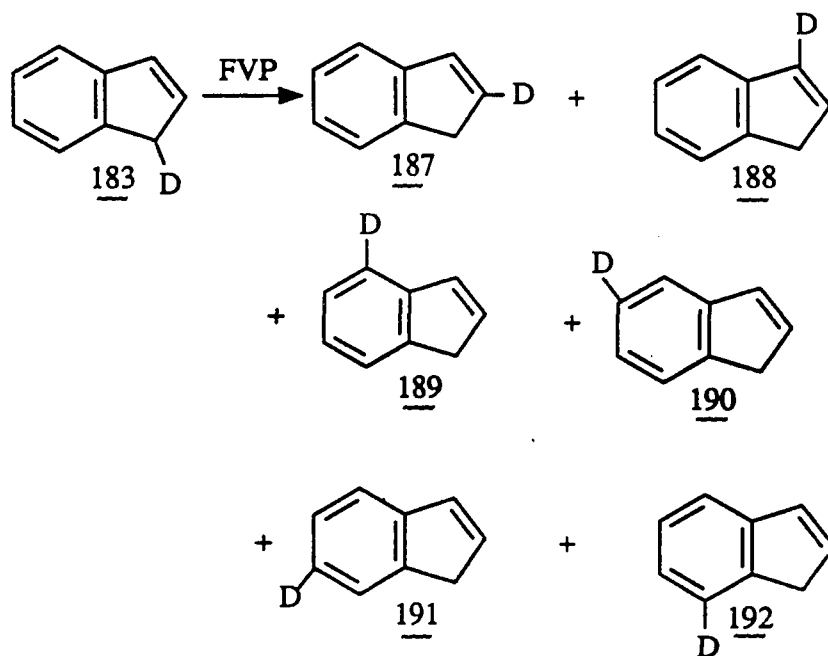
of this phenomenon and deduce the mechanism of this unusual
rearrangement, several labeling experiments were carried
out.

Since indene can be considered a derivative of
both styrene and toluene, α,β,β-trideuterostyrene 196
and α-deuterotoluene 198 were synthesized and pyrolyzed to
see if the deuterium atoms were incorporated into the
aromatic ring.

Acetophenone 193 was stirred over 0.12 M NaOD/D_2O
three times at 6 hour intervals to produce trideutero-
methylphenylketone 194 in 76% isolated yield containing
98.5% deuterium at the methyl carbon by 300 MHz ^{1}H NMR.
Reduction of ketone 194 by lithiumtetradeuteroaluminate

followed by aqueous workup yielded 1,2,2,2-tetradeutero-1-phenylethanol 195 in 84% yield. Alcohol 195 was converted to α,β,β-trideuterostyrene 196 in 37% yield using anhydrous $CuSO_4$ according to the method of Hoffman et al. (68).

Pyrolysis of 196 at 700°C, 800°C, and 900°C showed no incorporation of deuterium in the aromatic ring by ^{2}H-NMR. Thus, we concluded that the penultimate position of the aromatic deuteriums from the FVP of $1-^2$H-indene was probably not either of the olefinic position.
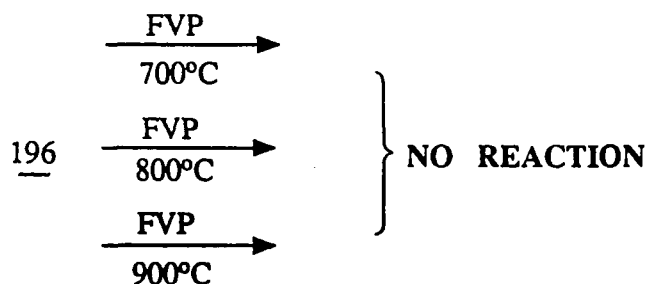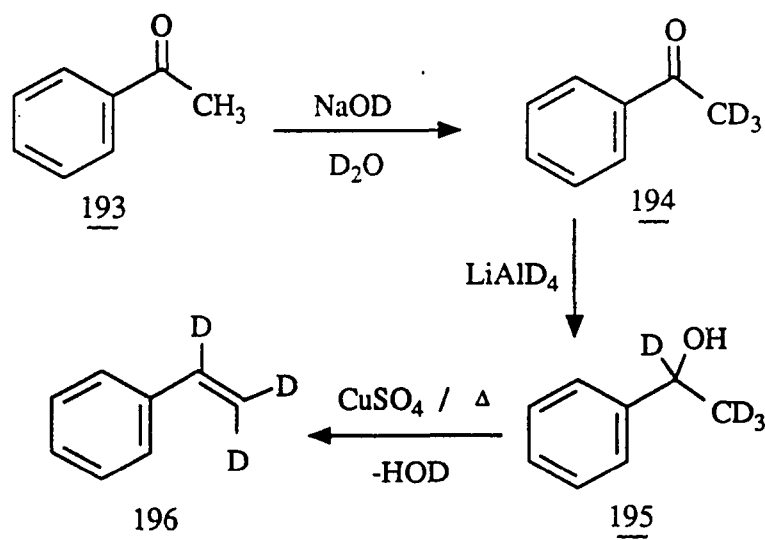
The other possible position of the deuterium is the 1-position of indene -- a "tolyl-type" position. Although we did not believe that α-^{2}H-toluene 198 would scramble a deuterium to any of the positions of the aromatic ring, we synthesized 198 from α-chloromagnesiotoluene and deuterium oxide in 21% isolated yield. FVP of 198 at 700°C, 800°C, and 900°C and analysis of the pyrolysates by ^{2}H-NMR showed only starting material.
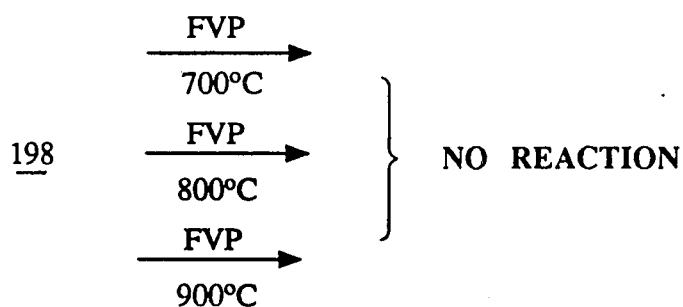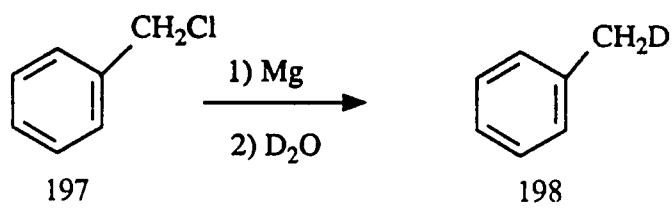
We reluctantly proposed a mechanism in which 2-^{2}H-isoindene 222, undergoes a very difficult 1,5-deuterium shift followed by two 1,5-hydrogen shifts to get to the two isomers 5- and 6-^{2}H-indene. However, this migration across the rigid planar carbon structure could not explain the 4- and 7-^{2}H-indene isomers.
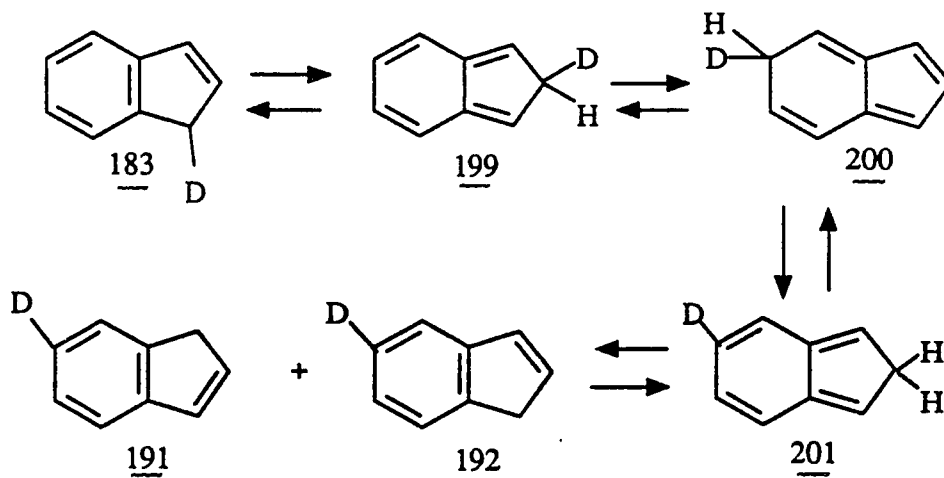
1,2-di-^{13}C-benzene 202 and disubstituted benzenes are
known to scramble their carbon framework at elevated
temperatures. Several research groups have observed this
phenomenon, although they do not agree on the mechanism of
rearrangement (69,70). This thermal isomerization of
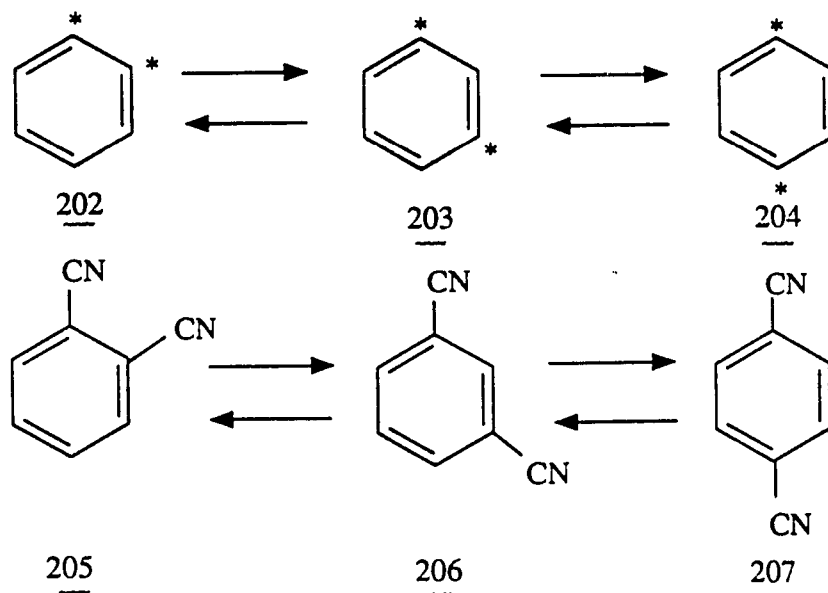
aromatic rings very nicely explains the formation of 4- and 7-^{2}H-indene from 5- and 6-^{2}H-indene. All that remains is to demonstrate that this aromatic automerization occurs under our conditions.

To demonstrate that our conditions facilitate this isomerization, 4-^{2}H-toluene 209 was prepared from 4-bromomagnesiotoluene and deuterium oxide in 52% isolated yield. FVP of 209 at 700°C, 800°C, and 900°C and analysis of the pyrolysates by ^{1}H-NMR and ^{2}H-NMR showed no change in starting material.

$$\text{CH}_3\text{-}C_6H_4\text{-Br} \quad \xrightarrow[\text{2) D}_2\text{O}]{\text{1) Mg}} \quad \text{CH}_3\text{-}C_6H_4\text{-D}$$

208   209

$$209 \quad \xrightarrow[\text{700°C}]{\text{FVP}} \quad \xrightarrow[\text{800°C}]{\text{FVP}} \quad \xrightarrow[\text{900°C}]{\text{FVP}} \quad \Big\} \text{ NO REACTION}$$
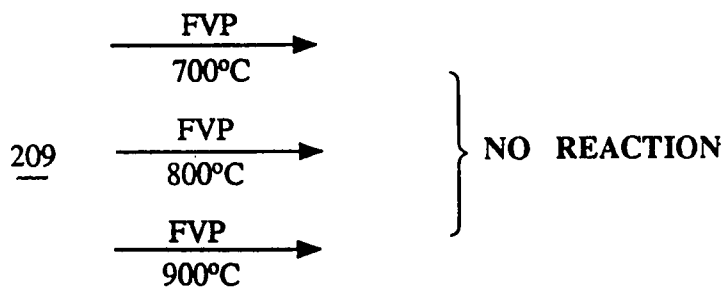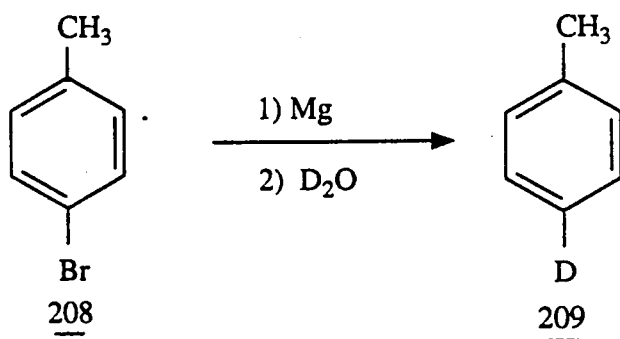
We then attempted to deduce an alternative mechanism for this unique rearrangement of indene. The six-electron

1,5-hydrogen migration from C1 to C2 of indene yields
isoindene 162. Isoindene, although of higher energy than
indene, may have some resonance stabilization owing to the
benzene ring of diyl resonance form 210.

163   210
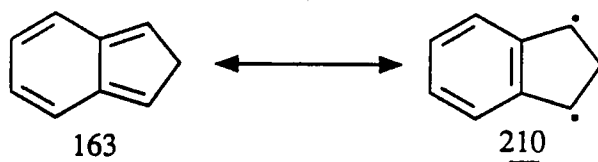
However, another possible 1,5-hydrogen migration is
available. The migration of a hydrogen from C1 to C8 would
yield isomer 211 in which all of the aromatic character of
the benzene ring would be destroyed. This isomerization
would require more energy than the formation of isoindene.

27   211
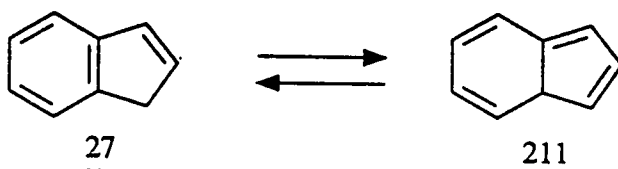
We propose that a 1,5-deuterium migration takes place to
totally destroy the aromatic character of the benzene ring
in the pyrolysis of 1-^{2}H-indene. Further migration occurs
to the other aromatic positions via previously unknown
1,9-migrations of hydrogen to reform the indene structure.

Although a 1,9-sigmatropic migration has been claimed
in the degenerate rearrangement of 7-acetyl-3-methyl-
anthranil shown below (71), we strongly agree with the
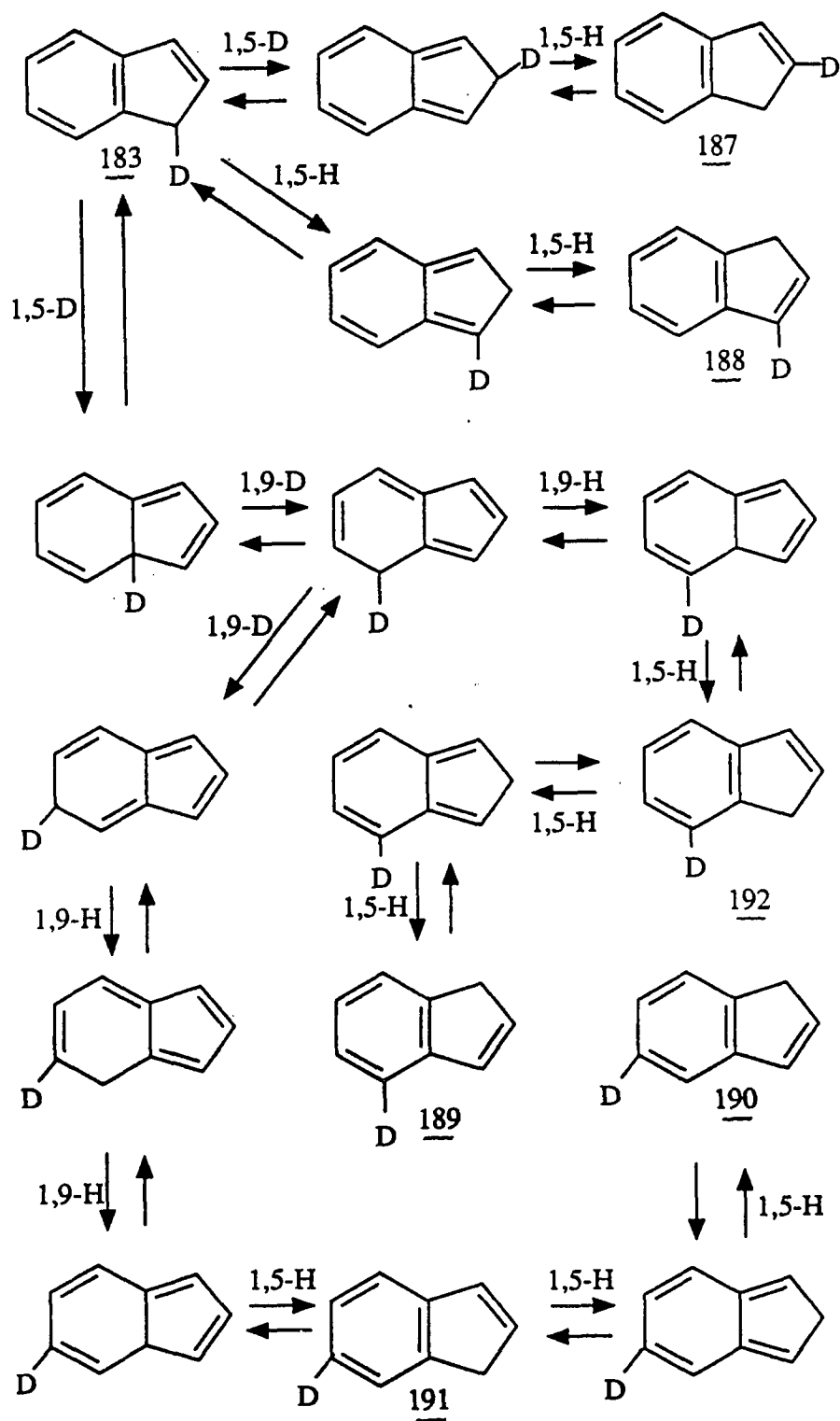
authors' suggestion that this can be considered an allowed $\pi 8s + \pi 2s$ or $\pi 8a + \pi 2a$ process. It is believed that the rigid planar structure of this molecule, which very much resembles our indene system, facilitates this rearrangement (72).

7-acetyl-3-methylanthranil
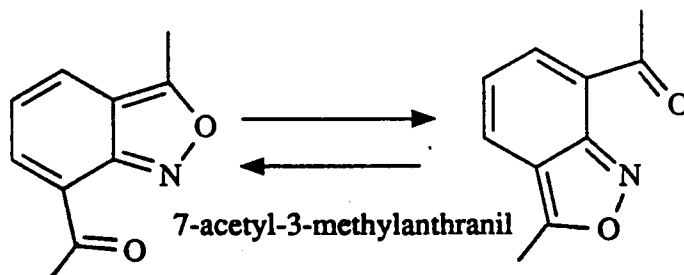
Another example of a possible 1,9-sigmatropic migration is a reasonable mechanism in the rearrangement of photochemical intermediate $\underset{\sim\sim\sim}{208}$ to indene derivative $\underset{\sim\sim\sim}{210}$ (73). Johnston and Scaiano propose either a six-electron electrocyclic ring opening followed by a 1,5-hydrogen migration or a direct 1,13-hydrogen migration. We believe that a 1,9-hydrogen migration would be an appropriate alternative and are at a loss to understand why the authors. chose to include the two additional π-bonds in their mechanism.

We sought to observe if the deuterium could be incorporated into an aromatic ring of molecules similar to indene. Since β-methylstyrene is capable of undergoing a

H
Ph
Ph

208

six
electron
electro-

cyclic
ring
opening

H

Ph
Ph

209

[1,5]-H

[1,9]-H

or

[1,13]-H

H

Ph
Ph

210
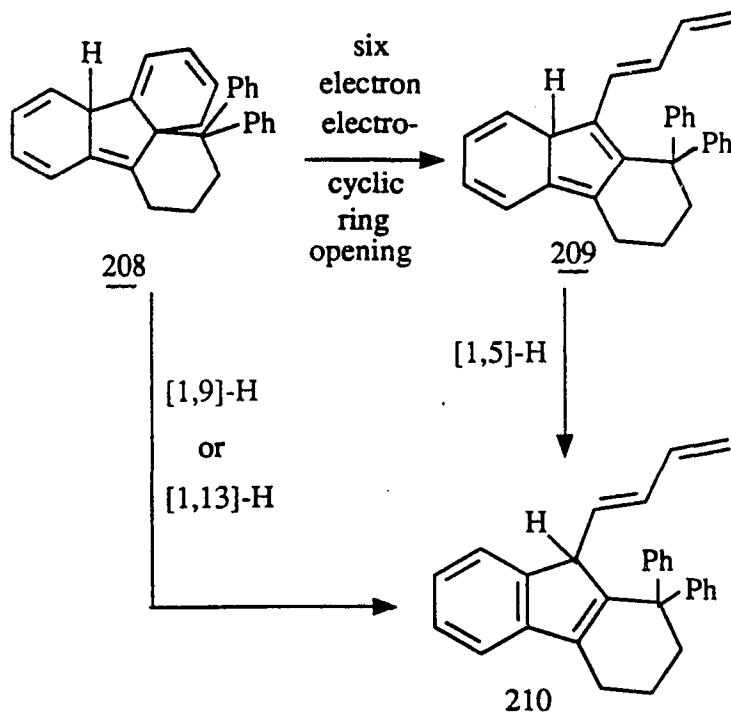
1,5-hydrogen migration into the aromatic ring, we
synthesized and pyrolyzed trans-β-deuteromethylstyrene at
700°C, 800°C, and 900°C. ^{2}H-NMR showed deuterium
incorporation into the aromatic ring at all three
temperatures but there were too many peaks to identify the
exact compound(s).

We then pyrolyzed trans-β-methylstyrene 211a at the same
temperatures. At 700°C and 800°C, cis-β-methylstyrene 211b
was the major product. At 900°C, 27 and 148 were also
observed. The loss of hydrogen in the following mechanism
is supported by the unusually long time that the pyrolysis
required to keep a constant pressure in the 10^{-4} range.

211a		211b	27
77%	700°C	23%	0%
69%	800°C	28%	1%
42%	900°C	19%	15%

148	213
0%	0%
1%	1%
14%	7%
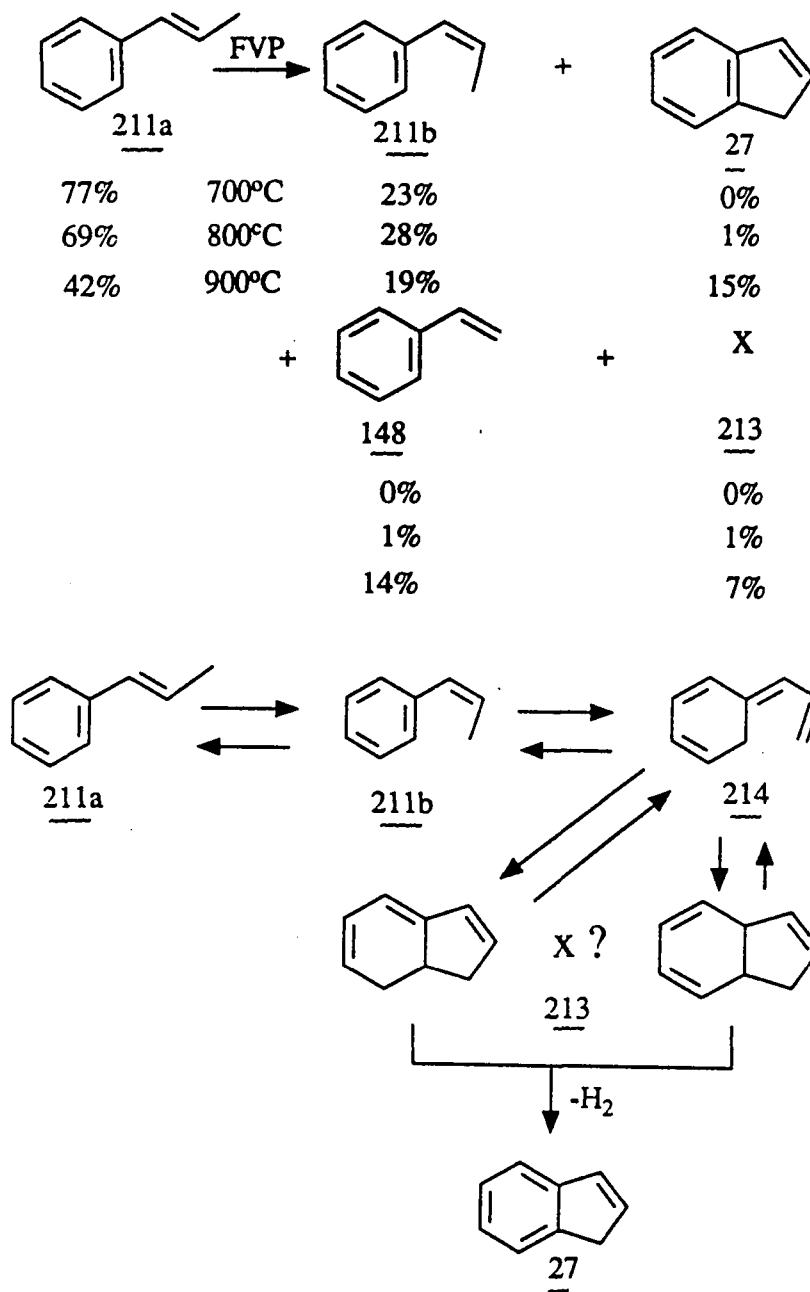
Given silicon's greater migratory aptitude, we studied the thermal chemistry of 1-trimethylsilyl indene. FVP of 215 at 600 °C yielded only 2- and 3-trimethylsilylindene. At higher temperatures, no additional isomers were observed

- only the decomposition products indene and a methylindene.

215 TMS   216   217

TMS = Si(CH$_3$)$_3$
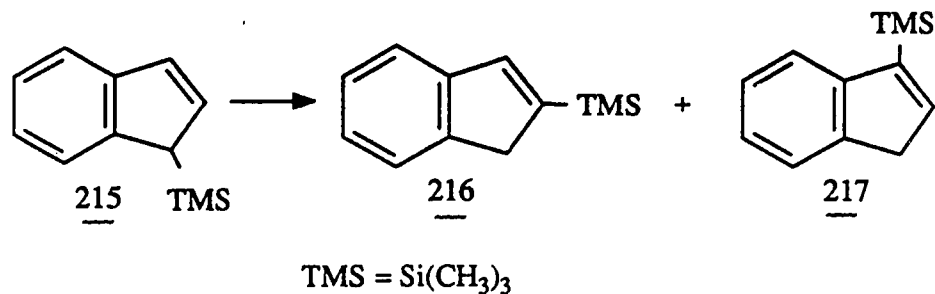
Rearrangements of Strained Organosilanes and Their

Hydrocarbon Counterparts

Since 2-methylene-1,1-dimethylsilacyclobutane 99 thermally ring expanded to form the two dimethylsilacyclopentene isomers 101 and 102 (3), we hypothesized that a methylenesilacyclopropane such as 2186 might ring expand in a similar manner to form a silacyclobutene 222.

Boatz et al. (4) reported that the strain enthalpies for three-, four-, five-, and six-membered saturated silacycles are 41.4 kcal/mol, 24.7 kcal/mol, 4.5 kcal/mol, and 4.0 kcal/mol and later calculates strain enthalpy for a silacyclobutene ring to be 26.3 kcal/mol (4). Therefore, expanding from a three- to a four-membered ring would lose roughly 15 kcal/mol of strain energy. This is close to the value gained in expanding from a four- to a five-membered ring -- roughly 20 kcal/mol.

If one could generate the methylenecyclopropane in situ, and high enough temperatures were used, a mechanistically

interesting one step synthesis of silacyclobutenes might be realized.
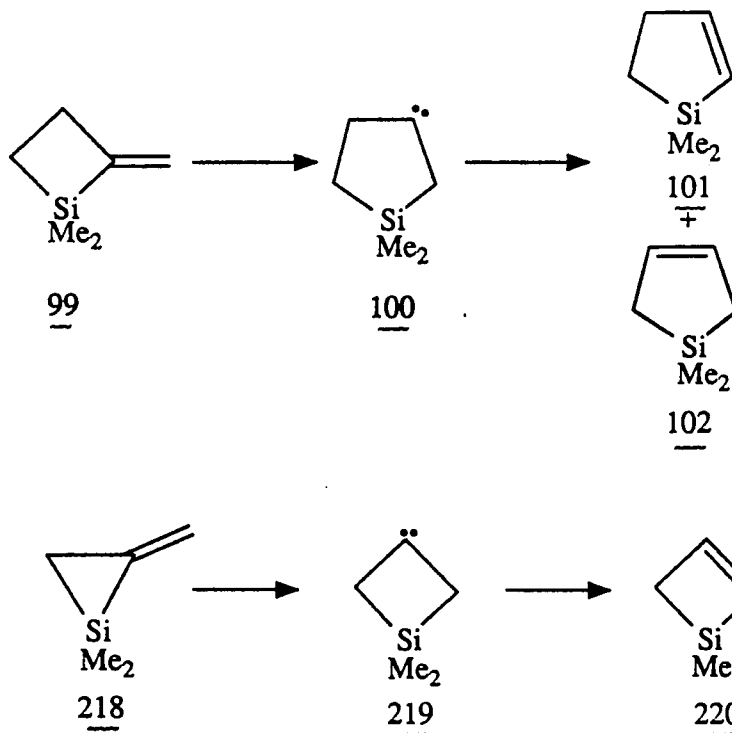
Allene 10 flow pyrolysis with known dimethylsilylene thermal generator 1-methoxy-1,1,2,2,2-pentamethyldisilane 221 followed by evaporation of allene yielded no adduct of dimethylsilylene and allene. Indeed the only silicon containing products observed were trimethylmethoxysilane 222 and a small amount of starting material 221.
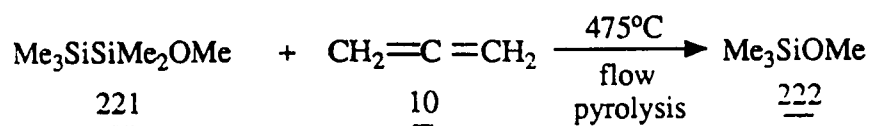
Raising the temperature did not improve the results. It was difficult for us to believe that the silylene did not add to allene given the propensity of silylenes to add to π-systems (74) and the usually high reactivity of allenes toward divalent species (75). However, we theorized that addition did occur to form the methylenesilacyclopropane 218, but that, reversibly, this intermediate extruded dimethylsilylene to reform allene.

$$Me_2Si: \quad + \quad CH_2{=}C{=}CH_2 \quad \underset{\longleftarrow}{\longrightarrow} \quad$$

10

218
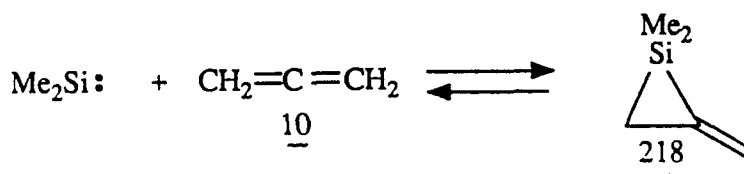
The experiment was then attempted under stirred flow reactor (SFR) conditions. A 100 fold excess of allene was copyrolyzed with 1-methoxypentamethyldisilane. The only products formed were trimethylmethoxysilane and 1-methoxyheptamethyltrisilane. The latter product is the insertion of dimethylsilylene into the Si-O bond of the starting disilane. Attempts to trap the silylene with a 10 fold excess of trimethylsilylacetylene were very successful. This proved that the silylene could be trapped under these conditions.

We then changed allenes. SFR experiments with 1,2-butadiene yielded an adduct with a molecular weight of 1/2 g/mol. Mass spectrum could not confirm whether this

adduct is a silacyclobutene or an isomer. Due to the low

boiling point of 1,3-butadiene, nitrogen flow pyrolysis

experiments did not produce the product that weighed 112

g/mol.

An allene that was easier to handle at room temperature

was then attempted. Copyrolysis of 1,2-dimethoxytetra-

methyldisilane 223 and 3-methyl-1,2-butadiene 224 yielded
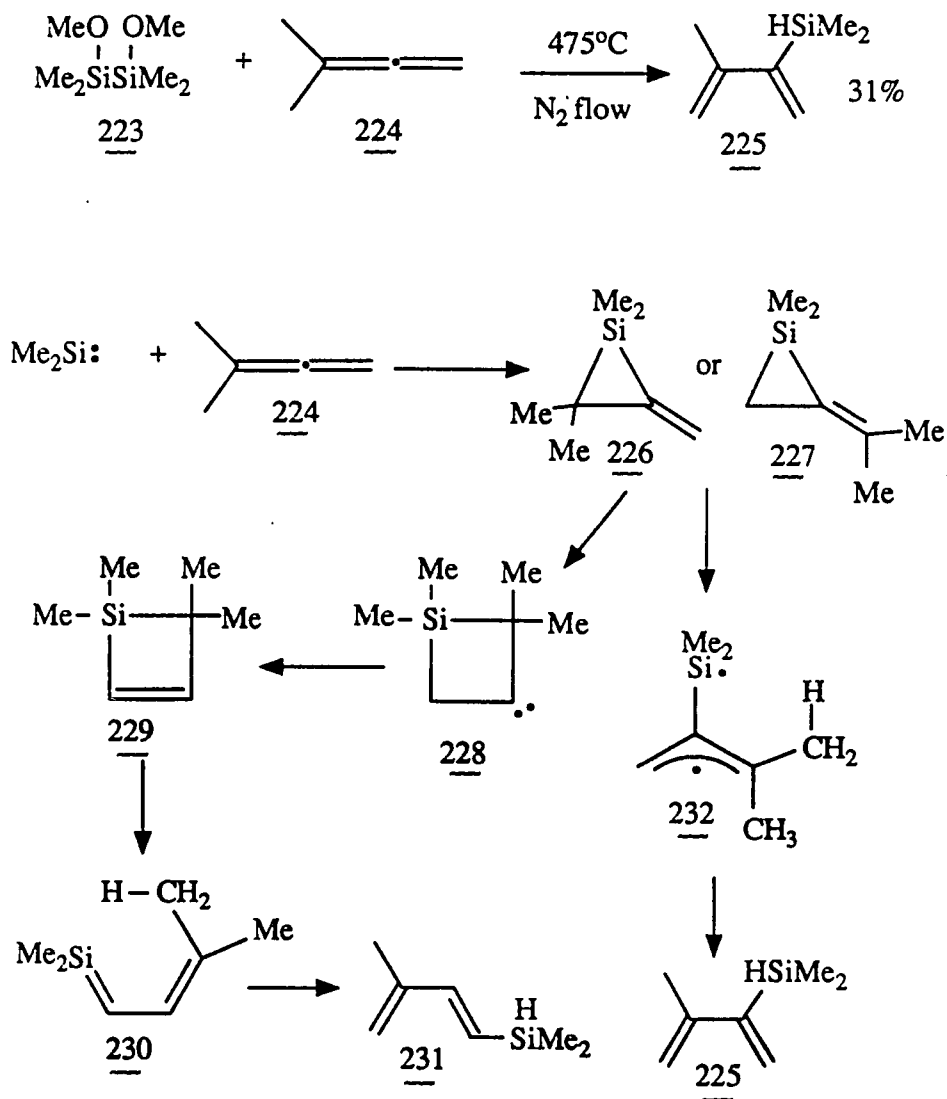
2-dimethylsilyl-3-methyl-1,3-butadiene 225 in 32% yield.

We, therefore, concluded that path b, the silamethylene-

methane pathway, was operative since carbene 228 cannot

undergo a 1,2-hydrogen shift that would go on to yield a

2-dimethylsilyl-1,3-butadiene. This carbene would probably

form 1-dimethylsilyl-1,3-butadiene 231 which was not

observed.

In 1986, Ando and Saso (76) reported the reaction of

photogenerated dimesitylsilylene with t-butylallene 233,

t-butyldimethylallene 234, and tetramethylallene 235. With

the two t-butyl-substituted allenes 233 and 234, one

alkylidenesilacyclopropane was isolated in each case. With

the methyl-substituted allenes 234 and 235, each produced an

isolable 1,3-butadiene in which C2 was substituted with a

dimesitylhydridosilyl group. These 2-(hydridosilyl)

substituted 1,3-butadiene products of this photochemical

reaction supports our claim for intermediacy of an

alkylidenesilacyclopropane in our thermal reaction.

Methylenecyclopropanes have been shown to undergo

structural isomerizations to exchange exo- and ring carbons

as in the reversible interconversion of 2-methylmethylene-

cyclopropane 246 to ethylidenecyclopropane 247 (77).

$\xrightarrow{h\nu}$ Mes$_2$Si: + t-Bu—⎓=•=⎓

233

Mes$_2$Si (236) + t-Bu

Mes$_2$Si

t-Bu **237**

Mes$_2$Si **238** t-Bu

+

t-Bu—C≡C—CH$_2$SiMes$_2$ (H)

239

Mes$_2$Si: + t-Bu—•=C(Me)Me **234** → Mes$_2$Si t-Bu **240** Me, Me

⇅

Mes$_2$Si Me, Me **241** t-Bu

→ HSiMes$_2$ Me, Me **242** t-Bu

Mes$_2$Si: + **235** → Mes$_2$Si Me, Me **243** Me, Me

↓

Mes$_2$Si• Me Me Me Me **244**

→ Me HSiMes$_2$ **245** Me, Me

$E_{act} = 42 \text{ kcal/mol}$

246   Me   247

Me   248

A trimethylenemethane
biradical
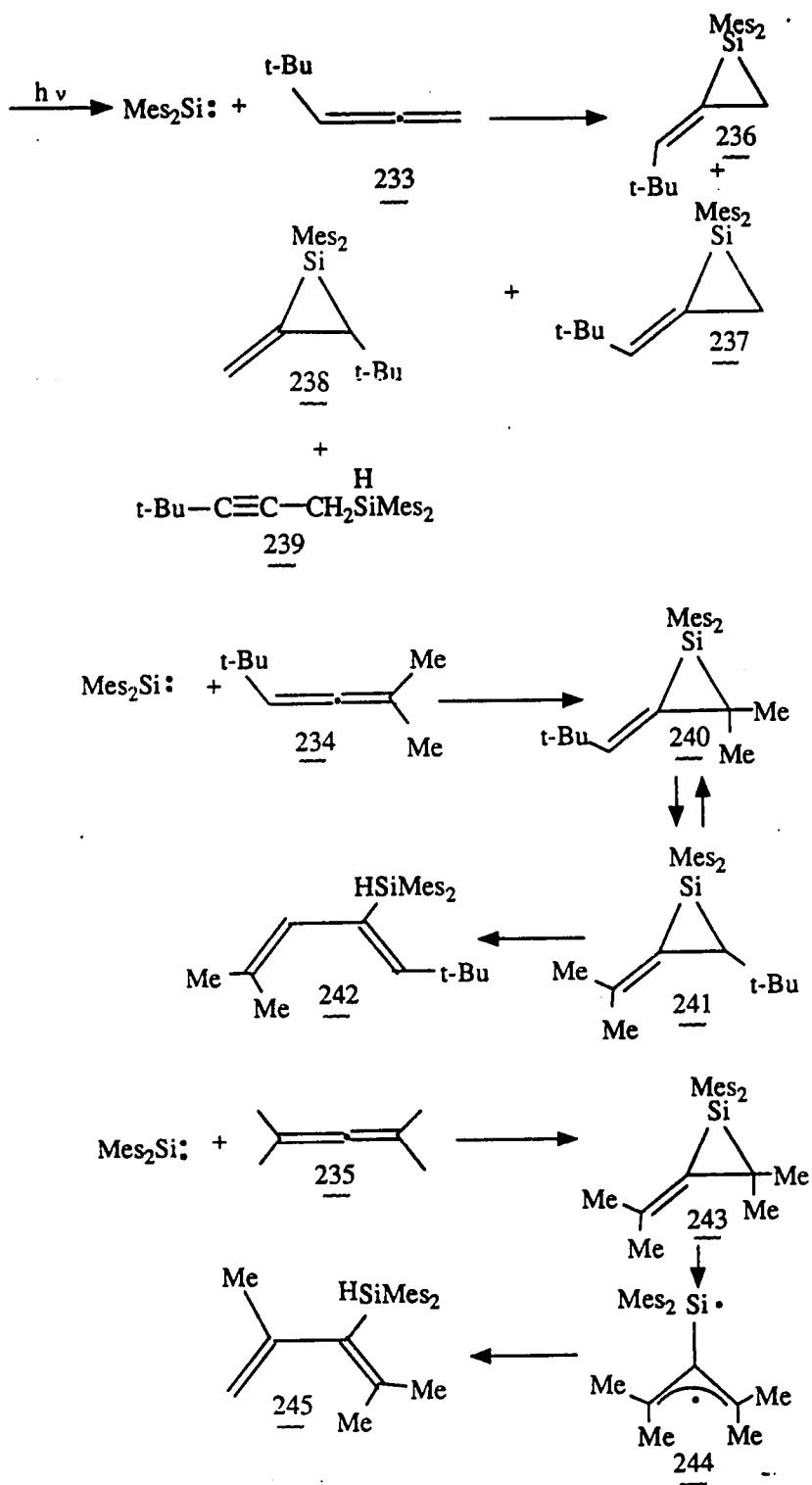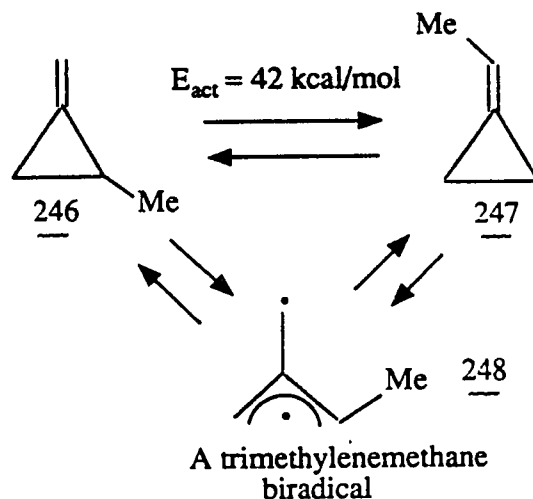
Other labeled methylenecyclopropanes have been observed
to undergo this rearrangement (78) and the kinetic studies
show all of these isomerizations to have an activation
energy of approximately 42 kcal/mol. The intermediate in
all of these rearrangements is believed to be a
trimethylenemethane (TMM) biradical, which has been
discussed in detail (79).

A higher energy process requiring approximately 54
kcal/mol of activation energy involves the formation of a
substituted 1,3-butadiene. Methylmethylenecyclopropane 246
forms isoprene 249 at temperatures higher than the
reversible structural isomerization mentioned above (80).
Diene 249 is believed to arise from an intramolecular
1,4-hydrogen abstraction process involving TMM biradical
248.

$$E_{act} = 54 \text{ kcal/mol}$$

248   249
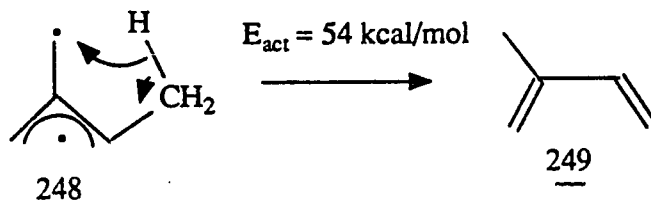
At the thermal upper limit of methylenecyclopropanes,
fragmentation to acetylenes and olefins is observed (81).
2,2-dimethylmethylenecyclopropane forms isobutene 252 and
acetylene with an activation barrier of 60 kcal/mol. This
process is suggested to proceed via the intermediacy of
vinylidene 251.

$$E_{act} = 60 \text{ kcal/mol}$$

250   251   252

$$H-C \equiv C-H$$
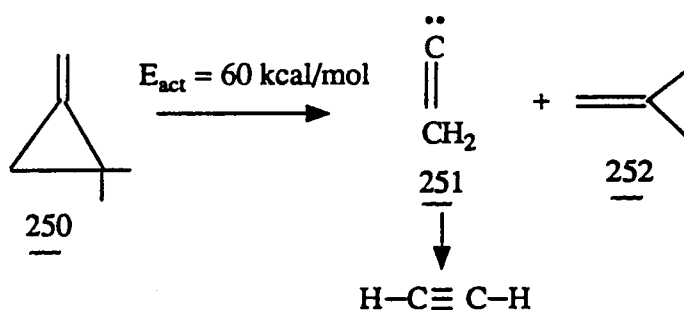
Sakurai et al. (54) and Conlin and Kwak's (57) work on
the thermolysis of trimethylsilylcyclopropane along with the
spectroscopic and theoretical results led us to question the
ring opening mechanism. In this mechanism, the shorter and,
therefore, possibly more stable bond in the ring is the sole
bond broken. Sakurai favors an anchimerically assisting
silicon atom in a concerted ring opening to
allyltrimethylsilane. Conlin adds the homolytic cleavage of

the shorter bond in the cyclopropane ring but does not rule
out Sakurai's mechanism.

Since Conlin had previously proposed a 1,2-silyl shift
to form a carbene (3), we were somewhat surprised to
discover that he did not propose a 1,2-silyl shift to break
the longer cyclopropane bond and form a γ-silyl carbene 253
which can easily C-H insert to form 117, the major product
of the pyrolysis.
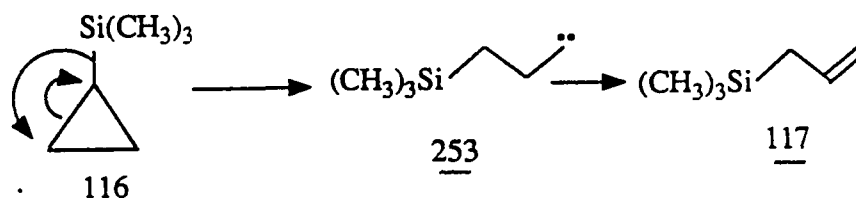
In order to test this mechanism, $1\text{-}^2\text{H}\text{-}1\text{-trimethylsilyl}$-
cyclopropane was synthesized and pyrolyzed. Vacuum
distillation through a packed quartz tube at 700°C and 2.0 x
10^{-4} mm Hg yielded mainly $2\text{-}^2\text{H}\text{-}3\text{-trimethylsilylpropene}$ as
detected by GC/MS and ^2H NMR. This shows that the major
pathway to decomposition of trimethylsilylcyclopropane does
indeed involve cleavage of the shorter C2-C3 bond.

256 $\xrightarrow{\text{FVP}}$ (CH₃)₃Si—CH₂—C(=CH₂)—CH₂D + (CH₃)₃Si—CH(D)—CH=CH₂

257 95%   258 5%
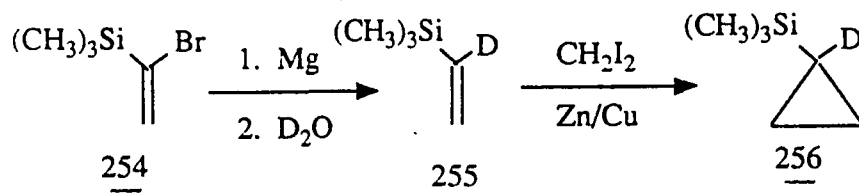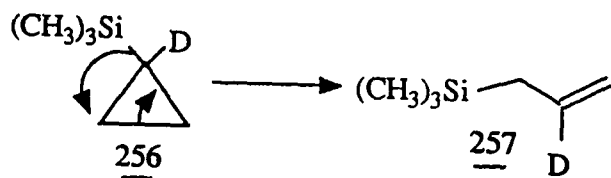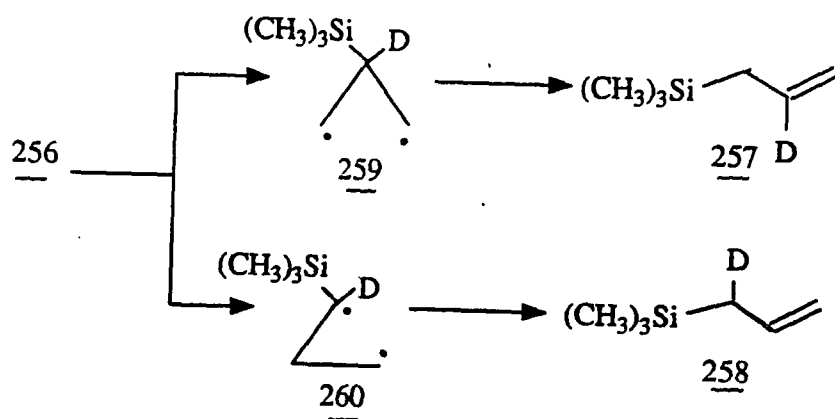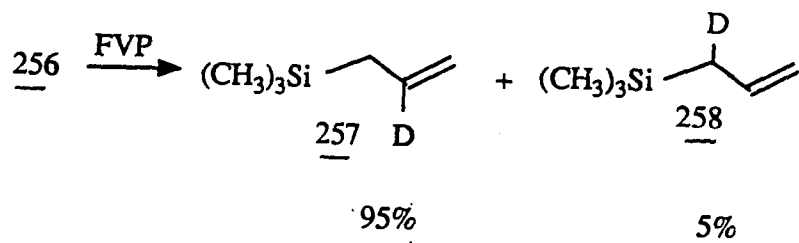
CONCLUSION

The products from the flash vacuum pyrolysis (FVP) of dimethylsilyldeuteroacetylene and dimethylsilylphenyl-acetylene support the intermediacy of silacyclopropenes. Formation of bis(dimethylsilyl)acetylene from the stirred-flow reactor (SFR) pyrolysis of dimethylsilylacetylene strongly suggests extrusion of dimethylsilylene from either starting material or from a silacyclopropene intermediate.

FVP of 1-phenylpropyne yielded phenylacetylene and the two isomeric products phenylallene and indene. ^{13}C-labeling experiments led us to propose the intermediacy of phenyl-substituted cyclopropene, vinylidenes, and vinylcarbenes.

^{13}C-labelled indene undergoes some rearrangement at high temperatures but not enough to account for all of the scrambling observed in the pyrolysis of 3-^{13}C-1-phenyl-propyne. 1-^{2}H-indene experiments fortuitously led us to the discovery of a hitherto unknown 1,9-sigmatropic migration of hydrogen and deuterium.

Addition of thermally generated dimethylsilylene to methyl-substituted allenes yielded 2-dimethylsilyl-1,3-butadienes. Formation of products most likely proceeded through a novel silatrimethylenemethane. Addition of thermally generated dimethylsilylene to allene yielded no adduct.

FVP of $1-^2H-1$-trimethylsilylcyclopropane yielded mainly 3-trimethylsilyl-2-^2H-propene. This product is consistent with the major decomposition pathway being cleavage of the shorter C2-C3 cyclopropane bond.

EXPERIMENTAL

Instrumentation

^{1}H NMR spectra were recorded on a Nicolet model NT-300 spectrometer. ^{13}C NMR spectra were recorded on either the Nicolet mentioned above or on a Bruker model WM-200 or WM-300 spectrometer. The Bruker model WM-300 was used in obtaining all ^{2}H NMR spectra. All chemical shifts are reported as parts-per-million (δ scale) using either tetramethylsilnae, benzene, chloroform, acetone, or methylene chloride as an internal standard. Infrared (IR) spectra were obtained on an IBM model IR/98 Fourier transform spectrometer. GCIR spectra were recorded on the same spectrometer coupled with a HP5880A capillary GC. All bands are reported in reciprocal centimeters (cm^{-1}). GC/MS data were obtained at 70 eV on a HP5970 mass selective detector coupled with a HP5890 capillary GC. All signals are recorded in m/e percent relative intensities.

Gas chromatographic analyses were performed on a HP5890 capillary GC. Preparatory GC purification was performed on a Varian Aerograph series 1700 equipped with 1/4" GC columns between 10% and 25% SE-30 as the stationary phase. Column lengths were between 10° and 20°.

Procedures and Results

General conditions for flash vacuum pyrolysis (FVP)

All samples were vacuum distilled from a bath maintained
at a temperature allowing slow introduction of the sample
into a horizontal quartz tube packed with quartz chips and
heated with an electric tube furnace. The heated zone of
the quartz tube was approximately 1.6 cm x 30 cm.
Pyrolysates were collected in a cold trap cooled with liquid
nitrogen. Pressures were measured by an ionization gauge
behind two liquid nitrogen cooled traps and do not
accurately reflect the actual pressures in the reaction
zone. However, experiments conducted on this apparatus have
shown that the pressure before the hot zone is approximately
an order of magnitude higher than at the ionization gauge.
Throughout the pyrolysis experiments, the pressure was
maintained below 6 x 10^{-4} mm Hg as measured at the
ionization gauge.

General conditions for flow pyrolyses

The oven and packed quartz tube were the same as used
for the FVP. During addition, the pyrolysis tube was
continually swept with a nitrogen stream of 40 mL/min unless
otherwise specified. The pyrolysates were collected in a
cold trap cooled to -78°C.

General conditions for stirred-flow reactor (SFR) pyrolyses

The plug stirred-flow reactor (SFR) used was designed after Baldwin's et al. (82). The quartz reactor had a volume of 3 cm^3. The helium flow through the reactor was 60 mL/min. The reactor temperature was controlled to 0.1°C by a Digi-Sense temperature controller. A Varian 6000 gas chromatographed, equipped with a 25° x 1/4" 25% SE-30 column was used to separate the products. A splitter after the column directed a fraction of the eluent stream to a quadr pole mass spectrometer (VG-SX300).

Samples were introduced from a vacuum manifold. The pressures were measured with a Baratron transducer. The samples were swept through the reaction vessel with the helium carrier gas. Approximate pressure inside the reaction vessel was 3 atmospheres. Approximate pressures of samples introduced was 0.1 torr. Concentration of the reactant in the reaction vessel is roughly 0.004%. This extremely low concentration in the helium flow gas maximizes collisions with helium, minimizes collisions with other reactant molecules and reactor walls, and, therefore, maximizes unimolecular reactions.

Synthesis of dimethylsilylacetylene 139

Calcium carbide was heated to 600°C in vacuo for five hours to yield black crystalline calcium carbide; 42.5 g of this solid was added slowly to a stirred round bottom flask

which contained 50.2 g deuterium oxide. The dideutero-
acetylene gas generated was bubbled for three hours into a
three neck round bottom containing 65 mL tetrahydrofuran
(THF) cooled to 0°C. After the gas had bubbled through the
solvent for 0.5 hr, 35 mL of a 3.0 M THF solution of
methylmagnesiumchloride was slowly added. After the gas was
stopped, the deuteroacetylenemonogrignard was quenched with
9.9 g of freshly distilled dimethylchlorosilane and allowed
to stir at 0°C for five hours. The product was distilled as
a THF solution. Yield by ^{1}H NMR was 41% as a 9% THF
solution. The product was purified as needed by preparatory
gas chromatography. Integration of the residual protons at
2.40 ppm versus the proton at 4.17 ppm showed the acetylene
to be 100.0% deuterated. ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.17 ppm
(heptet, J = 3.78 Hz, 1 H; 0.26 ppm (d, J = 3.86 Hz, 6 H).
Mass spectrum 85 (21), 84 (27), 70 (100), 59 (21), 58 (70),
54 (43), 43 (64).

FVP of dimethylsilyldeuteroacetylene 139

i. Dimethylsilyldeuteroacetylene, 6 mg, was vacuum
distilled through a 512°C quartz tube at a pressure of 1 x
10^{-4} mm Hg. The pyrolysate, 5 mg (83% mass recovery) was
analyzed by 300 MHz ^{1}H NMR. The ratio of 139 and an isomer,
dimethyldeuterosilylacetylene was 97 : 3 by NMR integration.

ii. Dimethylsilyldeuteroacetylene, 7 mg, was vacuum
distilled through a 700°C quartz tube at a pressure of 4.0 x

10^{-4} mm Hg. The pyrolysate, 5 mg (71% mass recovery) was analyzed by 300 MHz ^{1}H NMR. The ratio of 139 and an isomer, dimethyldeuterosilylacetylene was 89 : 11 by NMR integration.

iii. Dimethylsilyldeuteroacetylene, 9 mg, was vacuum distilled through a 750°C quartz tube at a pressure of 4.5 x 10^{-4} mm Hg. The pyrolysate, 9 mg (100% mass recovery) was analyzed by 300 MHz ^{1}H NMR. The ratio of 139 and an isomer, dimethyldeuterosilylacetylene was 81 : 19 by NMR integration. Some other products, dimethylsilane and trimethylsilane were observed by ^{1}H NMR and gas chromatography / mass spectrometry (GC/MS).

iv. Dimethylsilyldeuteroacetylene, 11 mg, was vacuum distilled through a 752°C quartz tube at a pressure of 3.0 x 10^{-4} mm Hg. The pyrolysate, 8 mg (73% mass recovery) was analyzed by 300 MHz ^{1}H NMR. The ratio of 139 and an isomer, dimethyldeuterosilylacetylene was 77 : 23 by NMR integration. The other products observed in iii above were also seen in this run.

A mass spectrometry experiment was done on this sample to estimate the percent isomerization. By analyzing the ration of m/e 53 (C_2HSi) to m/e 54 (C_2DSi) in the pyrolyzed and unpyrolyzed sample, it was calculated that 29.3% of the starting material was converted to its isomer. The contribution of the m/e 53 peak to the m/e 54 peak was taken

into consideration. Exact mass measurements confirm that the m/e 53 peak and the m/e 54 peak both contained one silicon. The possibility that m/e 54 consisted of C_2H_2Si instead of C_2DSi could not be ruled out by the exact mass measurement. However, since the mass spectrum of non-deuterated dimethylsilylacetylene does not show m/e 54, it seems reasonable that the m/e 54 peak does not arise from C_2H_2Si.

	Calculated Value	Deviation From Measured Value
C_2DSi	53.99103	9.8 ppm
C_2H_2Si	53.99258	38.5 ppm
C_4H_6	54.04695	1,045.0 ppm
C_4H_6D	54.04540	1,017.0 ppm
$C_3{}^{13}CH_5$	54.04578	1,024.0 ppm
Measured Value	53.9905	0.0 ppm

v. Dimethylsilyldeuteroacetylene, 7 mg, was vacuum distilled through a 800°C quartz tube at a pressure of 4.5 x 10^{-4} mm Hg. The pyrolysate, 6 mg (86% mass recovery) was analyzed by 300 MHz ^1H NMR. The spectrum was very messy, but the silylhydride region and the acetylene region were easily integrated. The ratio of 139 and an isomer,

dimethyldeuterosilylacetylene was 57 : 43 by NMR
integration.

SFR pyrolysis of dimethylsilylacetylene

Stirred-flow reactor pyrolysis of 0.5 torr at 650°C
yielded approximately 40% decomposition of starting
material. The major products of the pyrolysis was
bis(dimethylsilyl)acetylene and acetylene. The only other
identifiable products were traces of dimethylsilane and
methane. These produces were identified by mass
spectroscopy.

FVP of dimethylsilylphenylacetylene 145

i. Dimethylsilylphenylacetylene 145, 40 mg, was vacuum
distilled through an 800°C quartz tube at a pressure of 4.5
x 10^{-4} mm Hg. The pyrolysate, 31 mg (78% mass recovery),
was analyzed by 300 MHz ^{1}H NMR and GC/MS showed that a 77%
conversion of 142 had occurred to yield 96% phenylacetylene,
2.3% styrene, 1.2% indene, and 0.7% phenyldimethylsilyl-
acetylene. All products were identified by comparison of
their spectra with that of authentic material.

ii. Dimethylsilylphenylacetylene 145, 45 mg, was vacuum
distilled through a 850°C quartz tube at a pressure of 4.0 x
10^{-4} mm Hg. The pyrolysate, 11 mg (24% mass recovery), was
analyzed by 300 MHz ^{1}H NMR and GC/MS showed that an 88%
conversion of 142 had occurred to yield 91.3% phenyl-

acetylene, 2.9% styrene, 3.5% indene, and 1.7% phenyl-
dimethylsilylacetylene. All products were identified by
comparison of their spectra with that of authentic material.

FVP of 1-phenylpropyne 150

i. 1-phenylpropyne 150, 20 mg, was vacuum distilled
through a 700°C quartz tube at a pressure of 5 x 10^{-4} mm Hg.
Analysis of the pyrolysate, 19 mg (95% mass recovery) by 300
MHz ^{1}H NMR showed that no reaction had occurred.

ii. 1-phenylpropyne 150, 30 mg, was vacuum distilled
through an 800°C quartz tube at a pressure of 5 x 10^{-4} mm
Hg. Analysis of the pyrolysate, 29 mg (97% mass recovery)
by 300 MHz ^{1}H NMR showed traces of phenylallene and indene.

iii. 1-phenylpropyne 150, 50 mg, was vacuum distilled
through a 900°C quartz tube at a pressure of 5 x 10^{-4} mm Hg.
Analysis of the pyrolysate, 45 mg (90% mass recovery) by 300
MHz ^{1}H NMR showed a 50% conversion of the starting material.
The products formed were 28% phenylallene, 38% indene, and
34% phenylacetylene. The indene and phenylacetylene were
identified by comparison of the spectra with that of
authentic material. The phenylallene was identified by mass
spectrum 116 (65), 115 (100), 89 (13), 63 (15), 39 (12), and
by the olefinic protons at δ 6.159 ppm (apparent triplet, J
= 6.8 Hz, 1 H) and δ 5.140 ppm (d, J = 6.8 Hz, 2 H).

iv. 1-phenylpropyne 150, 29 mg, was vacuum distilled
through a 925°C quartz tube at a pressure of 5 x 10^{-4} mm Hg.

Analysis of the pyrolysate, 27 mg (40% mass recovery) by 300 MHz ^{1}H NMR showed that 62% of 150 had been converted to products. Yield of products 15% phenylallene, 51% indene, and 34% phenylacetylene.

v. 1-phenylpropyne 150, 120 mg, was vacuum distilled through a 1000°C quartz tube at a pressure of 5 x 10^{-4} mm Hg. Analysis of the pyrolysate, 48 mg (40% mass recovery) by 300 MHz ^{1}H NMR showed that 100% of the starting material was converted to products indene (50%) and phenylacetylene (50%).

Synthesis of 3-^{13}C-1-phenylpropyne 161

To a stirred THF solution of 0.713 g phenylacetylene (6.98 mmol) cooled to -78°C was added 3.0 mL of a 2.5 M hexanes solution of n-butyllithium. The reaction flask was allowed to come to room temperature over the next hour. The flask was then cooled to -78°C and a THF solution containing 1.0 g ^{13}C-methyl iodide was slowly added. The mixture was allowed to slowly warm to room temperature over the next 18 hours. Fifteen mL of pentanes were added along with 5 mL distilled water. The layers were separated and the organic layer washed an additional three times with 5 mL portions of distilled water. The solvent was removed by rotary evaporation and the product was purified by bulb-to-bulb vacuum distillation at room temperature to yield 0.448 g

(55%) isolated yield. Mass spectrum 117 (69), 116 (100), 90 (9), 64 (9), 63 (10), 58 (9).

FVP of 3-^{13}C-1-phenylpropyne 161

A sample of 161 (43 mg) was vacuum distilled through a 922°C quartz tube at a pressure of 4.5 x 10^{-4} mm Hg. The pyrolysate, 30 mg (70% mass recovery) was analyzed by ^{13}C NMR integration using a known quantity 1,4-dioxane as an internal standard. Three samples of non-labeled indene with known quantities of 1,4-dioxane were used as standard runs. The integration results are tabulated below. Seventy-five MHz ^{13}C shifts and peak heights in CD$_2$Cl$_2$ are as follows: 39.62 (8.89), 121.36 (3.08), 124.20 (2.87), 125.03 (4.76), 126.76 (1.55), 132.34 (9.89), 134.80 (11.95), 144.30 (0.73), 145.35 (0.31).

Carbon	Peak Area
1	9.822
2	7.713
3	8.419
4	1.959
5	4.044
6	3.579
7	1.859
8	0.325
9	0.394

The ^{13}C-label showed up in indene in the following amounts:
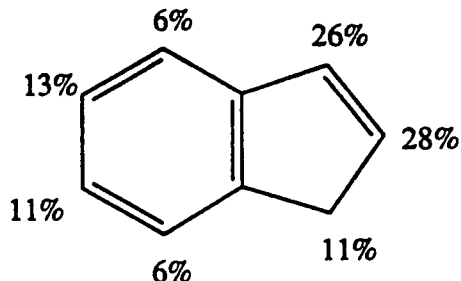
Synthesis of 1-^{13}C-3-phenylpropionic acid 166

A solution consisting of 3.60 g (19.45 mmol) 1-bromo-2-phenylethane and 5 mL THF was slowly added to a three neck round bottom flask containing 0.65 g magnesium turnings and 15 mL THF. After reaction had occurred, ^{13}C-labeled carbon dioxide (generated from the action of excess 10% hydrochloric acid on 3.90 g 99.99% ^{13}C-labelled barium carbonate) was bubbled into the flask containing the grignard reagent. After addition of the gas was complete, the reaction was allowed to stir for an additional two hours before the addition of excess 10% hydrochloric acid and 25 mL diethyl ether. The layers were separated and the organic phase was washed twice with 10 mL solutions of saturated ammonium chloride. The product was then extracted from the organic phase as its sodium salt with three 10 mL portions of 10% NaOH. The aqueous washings were combined and acidified with concentrated hydrochloric acid. The product

was extracted with three 30 mL portions of diethyl ether. The organic layers were combined, dried over anhydrous magnesium sulfate and the solvent removed by rotary evaporation to yield 0.60 g (20%) of an oil which crystallized to clear needles upon standing. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.15-7.35 ppm (broad multiplet, 5 H); 2.88-3.00 ppm (d of t, J = 4.1 Hz, 7.7 Hz); 2.60-2.71 ppm (apparent q, J = 7.5 Hz). Mass spectrum 151 (31), 105 (17), 104 (59), 103 (13), 91 (100), 79 (12), 78 (20), 77 (23), 65 (17), 51 (25), 50 (11), 46 (18).

Synthesis of 1-^{13}C-indanone from 166

The acid chloride prepared from 0.60 g (4.0 mmol) of labeled acid 166 was cyclized to the labeled indanone with trifluoromethanesulfonic acid using the procedure of Hulin and Koreeda (63) in 73% (0.38 g) crude yield and was used without purification in the next step.

Synthesis of 3-^{13}C-indene 168 from 167

1-^{13}C-indanone was converted to 3-^{13}C-indene using the method of Braun and Bernard (64) to yield 0.35 g isolated 168 (75% yield from 166). Mass spectrum 117 (90), 116 (100), 90 (16), 64 (19), 63 (24), 58 (19), 51 (14). The mass spectrum of the labeled indanol is an follows 135 (45), 134 (91), 118 (21), 117 (74), 116 (100), 91 (34), 77 (68), 63 (61), 58 (35), 56 (35), 59 (53).

FVP of 168

i. A sample of $3-^{13}C$-indene, 42 mg, was vacuum distilled through an 800°C quartz tube at a pressure of 3 x 10^{-5} mm Hg. The pyrolysate, 34 mg (81% mass recovery), was analyzed in the same manner as the pyrolysate of $3-^{13}C$-1-phenylpropyne. ^{13}C (75 MHz, CDCl$_3$) 39.02 (12.00), 120.89 (0.26), 123.64 (0.24), 124.47 (0.30), 126.15 (0.27), 131.99 (10.99), 132.44 (0.15). The integration of the carbon peaks is tabulated as follows:

Carbon	Peak Area
1	11.942
2	0.148
3	8.800
4	0.217
5	0.272
6	0.296
7	0.237

The ^{13}C-label was found in the following amounts in the indene molecule:
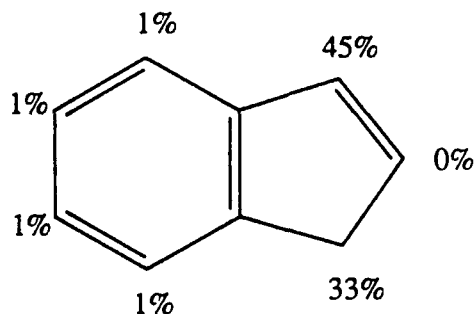
ii. A sample of 3-^{13}C-indene, 26 mg, was vacuum distilled through a 895°C quartz tube at a pressure of 1 x 10^{-4} mm Hg. The pyrolysate, 23 mg (88% mass recovery) was analyzed in the same manner as the pyrolysate of 3-^{13}C-1-phenylpropyne. ^{13}C (75 MHz, CDCl$_3$) 39.05 (7.54), 120.90 (1.44), 123.65 (1.50), 124.47 (1.64), 126.16 (1.63), 131.99 (12.00), 134.10 (1.20), 143.60 (0.56), 144.76 (0.19). Mass spectrum 118 (7.5), 117 (91), 116 (100), 90 (13), 89 (7.0), 64 (13), 63 (17), 58 (19). The integration of the carbon peaks is tabulated as follows:

Carbon	Peak Area
1	15.200
2	1.370
3	12.066
4	1.402
5	1.670
6	1.523
7	1.447
8	0.165
9	0.290

The ^{13}C-label was found in the following amounts in the indene molecule:
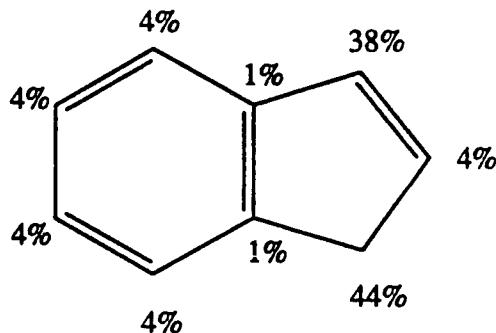
Synthesis of 1-^{2}H-indene 183

1-Indenyllithium, prepared via the method of Rakita and
Davison (27) from 3.009 g indene (25.9 mmol) and 10 mL of
2.5 M n-butyllithium, was quenched with deuterium oxide.
The mixture was washed with three 10 mL portions of
distilled water, dried over anhydrous magnesium sulfate, and
the solvent removed by rotary evaporation to yield 1.266 g
product (42% isolated yield). Mass spectrum 118 (20), 117
(100), 116 (91), 115 (14), 90 (8.9), 89 (6.5), 64 (6.1), 63
(9.2), 62 (4.6), 58 (8.7). ^{1}H NMR (300 MHz, CDCl$_3$) δ
7.10-7.50 ppm (broad mult., 4 H); 6.85-6.95 (broad d, 1 H;
6.50-6.57 ppm (broad d, 0.98 H); 3.35-3.45 ppm (broad s,
1.24 H). ^{2}H NMR (46 MHz, CHCL$_3$) δ 3.5 ppm (d, J = 4.0 Hz,
0.93 D); 7.0 ppm (s, 0.07 D).

FVP of 183

i. 1-Deuteroindene, 116 mg, was vacuum distilled
through a 700°C quartz tube at a pressure of 2 x 10^{-4} mm Hg.

The pyrolysate (99 mg, 85% mass recovery) was analyzed by ^{2}H NMR and mass spectrometry. ^{2}H NMR (46 MHz, $CHCL_3$) δ 7.1-7.8 ppm (4 s, 0.046 D); 6.5-7.1 ppm (2 s, 0.471 D), 3.5 ppm (d, J = 4 Hz, 0.483 D).

ii. 1-Deuteroindene, 47 mg, was vacuum distilled through a 805°C quartz tube at a pressure of 5 x 10 $^{-5}$ mm Hg. The pyrolysate (44 mg, 94% mass recovery) was analyzed by ^{2}H NMR and mass spectrometry. ^{2}H NMR (46 MHz, $CHCL_3$) δ 7.1-7.8 ppm (4 s, 0.347 D); 6.5-7.1 ppm (2 s, 0.333 D), 3.5 ppm (d, J = 4 Hz, 0.320 D). Mass spectrum 118 (20), 117 (100), 116 (90), 115 (14), 90 (8.9), 89 (6.1), 64 (6.2), 63 (9.1), 62 (4.6), 58 (7.8).

iii. 1-deuteroindene, 27 mg, was vacuum distilled through a 900°C quartz tube at a pressure of 5 x 10^{-5} mm Hg. The pyrolysate (44 mg, 94% mass recovery) was analyzed by ^{2}H NMR and mass spectrometry. ^{2}H NMR (46 MHz, $CHCL_3$) δ 7.1-7.8 ppm (4 s, 0.347 D); 6.5-7.1 ppm (2 s, 0.333 D), 3.5 ppm (d, J = 4 Hz, 0.320 D). Mass spectrum 118 (20), 117 (100), 116 (90), 115 (14), 90 (8.9), 89 (6.1), 64 (6.2), 63 (9.1), 62 (4.6), 58 (7.8).

iii. 1-Deuteroindene, 27 mg, was vacuum distilled through a 900°C quartz tube at a pressure of 5 x 10^{-5} mm Hg. The pyrolysate (26 mg, 96% mass recovery) was analyzed by ^{2}H NMR and mass spectrometry. ^{2}H NMR (46 MHz, $CHCL_3$) δ 7.1-7.8 ppm (4 s, 0.506 D); 6.5-7.1 ppm (2 s, 0.256 D), 3.5 ppm (d,

J = 4.Hz, 0.238 D). Mass spectrum 118 (24), 117 (100), 116 (93), 115 (19), 90 (9.4), 89 (6.7), 64 (6.4), 63 (10.1), 62 (4.7), 58 (9.7).

A mass spectrometry experiment was performed on the unpyrolyzed material and the pyrolysates from the 805°C and 900°C experiments. The average peak heights from at least three mass spectra runs were tabulated and the results for the largest peaks - namely the 115, 116, 117, and 118 masses - were compared. The change in the ratios of these peaks shows that a maximum value for non-deuterated material and dideuterated material is 0.2% for the 805°C experiment and 2.5% for the 900°C experiment.

Masses	Unpyrolyzed	805°C Sample	900°C Sample
115	13.50	13.90	18.57
116	91.21	90.41	92.67
117	100.00	100.00	100.00
118	19.86	19.97	24.21

Preparation of 0.116 M solution of sodium deuteroxide

Sodium metal, 0.266 g (11.6 mmol), was cautiously added to a beaker containing 100 mL deuterium oxide. After the reaction had stopped, the solution was transferred to a

stoppered bottle and used as needed without further purification.

Synthesis of trideuteromethyl phenyl ketone 194

Acetophenone, 7.656 g (63.7 mmol), was mixed with 10 mL of a 0.116 M solution of sodium deuteroxide in deuterium oxide and allowed to stir for six hours. This procedure was repeated three times -- each time discarding the spent aqueous layer and replacing with fresh. After the last six hours, the old layer was replaced with 10 mL deuterium oxide and stirred to remove any residual base. This was repeated once. The organic layer was separated and dried over anhydrous magnesium sulfate. The product was filtered from the drying agent to yield 5.986 g (76% yield) pure trideuteromethylphenylketone. The 300 MHz ^{1}H NMR (CDCl$_3$) agrees in every way with that of acetophenone except that the methyl signal is greatly reduced. Integration of the methyl proton versus the para-hydrogen of the phenyl ring shows that this deuteration experiment was 98.5% effective. ^{2}H NMR (46 MHz, acetone) δ 2.4 ppm (s).

Synthesis of 1,2,2,2-tetradeutero-1-phenylethanol 195

To a stirred suspension of 1.03 g (24.5 mmol) lithiumtetradeuteroaluminate in THF cooled to -78 °C was slowly added 5.174 g (42.0 mmol) of trideuteromethylphenyl-ketone. The solution was slowly allowed to come to room

temperature over the next three hours and 5 mL saturated
ammonium chloride was added along with 30 mL diethyl ether.
The layers were separated and the organic layer was washed
with two 5 mL portions of distilled water. The organic
layer was dried over anhydrous sodium sulfate and the
solution filtered from the drying agent. The solvent was
removed by rotary evaporation to yield 4.435 g (84%)
isolated alcohol $\underset{\sim\sim\sim}{218}$. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.1-7.4 ppm
(broad mult., 5 H); 1.76 ppm (s, 1 H). ^{2}H NMR (46 MHz,
acetone) δ 4.9 ppm (s, 1 D); 1.2 ppm, (s, 3 D).

Preparation of anhydrous copper sulfate

A 66.53 g (0.2665 mol) sample of copper sulfate
pentahydrate was placed in a porcelain dish and heated in a
muffle furnace between the temperatures of 200°C and 330°C
for four hours. While the heating process took place, the
solid material was stirred every 0.5 hr. After the four
hours of heating, the weight of the material showed a loss
equivalent to the weight loss of five moles of water per
mole of CuSO$_4$·5H$_2$O. The light, blue-gray powder, 42.50 g
(100% yield), was stored in a stoppered bottle in a
dessicator.

Synthesis of α,β,β-trideuterostyrene $\underset{\sim\sim\sim}{196}$

Alcohol $\underset{\sim\sim\sim}{195}$, 1.049 g (8.312 mmol), was converted
into α,β,β-trideuterostyrene using anhydrous copper sulfate

following the procedure of Hoffman et al. (68). Isolated

yield was 327 mg (37%). ^{2}H NMR (46 MHz, acetone) δ 6.68 ppm

(s, 1 D); 5.70 ppm (s, 1 D), 5.20 ppm (s, 1 D). Mass

spectrum 107 (100), 106 (35), 105 (17), 81 (20), 80 (37), 79

(33), 53 (22), 52 (38), 51 (39), 50 (25), 40 (15), 39 (19),

38 (12).

FVP of 196

i. A sample of α,β,β-trideuterostyrene, 61 mg, was

vacuum distilled through an 805°C quartz tube at a pressure

of 1 x 10^{-4} mm Hg. The pyrolysate, 60 mg (98% mass

recovery), was analyzed by ^{2}H NMR. The 46 MHz ^{2}H NMR was

identical to that of the unpyrolyzed material.

ii. A sample of α,β,β-trideuterostyrene, 113 mg, was

vacuum distilled through a 900°C quartz tube at a pressure

of 4 x 10^{-4} mm Hg. The pyrolysate, 107 mg (95% mass

recovery), was analyzed by ^{2}H NMR. The 46 MHz ^{2}H NMR was

identical to that of the unpyrolyzed material.

Synthesis of α-deuterotoluene 198

A solution of 2.85 g (22.5 mmol) of benzyl chloride in 5

mL diethyl ether was slowly added to a round bottom flask

containing 0.63 g (26.0 mmol) magnesium turnings in 10 mL

diethyl ether. After the reaction had subsided, the

grignard was quenched with 1.0 g deuterium oxide. The

reaction was allowed to stir for one hour before adding

concentrated hydrochloric acid to hydrolyze the excess magnesium and the magnesium salts. The layers were separated and the organic layer was washed three times with 10 mL portions of distilled water. The organic layer was dried over anhydrous magnesium sulfate, filtered from the drying agent, and the solvent removed by rotary evaporation. The product was separated from the bibenzyl impurity by bulb-to-bulb vacuum distillation at room temperature. ^{2}H NMR (46 MHz, acetone) δ 2.49 ppm (s). Mass spectrum 93 (64), 92 (100), 66 (11), 65 (7), 64 (8), 63 (8), 51 (9).

FVP of 198

i. A sample of α-deuterotoluene, 83 mg, was vacuum distilled through a 800°C quartz tube at a pressure of 3 x 10^{-4} mm Hg. The pyrolysate, 81 mg (98% mass recovery), was analyzed by ^{2}H NMR to show no change between the starting material and the pyrolysate.

ii. A sample of α-deuterotoluene, 33 mg, was vacuum distilled through a 900°C quartz tube at a pressure of 4 x 10^{-4} mm Hg. The pyrolysate, 33 mg (100% mass recovery), ws analyzed by ^{2}H NMR to show no change between the starting material and the pyrolysate.

Synthesis of 4-deuterotoluene 209

A solution containing 10.50 g (61.39 mmol) 4-bromotoluene was slowly added to a round bottom flask

containing 1.70 g (69.92 mmol) magnesium turnings. When the reaction has subsided, 2.0 g deuterium oxide was added and the mixture was allowed to stir for one hour. Concentrated hydrochloric acid was added to hydrolyze the excess magnesium and the magnesium salts. The layers were separated and the organic layer was washed with three 10 mL portions of distilled water. The organic layer was dried over anhydrous magnesium sulfate, filtered from the drying agent, and the solvent removed by rotary evaporation. The product was removed from the impurity 4-4'-dimethylbiphenyl by bulb-to-bulb distillation at room temperature. ^{2}H NMR 7.125 ppm (apparent t, J = 1.072 Hz). ^{1}H NMR (300 MHz, d_6-acetone) δ 7.219 ppm (apparent d, J = 7.5 Hz, 2 H); 7.153 ppm (apparent d, J = 7.8 Hz, 2 H); 2.298 ppm (s, 3 H).

NMR study of octadeuterotoluene

An NMR study was done to demonstrate that 46 MHz ^{2}H NMR could distinguish between ortho-, meta-, and para-deuterotoluene. After conducting ^{1}H NMR experiments on oluene in various deuterated solvents, it was concluded that hexadeuteracetone separated the phenyl shifts of toluene the best. A ^{2}H NMR experiment of octadeuterotoluene in acetone showed three phenyl shifts: 7.22 ppm (s, 2 D); 7.15 ppm (s, 2 D); 7.12 ppm (s, 1 D). These shifts were easily separated and it was concluded that the three isomers of deuterotoluene could probably be separated by this method.

FVP of 209

i. A sample of 4-deuterotoluene, 192 mg, was vacuum distilled through an 803°C quartz tube at a pressure of 4 x 10^{-4} mm Hg. The pyrolysate, 186 mm Hg (97% mass recovery), was analyzed by ^{2}H NMR and ^{1}H NMR to show no change between the pyrolysate and the starting material.

ii. A sample of 4-deuterotoluene, 217 mg, was vacuum distilled through a 902°C quartz tube at a pressure of 8.5 x 10^{-4} mm Hg. The pyrolysate, 204 mm Hg (94% mass recovery), was analyzed by ^{2}H NMR and ^{1}H NMR to show no change between the pyrolysate and the starting material.

Synthesis of trans-cinnamyl chloride

To a flask containing 13.9 g trimethylchlorosilane (128 mmol) was slowly added 16.40 g (122 mmol) trans-cinnamyl alcohol. After stirring for one hour, the product was separated from the excess trimethylchlorosilane by vacuum distillation to yield 12.0 g (65%) trans-cinnamyl chloride. Identification was made by comparison of ^{1}H NMR mass spectrum with that of authentic material.

Synthesis of trans-β-(deuteromethyl)-styrene

To a suspension of 0.48 g (45.7 mmol) lithium tetrahydroaluminate in 30 ml THF cooled to -78°C was slowly added 4.36 g trans-cinnamyl chloride. The mixture was allowed to come to room temperature and stir one additional hour.

After quenching with distilled water and extracting the organic product, much of the starting material remained. The mixture of product and starting material was redissolved in THF and treated with 1.20 g lithiumtetrahydroaluminate and the mixture refluxed for three hours. After aqueous workup, the trans-β-(deuteromethyl)-styrene was isolated in 82% yield (2.5 g). ^{1}H NMR (300 MHz, d_6-acetone) δ 7.3-7.4 ppm (d, J = 7.6 Hz, 2 H); 7.2-7.3 ppm (apparent t, J = 7.8 Hz, 7.2 Hz, 2 H); 7.1-7.2 ppm (apparent t, J = 7.1 Hz, 7.2 Hz, H); 6.41 ppm (d, J = 15.8 Hz, 1 H); 6.27 ppm (d of t, J = 15.8 Hz, 6.3 Hz, 1 H); 1.78-1.86 ppm (broad mult., 2 H). Mass spectrum 119 (71), 118 (100), 117 (16), 116 (34), 115 (12), 93 (19), 92 (35), 91 (24), 77 (16), 51 (15).

FVP of trans-β-(deuteromethyl)-styrene

i. A sample of trans-β-(deuteromethyl)-styrene, 49 mg, was vacuum distilled through a 703°C quartz tube at a pressure of 2 x 10^{-4} mm Hg. The pyrolysate, 44 mg (88% mass recovery), was analyzed by ^{2}H NMR. A very small amount of deuterium was present in the phenyl region of the ^{2}H NMR.

ii. A sample of trans-β-(deuteromethyl)-styrene, 45 mg, was vacuum distilled through an 800°C quartz tube at a pressure of 6 x 10^{-4} mm Hg. The pyrolysate, 42 mg (93% mass recovery), was analyzed by ^{2}H NMR. Approximately 10% of the ^{2}H signal was present in the phenyl region of the ^{2}H NMR.

iii. A sample of trans-β-(deuteromethyl)-styrene, 80 mg, was vacuum distilled through a 900°C quartz tube at a pressure of 6 x 10^{-4} mm Hg. The pyrolysate, 67 mg (84% mass recovery), was analyzed by ^{2}H NMR. Approximately 50% of the ^{2}H signal was present in the phenyl region of the ^{2}H NMR. There were too many shifts in the phenyl region to identify the compounds present in the pyrolysate. Gas chromatography showed that there was more than one compound present.

FVP of trans-β-methylstrene 211a

i. A sample of 211a, 73 mg, was vacuum distilled through a 700°C quartz tube at a pressure of 2.5 x 10^{-5} mm Hg. The pyrolysate, 69 mg (95% mass recovery), was analyzed by GC and 300 MHz ^{1}H NMR to show a 23% conversion to cis-β-methylstyrene.

ii. A sample of 211a, 72 mg, was vacuum distilled through an 800°C quartz tube at a pressure of 2 x 10^{-4} mm Hg. The pyrolysate, 71 mg (99% mass recovery), was analyzed by GC and 300 MHz ^{1}H NMR to show a 31% conversion to the following products: cis-β-methylstyrene, 28%; indene, 1%; styrene, 1%; and unidentifiable isomer of starting material, 1%.

iii. A sample of 211a, 86 mg, was vacuum distilled through a 900°C quartz tube at a pressure of 6 x 10^{-4} mm Hg. The pyrolysate, 72 mg (84% mass recovery), was analyzed by GC and 300 MHz ^{1}H NMR to show a 58% conversion to the

following products: cis-β-methylstyrene, 19%; indene, 15%; styrene, 14%; an unidentifiable isomer of starting material, 7%.

Synthesis of 1-trimethylsilylindene

1-trimethylsilylindene was prepared by the method of Rakita and Davison (27) and purified by preparatory GC. ^{1}H NMR (300 MHz, d_6-acetone) δ 7.1-7.5 (two complex multiplets, 4 H); 6.9 ppm (d of d, J = 5.4 Hz, 1.2 Hz, 1 H); 6.7 ppm (d of d, J = 5.3 Hz, 1.9 Hz, 1 H); 3.6 ppm (s, 1 H); -0.05 ppm (s, 9 H). Mass spectrum 188 (8), 173 (2), 115 (12), 75 (5), 74 (11), 73 (100), 45 (18), 43 (10).

Pyrolysis of 1-trimethylsilylindene

1-trimethylsilyl indene was vacuum distilled through a 600°C quartz tube at a pressure of 1 x 10^{-5} mm Hg. Analysis by ^{1}H NMR and GC/MS showed the presence of 3-dimethylsilyl-indene and another isomeric compound which could not be identified or separated from the reaction mixture.

Higher temperatures (650°C, 700°C) yielded the decomposition products indene and m/e 130 products mentioned in earlier research.

Copyrolysis of 1-methoxypentamethyldisilane 221 and allene 10

Ninety-seven mg of 221 was pyrolyzed through a 475°C quartz tube with 30 mL/min allene as the carrier gas. No

silicon containing products other than methoxytrimethyl-
silane were observed by GC/MS.

SFR pyrolysis of 221 and 10

i. SFR pyrolysis of 0.5 torr 221 and 5.0 torr 10 at
475°C yielded only methoxytrimethylsilane and the insertion
product of dimethylsilylene into starting material.
Identification was made by mass spectrometry.

ii. Repeat of i with 0.5 torr 221 and 50 torr 10 did
not change the results.

SFR pyrolysis of 221 and trimethylsilylacetylene

475°C SFR pyrolysis of 0.5 torr 221 and 5.0 torr
trimethylsilylacetylene yielded dimethylsilyltrimethyl-
silylacetylene by mass spectrometry demonstrating that
dimethylsilylene can be trapped under these conditions.

SFR of 221 and 1,2-butadiene

0.5 torr 221 and 5.0 mm 1,2-butadiene yielded an adduct
of m/3 112 by mass spectrometry. Mass spectrum 112 (5), 97
(40), 73 (20), 72 (18), 71 (40), 70 (18), 59 (100), 58 (40),
55 (22), 53 (22).

Copyrolysis of 223 and 3-methyl-1,2-butadiene 224

Copyrolysis of 373 mg 1,2-dimethoxytetramethyldisilane
and 1.254 g 3-methyl-1,2-butadiene yielded 39%
dimethyldimethoxysilane and 31% 2-dimethylsilyl-3-methyl-

1,3-butadiene. ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.8 ppm (d, J = 2.06 Hz, 1 H); 5.5 ppm (s, 1 H); 5.06 ppm (s, 1 H); 5.04 ppm (q, J = 1.25 Hz, 1 H); 4.26 ppm (heptet, J = 3.7 Hz, 1 H); 1.90 ppm (s, 3 H); 0.22 ppm (d, J = 3.8 Hz, 6 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ -3.67 (59), 21.07 (53), 114.80 (63), 125.77 (100), 145.43 (40), 149.50 (19). Mass spectrum 126 (15), 112 (11), 111 (100), 109 (22), 85 (28), 83 (38), 73 (12), 71 (14), 69 (14), 67 (19), 59 (89), 58 (25), 55 (17), 53 (21), 45 (21), 44 (15), 43 (85), 42 (14), 41 (24). Exact mass calculated for C$_7$H$_{14}$Si (M$^+$) 126.08648, measured 126.08699. GCIR 3094, 2970, 2129 (strong), 1258, 895 (very strong). Anal. Calcd. for C$_7$H$_{14}$Si: C, 66.64; H, 11.18. Measured: C, 66.44; H, 11.37.

Synthesis of 1-^{2}H-1-trimethylsilylethylene 255

To a flask containing 1.985 g (81.7 mmol) magnesium turnings and 50 mL THF was added a solution of 11.850 g (66.0 mmol) 1-bromo-1-trimethylsilylethylene and 10 mL THF. After the reaction subsided, the grignard was quenched with 10 g (500 mmol) deuterium oxide and allowed to stir for one hour. Concentrated hydrochloric acid was added to hydrolyze the excess magnesium and the magnesium salts. The layers were separated and the organic layer was washed with three 10 mL portions of distilled water and dried over anhydrous magnesium sulfate. The drying agent was removed via filtration and the solvent removed by rotary evaporation to

yield 4.8 g (72%) 1-^{2}H-1-trimethylsilylethylene. Mass spectrum 101 (3.2), 87 (9.3), 86 (100), 73 (17), 60 (42), 59 (89), 45 (23), 43 (56). ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.87-5.95 ppm (overlapping d of t, J = 3.6 Hz, 2.4 Hz, 1 H); 5.62-5.67 ppm (overlapping d of t, J = 3.3 Hz, 3.3 Hz, 1 H); 0.05 ppm (s, 9 H).

Synthesis of 1-^{2}H-1-trimethylsilylcycloopropane 256 from 291

This procedure is an adaptation of Seyferth's synthesis of trimethylsilylcyclopropane from vinyltrimethylsilane (83). Cuprous chloride, 1.130 g (11.42 mmol), zinc dust, 6.950 g (10.63 mmol), and methylene iodide, 16.250 g (60.67 mmol), were mixed in a round bottom flask along with 15 mL di-n-butyl ether. The mixture was heated to reflux and cooled to 65°C. A few crystals of sublimed iodine were added and the purple color was allowed to dissipate. After 0.5 hour, 3.679 g (36.18 mmol) 1-deutero-1-trimethylsilyl-ethylene was added and the reaction was kept at 65°C for 27 hours. The liquid was simply distilled from the salts to yield 2.54 g 1-^{2}H-1-trimethylsilylcyclopropane (2.54 g, 61% yield) as a solution in di-n-butyl ether. The product was purified by preparatory gas chromatography as needed. ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.509 ppm (broad s, 2 H); 0.142 ppm (broad s, 2 H); -0.750 ppm (s, 9 H). ^{2}H NMR (46 MHz, CHCl$_3$) δ -0.42 ppm (s). Mass spectrum 100 (83), 73 (100), 72 (27), 60 (46), 59 (44), 45 (36), 43 (58).

FVP of 256

1-deutero-1-trimethylsilylcyclopropane, 44 mg, was vacuum distilled through a 700°C quartz tube at a pressure of 2×10^{-4} mm Hg. The pyrolysate, 41 mg (93% mass recovery), was analyzed by mass spectrometry and 46 MHz ^{2}H NMR. Mass spectrum 115 (2), 100 (70), 74 (10), 73 (100), 60 (8), 59 (10), 45 (29), 43 (28). ^{2}H NMR (46 MHz, $CHCl_3$) 5.85 ppm (broad s, approximately 95% of total deuterium signals); 1.50 ppm (broad s, approximately 5% of total deuterium signals.

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