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The synthesis and cationic rearrangements of novel

organosulfur and organosilicon systems

by

Roland Calvin Kippenhan, Jr.

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1973

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DEDICATION

To Nancy

PART I. THE SYNTHESIS AND REARRANGEMENTS OF
ORGANOSULFUR SYSTEMS

# HISTORICAL

## Sulfenium Ions

In the history of carbonium ion chemistry distinct stages
of development can be recognized. Initially, the trivalent,
positively charged carbon atom was proposed as a reactive par-
ticle to explain a collection of observations on displacement
reactions (1). This was followed by a period of mechanistic
work including stereochemical studies, spectroscopic studies,
and kinetic measurements in various solvents (2). In the
most recent stage of development, properly substituted car-
bonium ions such as the tropylium ion (3) have been isolated
and studied directly.

In contrast to the extensive investigations on carbonium
ions, very little was known about the analogous divalent elec-
tron deficient nitrogen species until the work of Gassman (4)
in 1962. Subsequent work established the nitrenium ion as a
useful intermediate resembling a carbonium ion but much more
reactive, as would be expected from its greater electro-
negativity. The electronegativity of sulfur is between that
of carbon and nitrogen and one might expect similar behavior
for a monovalent, electron deficient sulfur species, to be
referred to as the sulfenium ion. Although the sulfenium
ion concept has been in the literature for more than a quarter
of a century, very little mechanistic work has been done on

the nature of sulfenium ions or their solvated forms.

It was first suggested by Foss (5) in 1947 that sulfenic acid derivatives in reactions with nucleophilic reagents eliminate the sulfenyl group as a monovalent cation, RS$\overset{\oplus}{}$. Foss pointed out that a comprehensive study by Kharasch et al. (6) on sulfenic acid derivatives failed to recognize that reactions such as thiosulfonic acid esters, $RSSO_2R$, with cyanide or mercaptide ions might involve the monovalent sulfur cation.

The mechanism of thiaxanthone formation (<u>1</u>) from the condensation of dithiosalicylic acid (<u>2</u>) with benzene was shown by Archer and Suter (7) to involve the protonated dithiosalicylic acid <u>3</u>.
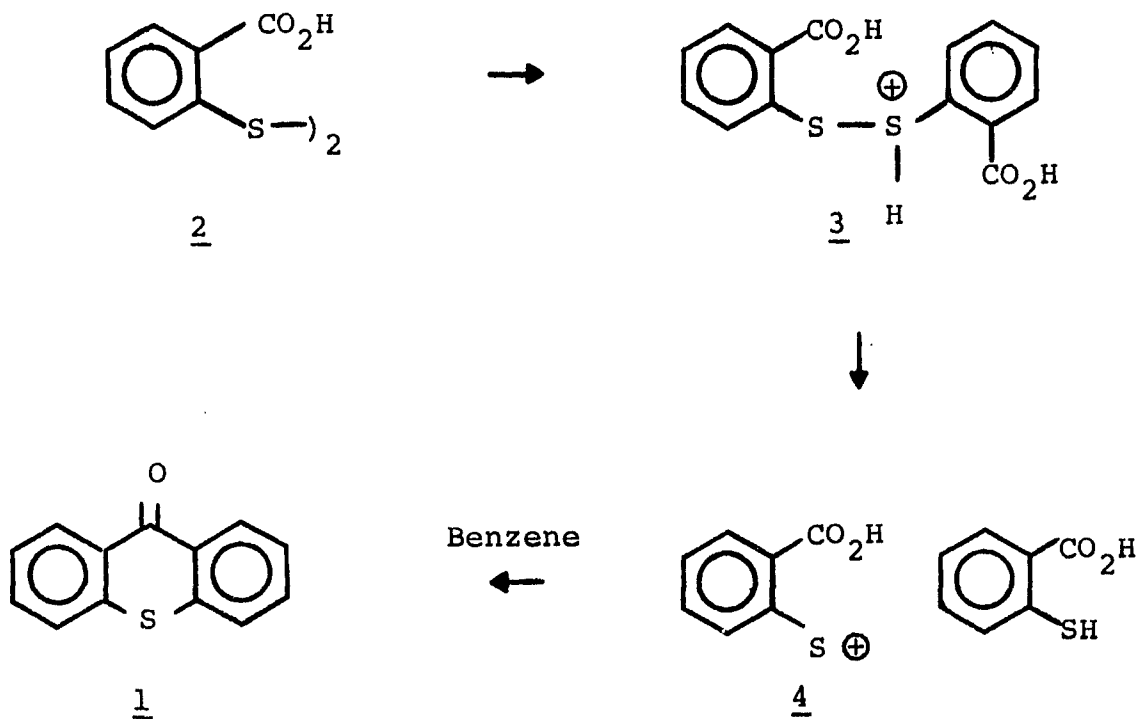
These authors commented that complete heterolysis of 3 would afford thiosalicylic acid and the ion 4 but were very hesitant to propose that the sulfur cation 4 had even a transitory existence because nothing was known about the behavior of such ions. A transitory existence of $RS^{+\cdot}$ was also proposed by Franklin and Lumpkin (8) in electron impact studies with thiols and disulfides.

In 1953 a historic work was published by Kharasch et al. (9) on the interaction of 2,4-dinitrobenzenesulfenyl chloride and sulfuric acid to form a red solution which he ascribed to the positive ion of sulfur and for which he suggested the name 2,4-dinitrobenzenesulfenium ion. Several lines of evidence were presented thereby removing the doubt that earlier workers had about the existence of this species. Kharasch proposed the following equilibrium for the formation of the sulfenium ion.



5                                    6
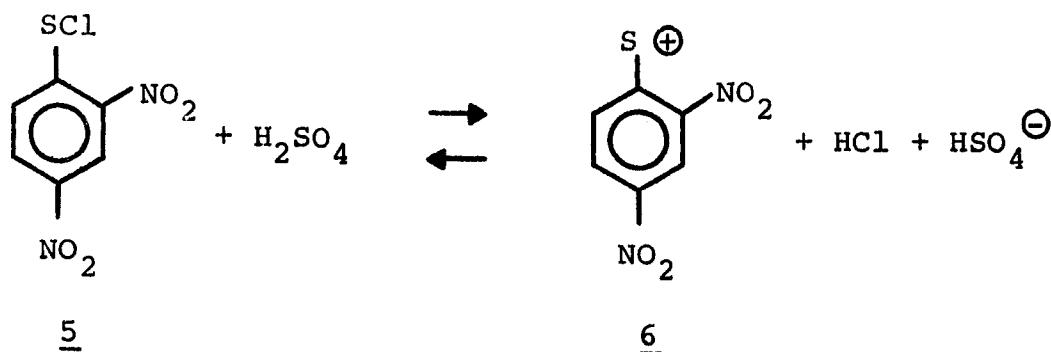
The formation of a bright red solution with the evolution of
hydrogen chloride upon dissolution of the yellow sulfenyl
chloride 5 pointed to the cleavage of the sulfur-chlorine
bond. Addition of bisulfite or dry hydrogen chloride to
dilute solutions of 5 in sulfuric acid entirely repressed the
development of the red color; this was corroborated by the
absorption spectrum, which was characteristic of 6 rather
than the red solution of 5 in sulfuric acid. It was found
that this red solution could also be generated by treating
solutions of 5 in dry ethylene chloride with aluminum
chloride or silver perchlorate. Additional evidence was the
migration of the red color to the cathode in electrolysis
experiments. Cryoscopic measurements were also consistent
with a sulfenium ion.

Since the work of Kharasch on the 2,4-dinitrobenzene-
sulfenium ion, sulfenium ions have been postulated in many
reactions (10). One example of the role of sulfenium ions is
found in an investigation of the mechanism of disulfide
interchange in acid solution (11),

RSSR + R'SSR' → 2 RSSR'

where the disulfides studied were cystine and bis-DNP cystine.
It was found that in neutral or basic solutions the addition
of a thiol increased the rate of reaction, but that in acidic

media the addition of thiols suppressed the interchange. This data is consistent with the sulfenium ion mechanism in acid solution, where addition of external thiol would lower the concentration of $RS^{\oplus}$ (Equation 3) and inhibit exchange.

1) initiation $\quad RSSR \quad + \quad H^{\oplus} \rightarrow RS^{\oplus} + RSH$

2) interchange $\quad RS^{\oplus} + \quad R'SSR' \rightarrow RSSR' \quad + R'S^{\oplus}$

3) inhibition $\quad RS^{\oplus} + \quad R'SH \rightarrow RSSR' \quad + H^{\oplus}$
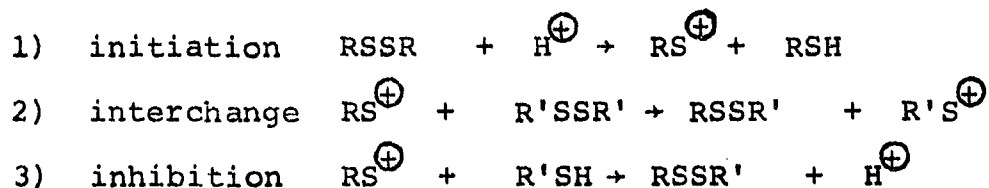
The rate of interchange was extremely sensitive to acid concentration. A number of substances regarded as precursors of sulfenium ions were found to catalyze the reaction including trichloromethanesulfenyl chloride and 2,4-dinitrobenzenesulfenyl chloride.

Only recently have attempts been made to generate sulfenium ions in organic solvents and to use them for synthetic purposes. Helmkamp and Owsley (12) have made use of "methane sulfenium ions" 7 prepared from the reaction of methanesulfenium bromide and silver benzenesulfonate in nitromethane or acetonitrile. The resultant species was trapped by cyclooctene to form an episulfonium salt 8 or by a sulfide to form an alkylated disulfide 9.

The covalency of the sulfur ligand bond is of greatest importance in these investigations. Conductivity studies of the "methane sulfenium ion" indicated an ionic character only when acetonitrile was used as a solvent, and it was suggested

$$MeBr \quad + \quad AgL \quad \rightarrow \quad AgBr \quad + \quad \overset{\oplus}{Me}S \; \overset{\ominus}{L}$$

$$\underline{7}$$

L = Trinitrobenzene Sulfonate

$$MeS\overset{\oplus}{} \quad + \quad Cyclooctene \quad \rightarrow$$



$$\underline{8}$$

$$MeS\overset{\oplus}{} \quad + \quad R_2S \quad \rightarrow \quad R_2S \; SMe$$
$$\overset{\oplus}{} \; \overset{\ominus}{L}$$

$$\underline{9}$$
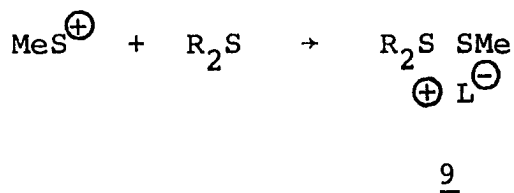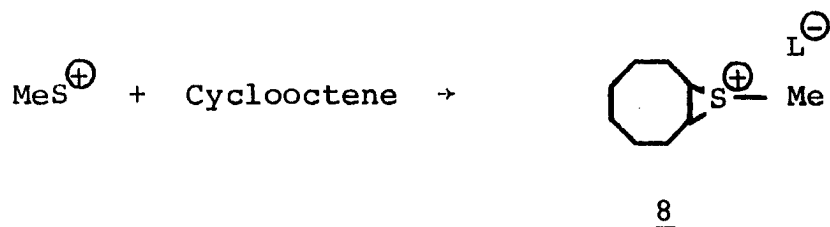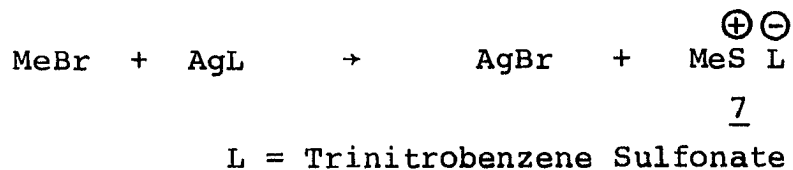
that the ion was coordinated with acetonitrile. In the absence of acetonitrile very low conductivities were observed, suggesting that the bonding is more covalent than ionic. Helmkamp concluded that he was dealing with a sulfenium ion transfer agent rather than a free ionic sulfenium ion. The nmr spectrum in nitromethane showed sharp lines for all protons which was taken as evidence for a singlet state, because a paramagnetic species would have caused line broadening. A chemical shift of $\delta$ 2.8 for the methyl protons also was consistent with covalent character. For comparison a methyl group alpha to a carbonium ion in

$HSO_3F-SbF_5$ is seen at $\delta$ 3.8 (13) and a methyl group alpha to a protonated thiol is observed at $\delta$ 3.0 (14).

Owsley and Helmkamp (15) have prepared a benzenesulfenium ion and have obtained evidence of its reaction with molecular nitrogen. Benzenesulfenyl bromide was treated with silver trinitrobenzenesulfonate in a nitrogen stream to isolate a crude impure nitrogen adduct. Elemental analysis and spectral data do show that the nitrogen has been incorporated, but the structure and bonding of this species remains to be determined. Additional evidence for sulfenium ions is found in the addition reactions of sulfenium halides to alkenes and alkynes, presented in the next section.

## Addition of Sulfenyl Halides to Alkenes and Alkynes

An examination of the products of the reaction of sulfenyl halides with unsaturated compounds suggests that the initial addition of $RS^{\oplus}$ is followed by attack of $Cl^{\ominus}$ and as such might proceed through a carbonium ion intermediate similar to other additions of HX. Early studies (16), however, on $\beta$-halo sulfides showed that sulfur has a very strong neighboring group effect. It was suggested that these reactions were different from the additions of HX to olefins in that a discrete intermediate, the thiiranium ion 10 or episulfonium ion was involved (17, 18).

R
|
S⊕



10
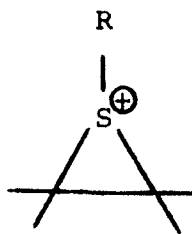
Evidence for the thiiranium ion was obtained in a study of sulfenyl halide additions to cis- and trans-2-butene (19). The products were analyzed and found to result from stereospecific trans addition to the double bond, and argued very strongly against open carbonium ions. Additional evidence for thiiranium ions as intermediates is found in recent studies in which stable crystalline thiiranium salts such as the cyclooctene methylsulfenium ion salt 8 have been isolated (12). A kinetic study of the reactions of aromatic sulfenyl halides with cyclohexene found a rho value of -0.714 when $\sigma^+$ constants were used. The correlation with $\sigma^+$ constants is consistent with charge development in the transition state and is good evidence for a thiiranium ion (20).

Although the trans mode of addition is well established (21), the orientation of the addition of sulfenyl halides to olefins is a more complicated area. The orientation will be referred to as "Markovnikov" or "anti-Markovnikov" by analogy to additions of HX to olefins. With terminal olefins steric factors are very important in controlling the product

distribution. The kinetic products formed in a study by
Mueller and Butler (22) were predominantly anti-Markovnikov
with the selectivity increasing with the size of alkyl
substituents.

Buess and Kharasch (23) reported that only Markovnikov
type products were formed with aryl olefins, but later
investigations showed that a post-isomerization was often
occurring (21). Kinetic products formed at lower temperatures
were missed when the reactions were carried out at room
temperature, and only the thermodynamic products were isolated.
Phenyl substituents on the olefin, particularly, complicate
the mechanism in that ring opening occurs at the benzylic
carbon leading to Markovnikov products.

A recent paper by Schmid et al. (24) investigated the
problem of mechanism in a careful study of the addition of
aromatic sulfenyl chlorides to cis- and trans-1-phenylpropene.
Addition to the cis-1-phenylpropene gave only threo-
Markovnikov 11 and threo-anti-Markovnikov products 12 while
trans gave only the erythro-Markovnikov product 13. This
can be contrasted with the additions of bromine and chlorine
to 1-phenylpropene which are completely nonstereospecific and
involve an open benzylic carbonium ion (25). The difference
in orientation of products from cis and trans-isomers can
be explained on the basis of steric crowding. The crowding
is more severe in the case of the thiiranium ion formed by
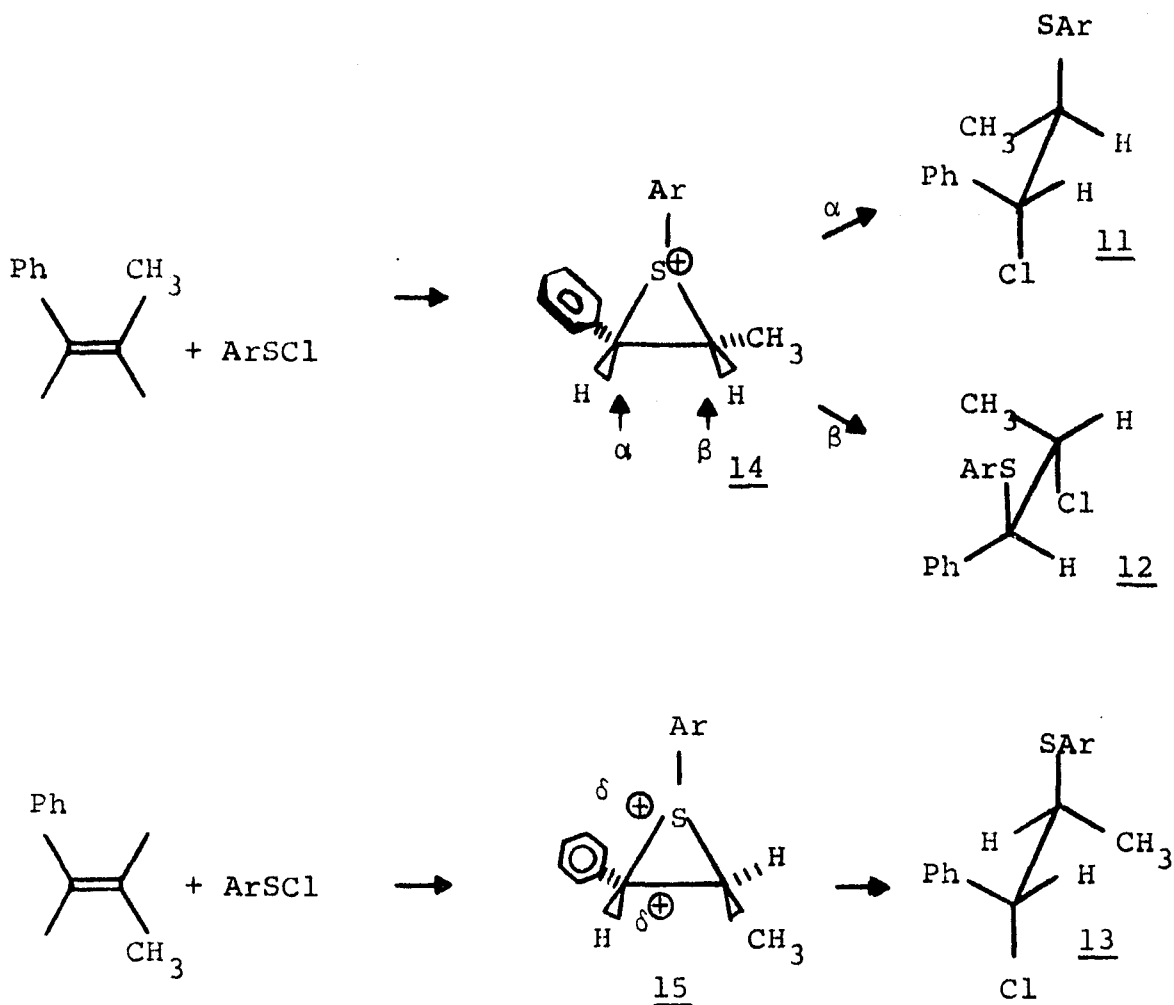
addition to the cis 14 than to the trans olefin 15. The

phenyl ring is now unable to rotate to a position such that

a positive charge on the benzylic carbon can be stabilized.

Therefore, attack on the carbons labelled α or β proceeds

through transition states of comparable energy and the mixture

of Markovnikov and anti-Markovnikov products is observed. In

the case of the trans olefin the transition state for attack

at the benzylic carbon is stabilized by the phenyl ring which

is now not restricted in its rotation, resulting in the formation of only the Markovnikov product. This steric crowding also affects the rate determining step in that the trans isomer reacts faster than the cis. Variable temperature nmr studies (26) show that at 146° some interconversion of threo and eryth o isomers takes place but suggests that there is a significant difference in activation energy for the formation of the open ion compared to the bridged ion.

In summary, the thiiranium ion is required in the rate determining step to explain the completely stereospecific reaction. Depending on the nature of the substituents, however, a significant amount of positive charge can reside on the adjacent carbon and will be very important in determining the product distributions.

Sulfur dichloride also undergoes addition to alkenes to form initially a β-chlorosulfenyl chloride (27). The mechanism is assumed to involve a chlorothiiranium ion, but detailed studies have been hampered by the competing reaction in which the sulfenyl chloride adds to another molecule of the alkene to form a β-chloro sulfide. Barton and Zika (28) found that sulfur dichloride and trans-stilbene in methylene chloride formed a 2:1 adduct 16. Using an excess of sulfur dichloride, reaction with trans-stilbene gave the β-chlorosulfenyl chloride 17 in which the stereochemistry is assumed to result from trans addition.

17

16
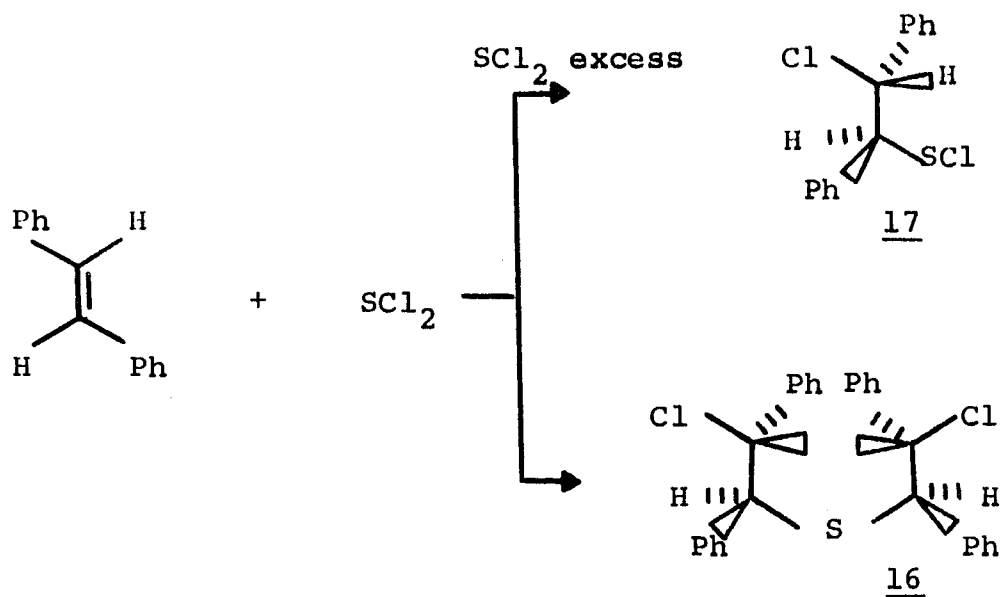
Sulfur dichloride additions to cyclic diolefins have also been investigated in the last five years as routes to novel heterocyclic systems (29). Norbornadiene undergoes endo attack through the endo-thiiranium ion intermediate 18 followed by attack of chloride to give the trans bridged dichloride 19. Similar transition states have been proposed in the transannular addition of sulfur dichloride to 1,4-cyclohexadiene (30) and 1,5-cyclooctadiene (31).

The reaction of sulfur dichloride with a linear diolefin was reported in 1967 by Lautenschlager (32). The size of



18                                    19
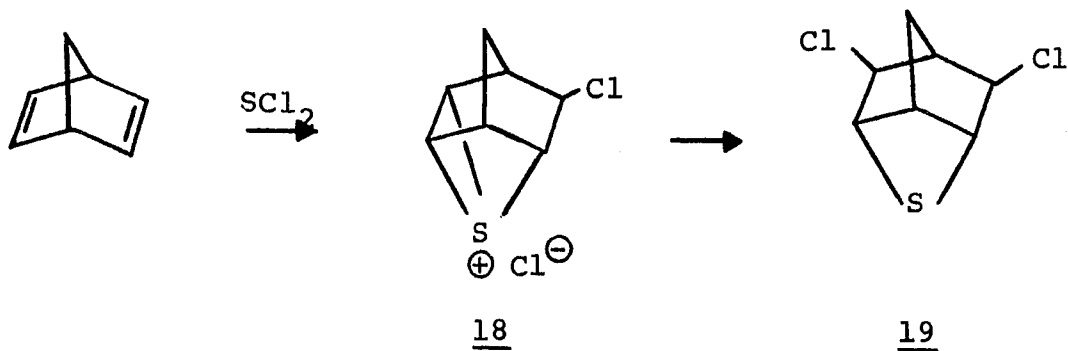
the resulting ring and its stereochemistry could be explained on the basis of thiiranium ion formation and the product determining ring opening mechanism, shown in Scheme 1. The addition of sulfur dichloride to 1,5-hexadiene was expected to proceed through both intermediates 20 and 21. Intramolecular attack on the second double bond would lead to the intermediates 22 and 23. Chloride attack at the least hindered carbon would then afford the five- and six-membered heterocycles 24 and 25. The cis-five membered heterocycle 24 was the only product isolated in this reaction and was explained by a post-isomerization of 25 through the ion 22 followed by chloride attack at the least hindered site to afford the thermodynamic product 24. No evidence was found, however, for the formation of the pre-isomerized products 25 and 26.

A mechanistic study of the addition of sulfenyl halides to terminal acetylenes was reported by Modena and Scorrano (33), who found only the trans anti-Markovnikov type of addition. The initial study of the electrophilic addition of sulfenyl halides to aryl acetylenes was done by Kharasch and Assony (34) who reported only Markovnikov products. These results were disputed by Calo et al. (35) and also by Schmid and Heinola (36).

Aromatic sulfenyl halides were found to add to acetylenes such as 1-phenyl propyne in an exclusive trans fashion (36).

Scheme 1



$\underline{20}$

$\underline{21}$

$\underline{22}$

$\underline{23}$

$\underline{24}$

$\underline{25}$

$\underline{26}$
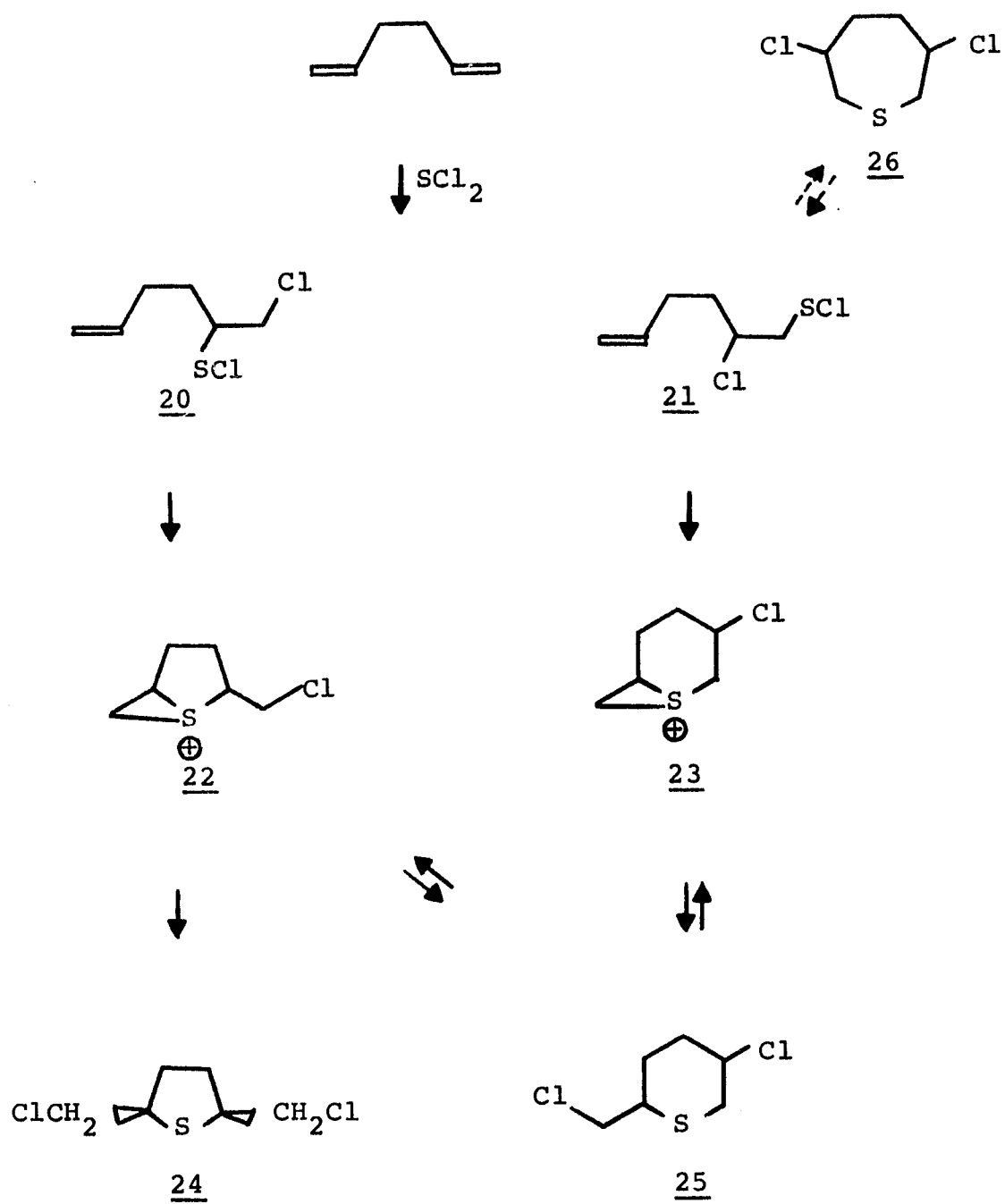
A detailed product analysis showed that the major orientation was Markovnikov, but that the anti-Markovnikov product was also formed. A second order rate expression was found, first order in both the sulfenyl halide and acetylene. The stereo-specific nature of addition, by analogy to the reaction with alkenes, implicates the thiirenium ion **27** as an intermediate.



Thiirenium ion         Thiovinyl cation
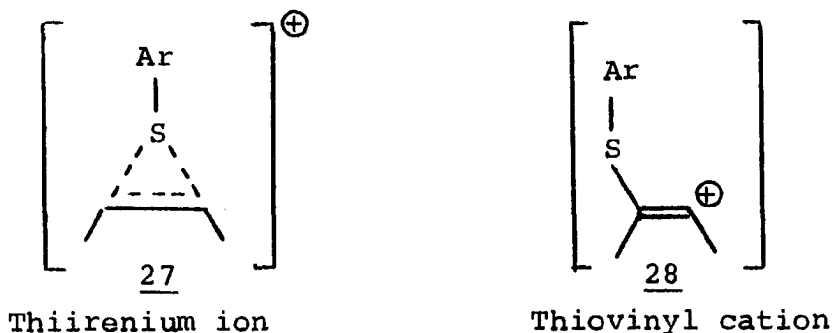
The high Markovnikov/anti-Markovnikov product ratio suggests that the thiirenium ion is not a symmetrical species for aryl acetylenes.

In contrast to the thiiranium ion, no examples of stable thiirenium ions have been isolated and much less is known about their chemistry. Denes et al. (37) have done a theoretical study on the relative stability of the β-thio-vinyl cation **28** and the thiirenium ion **27** using a SCF-MO calculation. The bridged thiirenium ion **27** was found to be 65.9 kcal/mole more stable than the linear ion **28** in contrast to protonated acetylenes in which the open cations were more stable than the bridged form by 18.5 kcal/mole.

Thiirenium ions have also been postulated as transient intermediates in solvolysis reactions (38). The trans-aryl thiovinyl sulfonate 29 was labelled with $^{14}C$ at the β carbon and solvolyzed. The isolated products showed that complete $^{14}C$ scrambling had occurred between the two ethylenic carbons,

$$Ar—S \underset{Ar}{\overset{Ar}{\diagdown}} C=C \underset{Ar}{\overset{OSO_2R}{\diagup}}$$

29
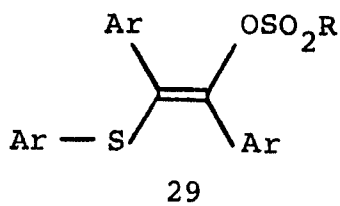
consistent with a thiirenium ion 27.

The precise nature of the thiirenium ion intermediate may vary with the type of substituents and with the solvating power of the medium. A π complex or various ion pairs with differing amounts of covalent character may be involved.

The first report of sulfur dichloride addition to alkynes appeared in 1961 with the work of Brandsma and Arens (39). Addition to an excess of propyne formed the symmetrical divinyl sulfide 30 where no stereochemistry was designated.

$$CH_3—\!\!\!\equiv\!\!\!—H + SCl_2 \longrightarrow \left( \underset{Cl}{\overset{CH_3}{\diagdown}} C=C \underset{H}{\overset{}{\diagup}} \right)_2 S$$

30
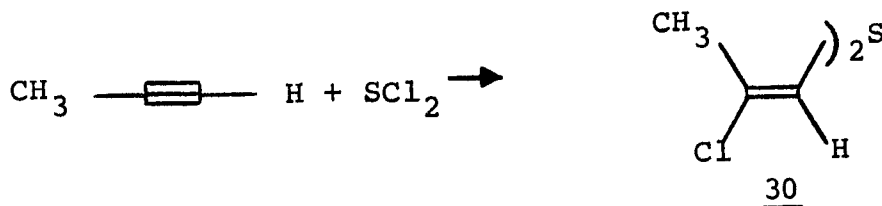
Barton and Zika (40) investigated the adducts of acetylenes and sulfur dichloride and found that under certain conditions it was possible to isolate an intermediate vinylsulfenyl chloride 31 without formation of the divinyl sulfide
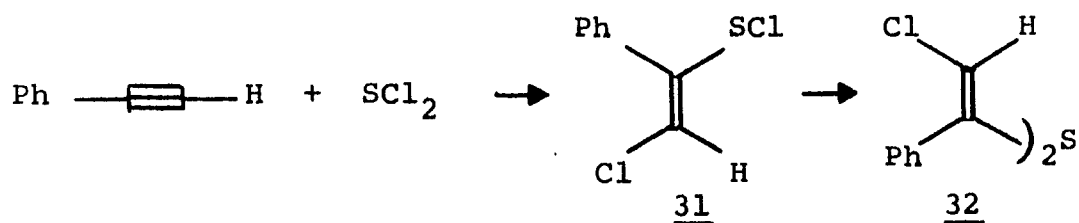


32. The stereochemistry of the reaction was assumed to be trans, and the orientation was mostly anti-Markovnikov. The results were explained on the basis of an initial complex formation which could be either a covalent 33 or ion paired 34 intermediate. Depending on the nature of the substituents
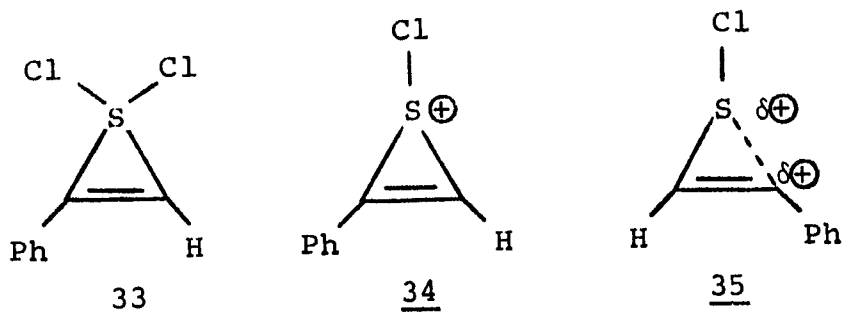


and the solvent an unsymmetrical intermediate 35 was also proposed. These results were surprising in view of the reports of Kharasch and Yiannios (41) that acetylenes are more reactive to sulfenyl halide attack than olefins. Presumably, the low reactivity of the chlorovinylsulfenyl halides is due to deactivation by the electronegative

chlorine group.

## Thiepin

Heterocyclic systems which do not fit the Huckel rule
have been a topic of great interest to organic chemists.
Seven-membered cyclic 8π systems in which the heteroatom is
nitrogen (azepin) and oxygen (oxepin) have been successfully
synthesized and quite well studied (42). The sulfur analog
(thiepin), however, has been more evasive, and until recently
only examples of annulated thiepins were known. In 1972
Dewar and Trinajstic (43) reported MO calculations in which
the thiepins were predicted to be antiaromatic. A severe
problem in the synthesis of thiepins is the facile extrusion
of sulfur which probably occurs from a thianorcaradiene
valence isomer 36 to give the corresponding benzene derivative
37 (44).

36          37
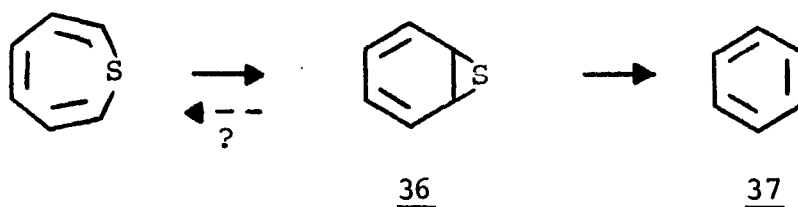
Although benzothiepins have been prepared, the synthetic
challenge remains to prepare the unsubstituted annulated
systems. The substituents often bias the ring system or
prohibit observations to be made on the physical properties

relating to aromaticity or antiaromaticity. The substituted benzo[b]thiepin ring system 38 has been examined by several workers. Neckers et al. (45) found that pyrolysis of a



39                                   38
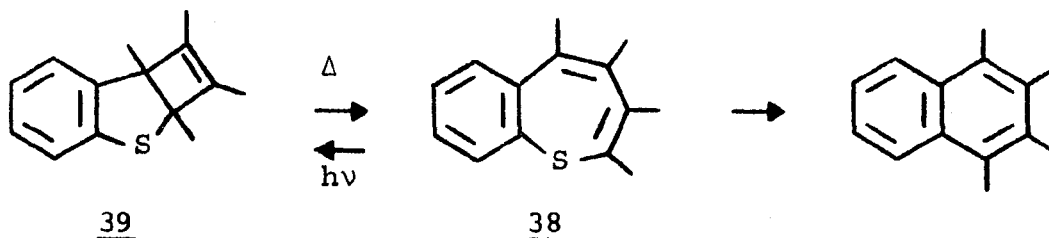
substituted thiabicyclo[3.2.0]heptadiene derivative 39 afforded substituted napthalene presumably via the thiepin 38. In 1972 Hofmann and Meyer (46) found that a substituted benzo[b]thiepin could be isolated and that photolysis closed the ring system to the thiabicyclo[3.2.0]heptadiene derivative 39.

Addition of sulfur dioxide to cis-hexatriene, followed by bromination and dehydrohalogenation afforded the first unsubstituted thiepin dioxide (47) 40. The thiepin 1,1-dioxide was found to be very easily hydrogenated and de-



40
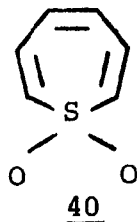
composed at 100° with formation of benzene and sulfur dioxide, indicating a conjugated triene with no benzenoid character.

X-ray studies (48) showed a boat conformation with bond lengths and angles typical of a cyclic polyene, although an nmr study (49) of inversion barriers suggested some conjugation might be present.

The first nonbenzo fused thiepin was prepared by Hoffman and Schlessinger (44), but a dihydrofuran ring was fused to the thiepin and complicated any conclusions on structure and bonding. Barton and co-workers (50) recently reported an attempt to prepare a totally unsubsituted thiepin by dehydrohalogenation of 3,4-dibromo-7-thiabicyclo[4.1.0]heptane. Although the intermediacy of a thiepin was a possibility, only sulfur extrusion products were isolated.

Recently, two groups of Dutch workers independently reported the first synthesis of a mono-cyclic thiepin. Helder and Wynberg (51) found that, contrary to organic textbook statements, thiophenes will undergo Diels-Alder reactions with activated dienophiles, shown in Scheme 2. Tetramethylthiophene reacted with dicyanoacetylene at 60-120° to give tetramethyl-phthalonitrile 41. A thiabicycloheptadiene 42 was proposed as an intermediate. Using an aluminum chloride catalyst (52), reaction was found to occur at room temperature, and the substituted thiepin 43 was reported. Heating in refluxing xylene gave the thiabicyclo[3.2.0]heptadiene 44 which when pyrolyzed at 300° again extruded sulfur to tetramethyl-phthalonitrile.

Scheme 2



DCA = NC —▭— CN



DMAD = MeO$_2$C —▭— CO$_2$Me
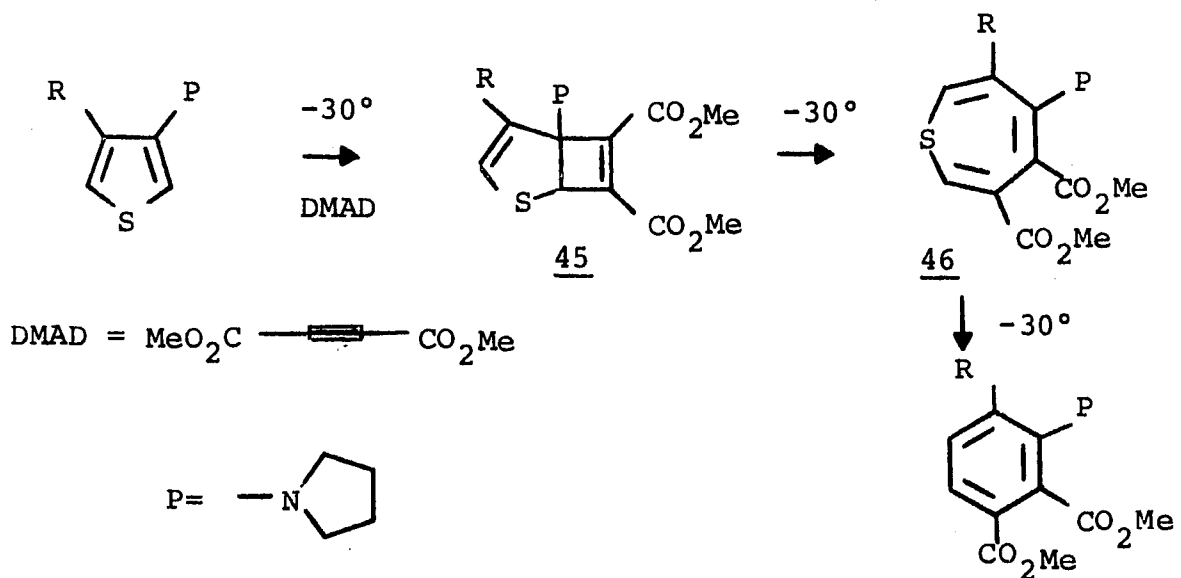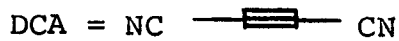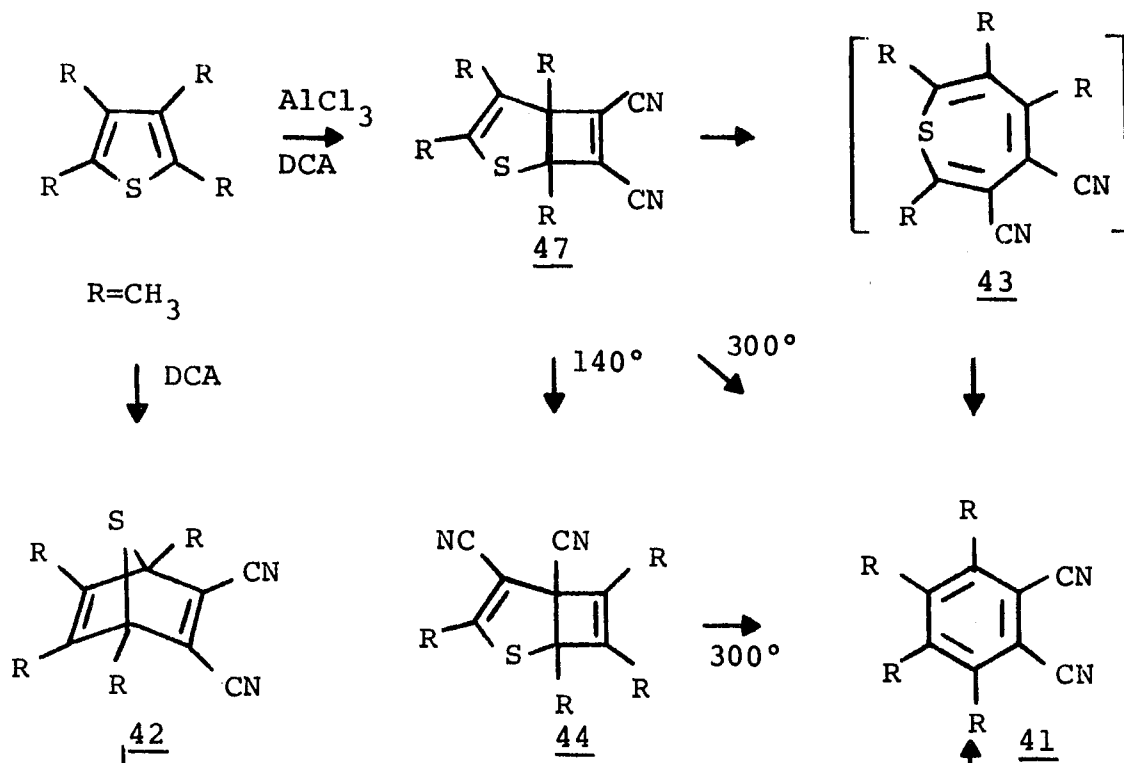
P= —N⟩ (pyrrolidine)

Reinhoudt and Kouwenhouven (53) investigated a cycloaddition of dimethylacetylene dicarboxylate with a pyrrolidino-thiophene at -30° by low temperature nmr and ir spectroscopy. The initially formed thiabicyclo[3.2.0]heptadiene 45 rearranged to the thiepin 46 which slowly extruded sulfur at -30°. The difference in stability of thiepins 43 and 46 motivated Reinhoudt et al. (54) to reinvestigate the work of Wynberg and Helder. $^{13}$C nmr spectra showed that 43 and 44 had the same structural skeleton with two bridgehead sp$^2$ carbon atoms and the initial adduct was therefore reassigned as 47, instead of the thiepin 43.

## RESULTS AND DISCUSSION

Previous workers in organosulfur chemistry sought to generate a stable monovalent, positively charged sulfur species, the sulfenium ion, in order to learn more about the nature of this cation in the chemistry of divalent sulfur. The problem of covalency in these species involving either a nucleophilic counterion or solvent molecules thwarted the success of these attempts. It seemed that a good approach to the problem would employ some nonnucleophilic counterion. A positive charge on sulfur might be further stabilized by an adjacent π center, but this would require the synthesis of a vinylsulfenyl halide as a convenient precursor. Recently a very general route to vinylsulfenyl halides has been reported utilizing sulfur dichloride and various acetylenes (40).

The motivation for generating a vinylsulfenium ion is summarized in Scheme 3. It was expected that the initial ion 48, a hetero allyliccarbonium ion, would be stabilized by contributions from the resonance form 49. Hydride transfer was expected to form the thiocarbonyl compound 50 either directly or by tautomerization of the vinyl mercaptan 51. A hydride abstraction by the rearranged cation 52 was considered as a route to thiiranes 53. Another possibility was to use a basic counterion such that a proton loss from the rearranged cation would provide a route to the thiirene ring system (55) 54 which is known only as a transient intermediate.

Scheme 3
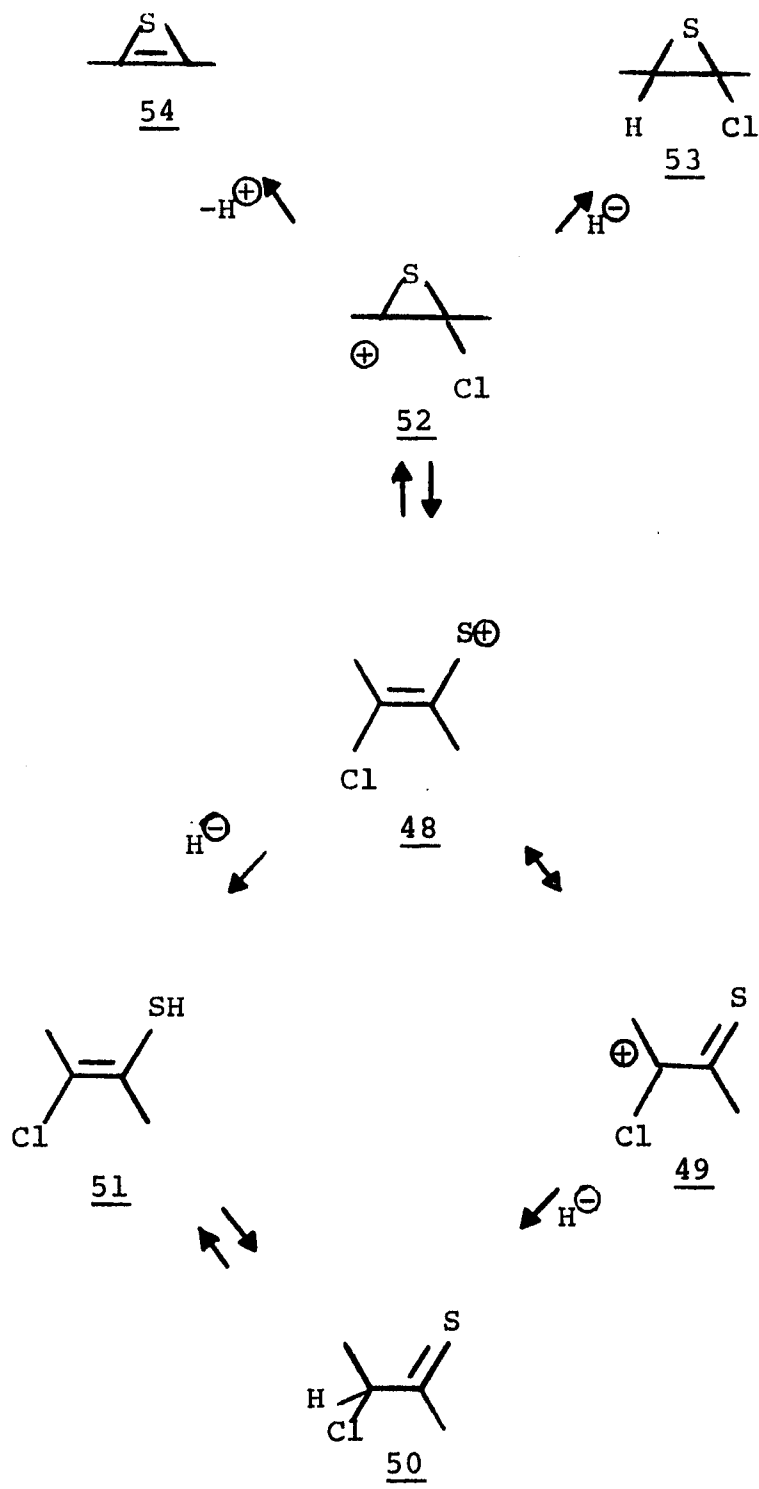
The acetylene chosen for our initial studies was tert-butyl acetylene which added sulfur dichloride under high dilution conditions to afford E-1-chloro-3,3-dimethylbut-1-enesulfen-2-yl chloride (55), shown in Scheme 4. The stereochemistry of the products is assumed to be trans and anti-Markovnikov on the basis of the analogous additions of sulfenyl halides to acetylenes outlined in the Historical Section.

The vinylsulfenyl halide was very unstable, and therefore characterization was carried out on bis-E-1-chloro-3,3-dimethyl-but-1-enesulfen-2-yl sulfide (56). Oxidation of the sulfide with m-chloroperbenzoic acid afforded E-1-chloro-3,3-dimethylbut-1-enesulfen-2-yl sulfone (57). Complete spectral and microanalytical data were obtained on the sulfone. Evidence that the addition of sulfur dichloride to acetylenes proceeded with the same stereochemistry as additions of sulfenyl halides to acetylenes is seen in the symmetrical nature of the sulfide and sulfone which exhibit only one signal in the nmr spectrum for the two sets of equivalent tertiary butyl protons.

Treatment of the tert-butyl vinylsulfenyl chloride 55 with silver tetrafluoroborate at 0° gave an immediate precipitate of silver chloride which was suggestive of the formation of E-1-chloro-3,3-dimethylbut-1-ene-3-yl sulfenium tetrafluoroborate (58). Studies were then carried out with hydride donors to take advantage of the expected electro-

Scheme 4



$AgCl +$ [ structure with Cl, R', R, $S^{\oplus}$ ] $L^{\ominus}$
$\underline{58}$ R=H, R'=$\underline{t}$-Bu
$\underline{62}$ R=R'=Me

↑ AgL

$\underline{55}$ R=H, R'=$\underline{t}$-Bu
$\underline{60}$ R=R'=Me

structure with Cl, R', R, SCl

R——R'  $\xrightarrow{SCl_2}$

↓ R——R

$\underline{56}$ R=H, R'=$\underline{t}$-Bu
$\underline{61}$ R=R'=Me

structure with Cl, R', R, $)_2S$

m-chloroperbenzoic
acid ↓

structure with Cl, R', R, $)_2SO_2$

$\underline{57}$ R=H, R'=$\underline{t}$-Bu
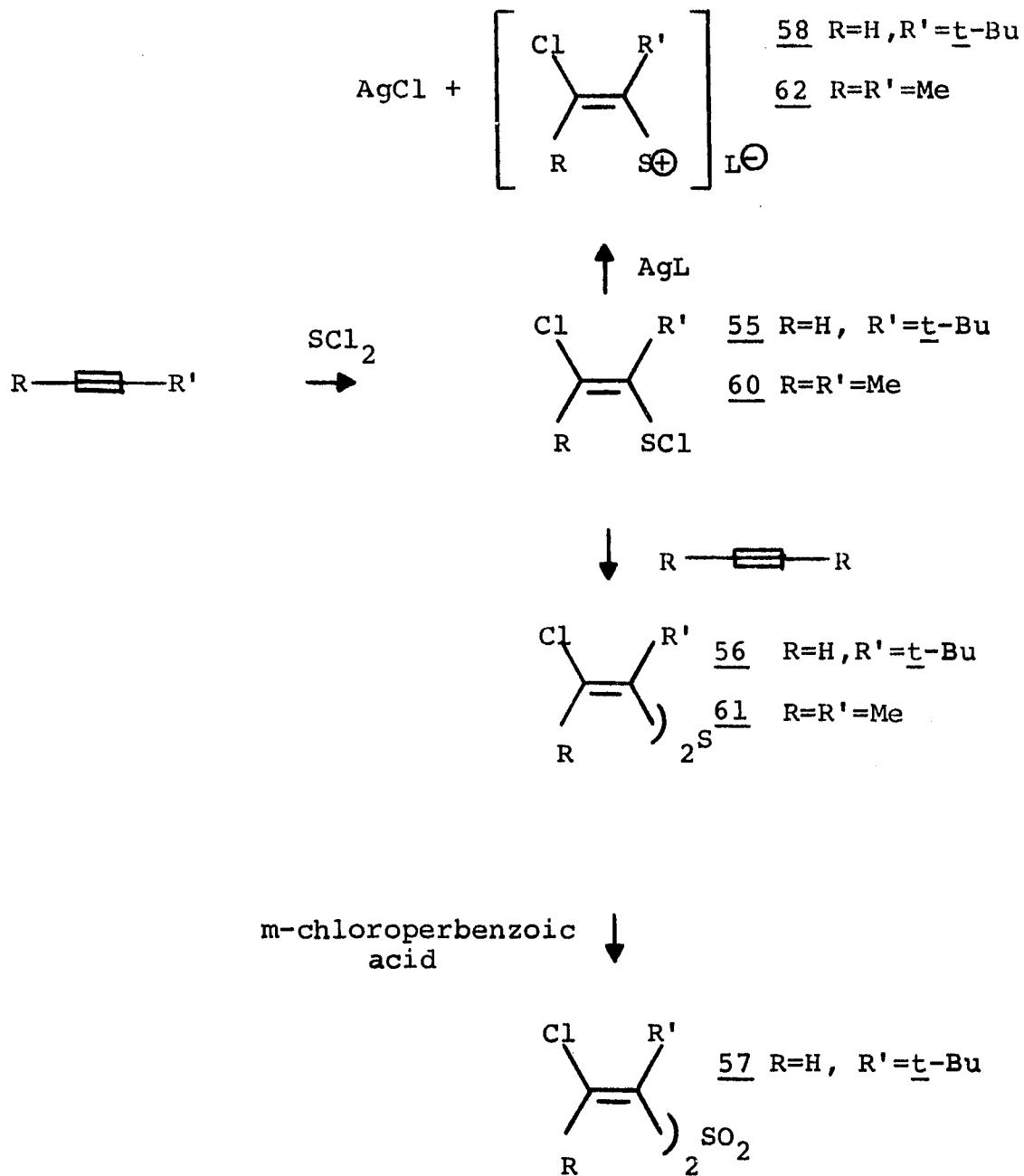
philicity of the positive sulfur, as shown in Scheme 5. The sulfenium ion solution, at 0°, was decanted into a solution of cold cycloheptatriene, and from this reaction a 12.5% yield of tropylium tetrafluoroborate (59) was isolated showing that a hydride ion was definitely removed from cycloheptatriene. An investigation of the hydride acceptor products, however, was thwarted by very complex product mixtures which could not be separated. Extensive investigations to increase the yield of tropylium cation and thereby obtain a cleaner reaction were unsuccessful. Different solvent systems were tried but the sulfenyl chloride was found to react with acetone, benzene, sulfur dioxide, acetonitrile, and dimethyl sulfoxide and limited the use of these solvents. Methylene chloride and nitromethane were also usable solvents but the yields of tropylium cation were no higher than those obtained using ether. A nonterminal acetylene was therefore investigated as an alternative.

Addition of sulfur dichloride to 2-butyne gave E-2-chlorobut-2-enesulfen-3-yl chloride (60) which was characterized by formation of bis-E-2-chlorobut-2-en-3-yl sulfide (61). The reaction of dimethylvinylsulfenyl chloride 60 with silver hexafluorophosphate or silver tetrafluoroborate precipitated silver chloride, showing the generality of the reaction. When E-2-chlorobut-2-ene-3-yl sulfenium hexafluorophosphate or tetrafluoroborate (62) was added to cyclo-

heptatriene, yields of tropylium fluorophosphate (63) or tropylium fluoroborate (59) of up to 48% were determined by nmr analysis. Gas chromatography of the reaction mixture showed the formation of 2-chloro-3-butanone (64) and 2,2-dichloro-3-butanone (65) by comparison with authentic samples. When the same reaction was carried out without cyclohepta-triene, bis-E-2-chlorobut-2-en-3-yl disulfide (66) was isolated in good yield. The following mechanism is proposed to explain these observations in Scheme 5. The dimethyl-vinylsulfenium ion 62 or the resonance contributor or 67 can accept a hydride ion to form the vinyl mercaptan 68 or the thioketone tautomer 69. Hydrolysis of the thioketone 68 in the workup is expected to form the observed 2-chloro-3-butanone (64) on the basis of the well known hydrolysis reactions of thiocarbonyls. The low recovery of any char-acterizable products is also understandable in light of the known instability of thiocarbonyl compounds (56). Although the instability of thioketones has hampered previous workers, Mayer et al. have reported that the thiocarbonyl-vinyl mercaptan equilibria lies far on the thiocarbonyl side (57).

Formation of 2,2-dichloro-3-butanone in the reaction mixture in a parallel pathway can be explained by chloride attack on 67 to form dichlorothioketone 70, followed by hydrolysis to 65. A mechanism for the formation of the divinyl disulfide 66 is a more challenging question although

Scheme 5
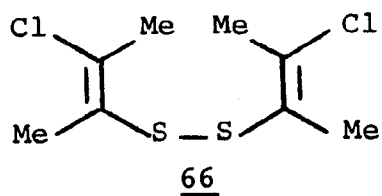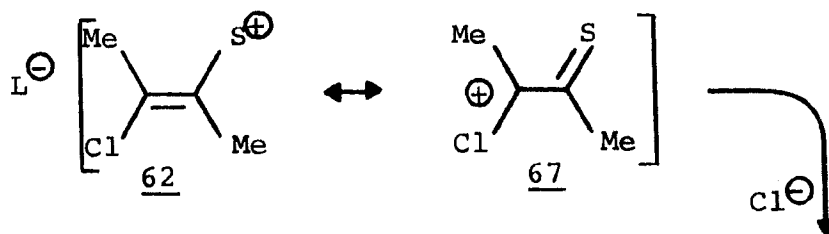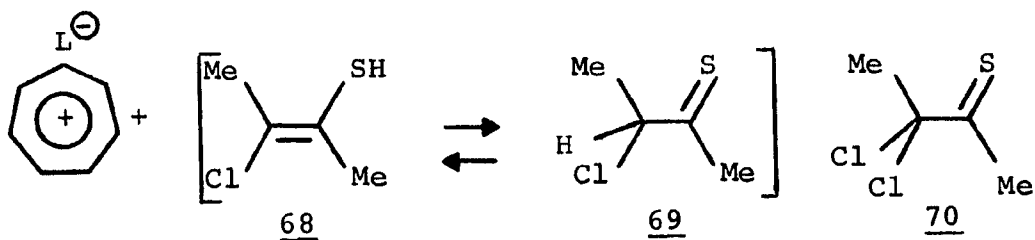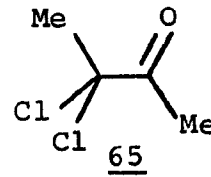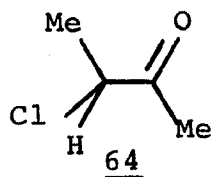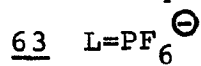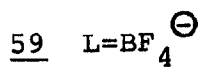
oxidation of the vinyl mercaptan is one possible pathway. No evidence of any rearranged heterocyclic products was obtained in these reactions.

Substituting silver acetate for silver hexafluorophosphate or silver tetrafluoroborate in the reaction with the dimethyl-vinylsulfenyl chloride and cycloheptatriene formed no tropylium cation. The competitive pathway was also operative here, and a 27% yield of divinyl disulfide 66 was obtained. The other product isolated and characterized was acetic anhydride. Tri-phenylmethane was substituted for cycloheptatriene as a hydride donor, but no triphenylmethane cation was detected. Good yields of unreacted triphenylmethane were recovered.

Low temperature nmr studies were carried out in an attempt to observe the sulfenium ion directly. The dimethyl-vinylsulfenyl chloride 60 was treated with silver tetra-fluoroborate at -15° in a nmr tube which was centrifuged (cold) to remove solids and then rapidly transferred to the pre-cooled probe. Only broad lines were observed from $\delta$ 1.00 to 3.00, although addition of cycloheptatriene to this solution formed the tropylium cation.

Reactions of arylsulfenyl chlorides with various silver salts were studied in order to determine the relative stability of the dimethylvinylsulfenium ion. A small amount of tropylium cation was isolated when 2,4-dinitrobenzenesulfenyl chloride was treated with silver hexafluorophosphate and cyclohepta-

triene. No other products could be identified. The p-methoxy-benzenesulfenyl chloride was considered as a system in which the electron donating p-methoxy substituent would stabilize the corresponding sulfenium ion more than the initially investigated dinitro substituents. Treatment of p-methoxy-benzenesulfenyl chloride with silver hexafluorophosphate followed by addition of cycloheptatriene resulted in the formation of tropylium hexafluorophosphate. Column chromatography on silica gel cleanly afforded one product which was identified as bis-p-methoxybenzene sulfide by comparison with an authentic sample. A more detailed investigation, however, showed that a completely different product was formed prior to chromatography, which lost elemental sulfur on the column. Comparison with authentic samples showed the pre-chromatography product was not a disulfide or trisulfide, but was assumed to be a higher polysulfide. Mass spectrometry showed only the presence of bis-p-methoxybenzene sulfide, and all attempts at purification of the pre-chromatography material resulted in loss of sulfur.

It was also desired to prepare 2,4-dimethoxybenzene-sulfenyl chloride both by chlorination of the disulfide and the mercaptan. These experiments as well as an attempted trapping experiment with cyclohexene at -10° afforded only a white polymer.

These results prompted a comprehensive literature search

which revealed that 2,4-dimethoxybenzenesulfenyl chloride had never been prepared. In 1964 Mayer and Frey (58) found that the stability of aromatic sulfenyl halides decreased with increasing electron donating substituents on the aromatic ring. For example, p-methoxybenzenesulfenyl chloride decomposed completely in 10 minutes at 90°, whereas nitro substituents greatly hindered decomposition at the same temperature. The products of these decompositions were the corresponding aryl chloride, symmetrical diaryl disulfide and sulfur monochloride. Some aliphatic sulfenyl chlorides were also decomposed to the corresponding alkyl chloride, but yields were reportedly much lower.

Douglass et al. (59) reported that methanesulfenyl chloride thermally decomposed into methyl chloride, methyl-disulfur chloride, methyl disulfide, methyl trisulfide, methyl tetrasulfide, methyl chloromethyl disulfide and dichloro-methyl methyl sulfide, and reported that a mechanism of decomposition could not be discerned. Barton and Zika (28) studied the thermal decomposition at 200° of erythro-2-chloro-1,2-diphenylethylsulfenyl chloride (71) and found meso-1,2-dichloro-1,2-diphenylethane (72) and stilbene as major products. Two mechanisms of sulfenyl halide decomposition were then proposed involving either a frontside displacement by the sulfenyl chloride chloride 71 or a novel double backside displacement involving the β-chloro

71
Frontside

73
Double Displacement

Δ 200°

72
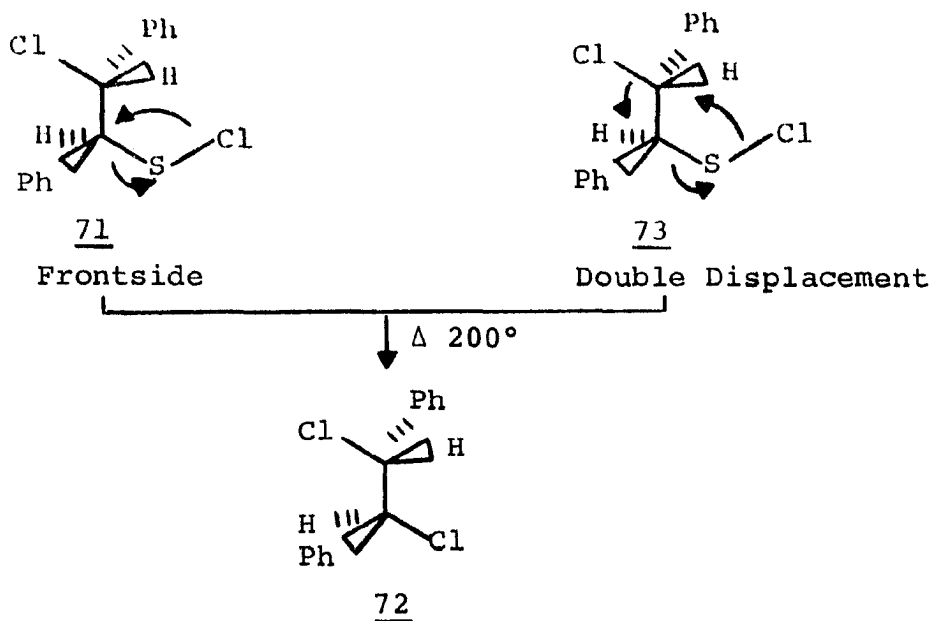
chloride 73.

In order to determine the mechanism of decomposition of sulfenyl halides, an experiment was designed in which an optically active sulfenyl halide could be obtained with sulfur directly bonded to the asymmetric carbon atom. The commercial availability of optically active 2-octanol prompted a preparation of octanesulfen-2-yl chloride by chlorination of bis-octan-2-yl disulfide. A derivative of the sulfenyl halide was prepared by reaction with cyclohexene for which satisfactory spectral and microanalytical data were obtained. Pyrolysis of octansulfen-2-yl chloride at 450° afforded only the disulfide and no octyl chloride or 2-octene. Higher

temperatures decreased the yields of bis-octan-2-yl disulfide.
At these temperatures, however, the elimination reaction to
form 2-octene became the major competing reaction. The small
amount of 2-octyl chloride formed in this pyrolysis limited
any investigations on an optically active sulfenyl halide,
and the nature of sulfenyl halide decompositions remains un-
known.

Several investigations on the addition of sulfenyl
chlorides to alkyl-substituted terminal olefins have con-
cluded that steric factors control the direction of ring
opening of the cyclic thiiranium cation by chloride, thus re-
sulting in anti-Markovnikov products, as outlined in the
previous section. However, the product ratio can be drastical-
ly changed by the presence of a phenyl group. For example,
styrene, which is capable of forming a benzyl cation, af-
fords Markovnikov addition products with greater than 98%
selectivity (60). The reaction of o-divinylbenzene with
sulfur dichloride was investigated in anticipation of forming
the cyclic dichlorosulfide 74 which is essentially a double
Markovnikov addition product. The dehydrohalogenation of 74
was viewed as a likely route to the unknown benzo[d]thiepin,
a molecule for which extensive MO calculations have recently
been reported (43).

Under high dilution conditions, simultaneous addition of
$SCl_2$ and o-divinylbenzene 75 afforded a 98% yield of an un-

stable product whose complex, unsymmetrical nmr spectrum strongly suggested a mixture of the cis and trans isomers of 1,3,4-H-1-chloromethyl-4-chloro-2-benzothiopyran (76), shown in Scheme 6. Oxidation of 76 with m-chloroperbenzoic acid afforded the sulfone 77 in 90% yield as a mixture of cis and trans isomers from which a single isomer 77a (mp 98-100°) was isolated by fractional recrystallization. The structure of 77a was deduced from nmr analysis (vide infra), facilitated by spin-decoupling experiments summarized in Table 1.

Table 1.  Results of spin-decoupling experiments on 1,3,4-H-1-chloromethyl-4-chloro-2-benzothiopyran-2,2-dioxide (77a)
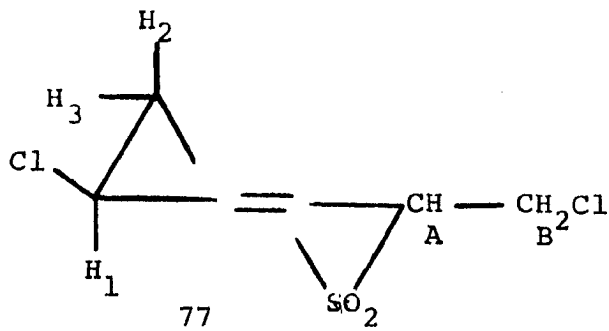


| Irradiation Frequency | $H_1$ $\delta$ 4.85 | $H_2$ $\delta$ 4.40 | $H_3$ $\delta$ 4.15 |
|---|---|---|---|
| no irradiation | d of d $J_{1,2}$=6.6 Hz $J_{1,3}$=4.0 Hz | d of d $J_{2,3}$=11.5 Hz $J_{1,2}$= 6.6 Hz | d of d $J_{2,3}$=11.5 Hz $J_{1,3}$= 4.0 Hz |
| $H_1$ 291 Hz | | d $J_{2,3}$=11.5 Hz | d $J_{2,3}$=11.5 Hz |
| $H_3$ 248 Hz | d $J_{1,2}$= 6.6 Hz | | |

Scheme 6



DBU ↑ -2HCl



75

$\xrightarrow[\text{MeCl}_2]{\text{SCl}_2}$

76 $CH_2Cl$

$\xrightarrow{RCO_3H}$

77 $CH_2Cl$

silica gel

78

$RCO_3H$

79

$\xrightarrow{\text{Vitride}}$

80 $CH_3$

DBU

81
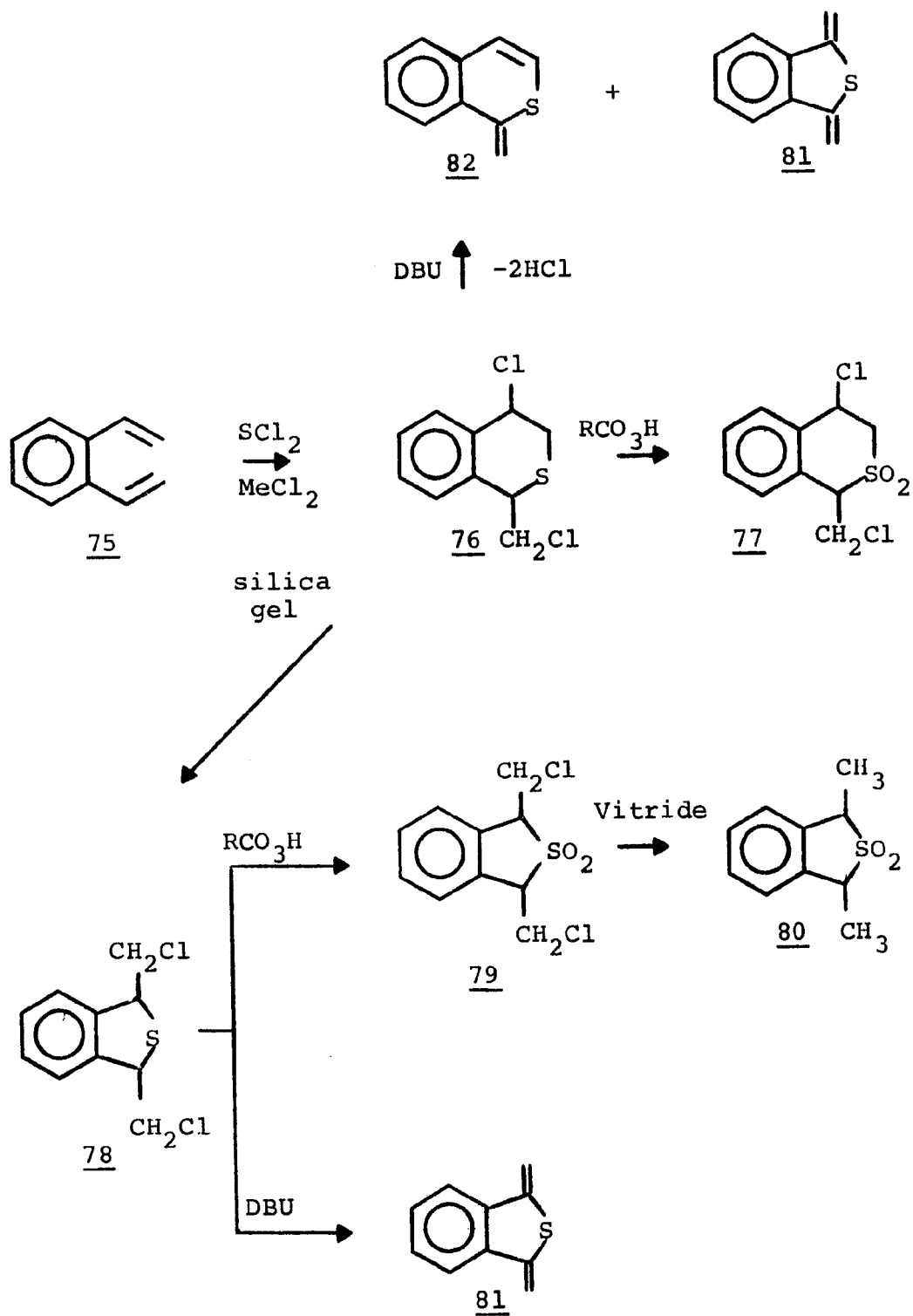
Upon standing at room temperature 76 rearranged to a mix-
ture of 76 and an isomer 78. Complete destruction of 76 was
effected by percolation of a solution of 76 through a silica
gel column, a procedure which afforded 78 (cis, trans isomer
mixture) as the sole isolable product. The nmr spectrum did
not by itself allow conclusive differentiation between 78
and 74.

Structure 74 was ruled out through peracid oxidation of
78 to sulfone 79 (85% yield) followed by reductive dechlori-
nation to 80. The nmr spectrum of 80 showed two methyl
doublets (δ 1.61 and 1.59, J = 7 Hz) thereby eliminating
structure 74 from consideration and establishing the di-
hydrobenzo[c]thiophene system 78 as the rearrangement product
from 76.

Additional evidence for the proposed structures was
found in the DBU-dehydrochlorination of a mixture of cis-
and trans-isomers of 78 to clearly provide only one un-
saturated product, 81. While the extreme instability of
neat 81 precluded isolation, the nmr spectrum was unambiguous.
Similar treatment of 76 with DBU afforded 82 along with 81,
the latter presumably arising from partial isomerization of
76 to 78 under the reaction conditions.

A mechanism for this reaction is proposed in Scheme 7
by analogy to the reports by Lautenschlager (32) on the addi-
tion of sulfur dichloride to 1,5-hexadiene. Only one

Scheme 7
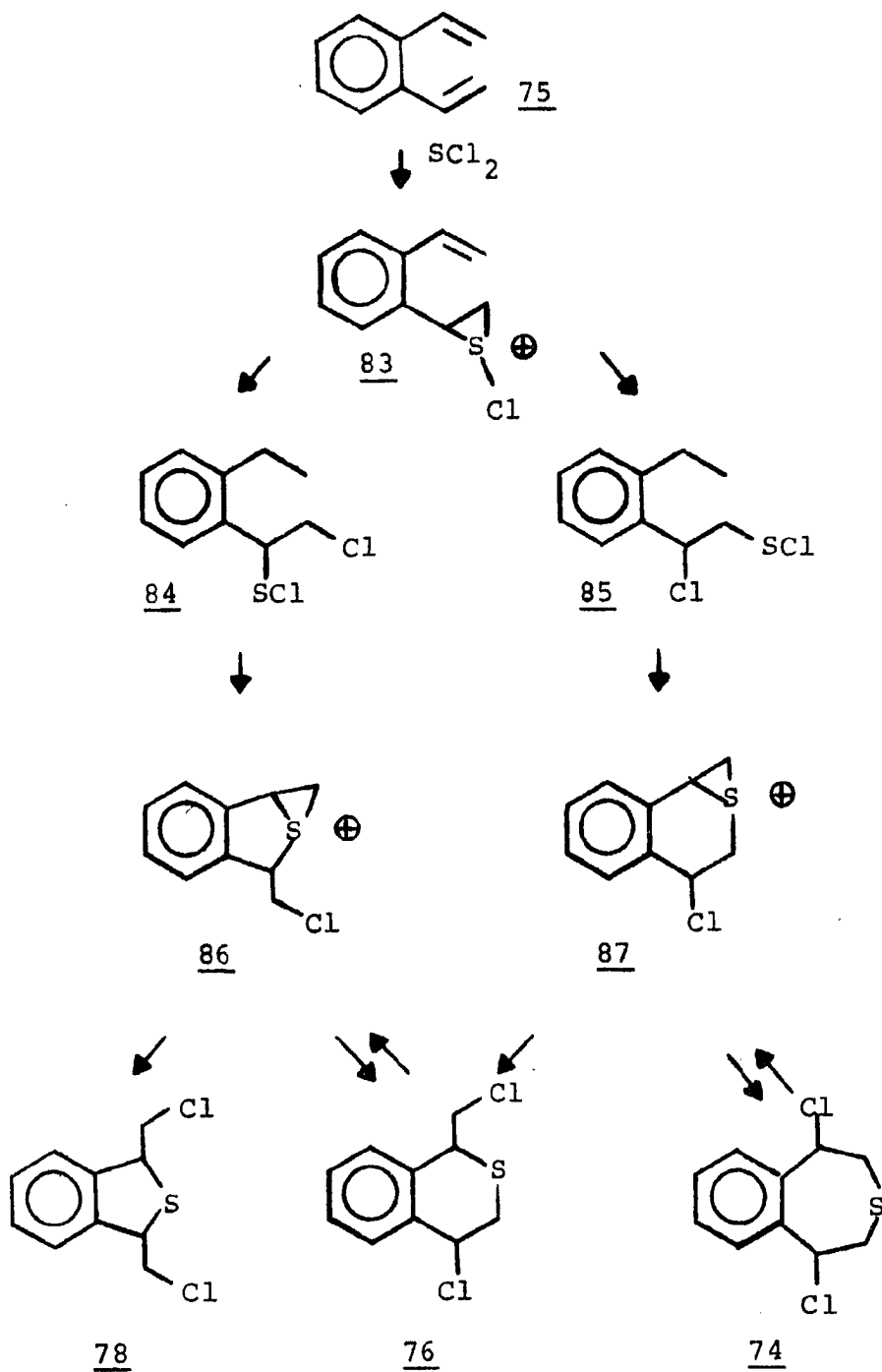
thiiranium ion 83 can be formed in the initial addition of sulfur dichloride, which can open in two ways to the intermediates 84 and/or 85. The anti-Markovnikov ion 86 can also be attacked in two ways to form a double anti-Markovnikov addition product 78 or the mixed benzothiopyran 76, as a kinetic product. Post-isomerization of the kinetic product 76 through the thiiranium ion 86 would then lead to the observed dihydrobenzo[c]thiophene 78. An alternate pathway is through the mixed thiiranium ion 87 to the benzothiopyran ring system. The same post-isomerization would explain the observed products.

A remarkable finding of this study was the lack of influence of the benzene ring in stabilizing contributions from the open benzylic carbonium ion. The determining thermodynamic factor seems to be the heterocyclic ring size which Lautenschlager established as 5>6>7. The isolation of the benzothiopyran 76 contributes to the credibility of this mechanism as well as to the similar mechanism proposed for 1,5-hexadiene, Scheme 1, in which the corresponding intermediate was not found in the reaction mixture. The finding that the six-membered ring sulfide 76 was the initially observed product, therefore, does not rule out the possibility that 74 is the initial product. Indeed the results do not deny the possibility of initial formation of 74 rearrangement to 76 and a slower rearrangement to 78. However, attempts

to observe $\underline{74}$ under quite mild conditions have been uni-
formly unsuccessful.

## EXPERIMENTAL

Infrared spectra (ir) were recorded on a Beckman 12 spectrophotometer. Routine nmr spectra were determined on a Varian model A-60 or a Hitachi R20-B spectrometer, and chemical shifts were reported as parts per million ($\delta$ scale) from tetramethyl silane as an internal standard. Decoupling and low temperature studies were recorded on the Hitachi R20-B spectrometer. The Varian HA-100 spectrometer was used to record all 100 MHz spectra. Routine mass spectra were obtained on an Atlas CH-4 spectrometer. High resolution mass spectra were recorded on a MS-902 mass spectrometer manufactured by AEI. Ultraviolet spectra (uv) were recorded using a Cary model 14 spectrophotometer. All melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, West Germany.

### E-1-Chloro-3,3-dimethylbut-1-enesulfen-2-yl chloride (55):

A solution of 8.20 g (0.10 mol) of t-butylacetylene in 175 ml of dry methylene chloride was added dropwise to a refluxing solution of 11.30 g (0.11 mol) of freshly distilled sulfur dichloride in 700 ml of methylene chloride. After 2.0 hr of addition time the solvent was removed and the residual red-orange liquid (stench) was distilled at reduced pressure

to give 12.65 g (68.5%) of product: bp 32-34° (0.1 mm);
nmr (CCl$_4$) δ 1.42 (s, 9H), 7.16 (s, 1H).

Bis-E-1-chloro-3,3-dimethylbut-1-enesulfen-2-yl sulfide (56):

To a solution of 3.51 g (19.0 mmol) of E-1-chloro-3,3-dimethylbut-1-enesulfen-2-yl chloride (55) in 120 ml of methylene chloride was added 1.58 g (19.2 mmol) of t-butyl-acetylene in 30 ml of methylene chloride and the resulting solution refluxed for 30 min. After rotary evaporation of ether the residual yellow liquid was distilled at reduced pressure to afford after two distillations 2.80 g (55.1 %) of 56 as a yellow liquid: bp 75-76° (0.13 mm); nmr (CCl$_4$) δ 1.33 (s, 9H), 6.00 (s, 1H); ir (film) 785, 1360, 1395, 1460, 1475 cm$^{-1}$; mass spectrum (70 eV) m/e 266 M$^+$.

Bis-E-1-chloro-3,3-dimethylbut-1-enesulfen-2-yl sulfone (57):

To a solution of 1.53 g (11.0 mmol) of 85% m-chloro-perbenzoic acid in 15 ml of chloroform was added 1.49 g (5.55 mmol) of bis-E-1-chloro-3,3-dimethylbut-1-enesulfen-2-yl sulfide (56) in 4 ml chloroform at room temperature. The reaction was exothermic with the temperature increasing to 48°C. After 2 hr m-chlorobenzoic acid was removed by filtration. The filtrates were washed twice with two 30 ml portions of 10% sodium bicarbonate and dried over anhydrous magnesium sulfate. The filtrates were concentrated to afford 1.08 g (64.8%) of white solid. Recrystallization from hexane gave

white prisms of <u>57</u>: mp 124-125°; nmr (CCl$_4$) δ 1.44 (s, 9H), 7.44 (s, lH); ir (KBr) 1570 (m), 1280 (s), 1123 (s), 962 (m), 855 (m), 822 (m) cm$^{-1}$; mass spectrum (70 eV) <u>m/e</u> (rel intensity) 300 (3), 298 (8) M$^+$, 117 (100).

<u>Anal</u>. Calcd for C$_{12}$H$_{20}$Cl$_2$O$_2$S: C, 48.16; H, 6.74; Cl, 23.69. Found: C, 48.07; H, 6.78; Cl, 23.52.

## E-2-chlorobut-2-enesulfen-3-yl chloride (60):

To a stirred solution of 45.0 g (0.44 mol) of freshly distilled sulfur dichloride in 1-liter of dry ether was added a solution of 12.5 g (0.23 mol) of 2-butyne in 125 ml of dry ether over a period of 4 hr at room temperature. After removal of ether by rotary evaporation the residual red liquid (stench) was purified by trap to trap distillation at room temperature (0.3 mm) to afford 30.9 g (86.0%) of the title compound. The sulfenyl chloride was unstable toward small amounts of acid and moisture. All transfer operations were carried out under nitrogen and the product was stored over sodium carbonate at freezer temperatures: nmr (CDCl$_3$) δ 2.28 (q, 3H), 2.50 (q, 3H, <u>J</u> = 1.5 Hz).

## Bis-E-2-chlorobut-2-en-3-yl sulfide (61):

A solution of 2.93 g (18.7 mmol) of E-2-but-2-enesulfen-3-yl chloride (<u>60</u>) in 50 ml of dry methylene chloride was added to a solution of 1.01 g (18.7 mmol) of 2-butyne in 100 ml of methylene chloride over a period of 20 min at room

temperature. After 4 hr the solvent was removed to afford 3.27 g (83.1%) of the title compound which was distilled at reduced pressure: bp 44-46° (0.1 mm); nmr (CCl$_4$) $\delta$ 2.00 (q, 6H), 2.35 (q, 6H); ir (film) 1620, 1375, 1060 cm$^{-1}$; mass spectrum (70 eV) m/e 210 M$^+$.

Anal. Calcd for C$_8$H$_{12}$Cl$_2$S:  C, 45.51; H, 5.73; Cl, 33.58. Found:  C, 45.41; H, 5.73; Cl, 33.60.

## Reaction of E-1-chloro-3,3-dimethylbut-1-enesulfen-2-yl chloride with silver fluoroborate and cycloheptatriene:

A solution of 1.00 g (5.41 mmol) of E-1-chloro-3,3-dimethyl-but-1-enesulfen-2-yl chloride (55) in 5 ml of dry ether and a suspension of 1.05 g (5.41 mmol) of silver tetra-fluoroborate in 5 ml of dry ether were prepared under argon, protected by drying tubes, and cooled to 0°. Addition of the vinyl sulfenyl halide to silver fluoroborate resulted in the immediate formation of a white solid in a yellow solution. The solids were centrifuged to the bottom of the centrifuge tube, and the liquid was decanted into a solution of 0.49 g (5.41 mmol) of cycloheptatriene in 10 ml of ether at 0°.

The solids were dissolved in ammonia then added dropwise to nitric acid to precipitate 0.62 g (80.0%) of silver chloride. The residual ether solution was concentrated to a dark oil from which was isolated 0.120 g (12.5%) of tropylium fluoroborate as an off-white solid by crystallization from ether-hexane. The isolated tropylium fluoroborate was identical to an authentic

sample (61): mp 200° (decomposition); nmr (CD$_3$CN) δ 9.23 (s).

The experiment was also carried out in nitromethane, and yields of tropylium fluoroborate up to 32% were obtained as determined by nmr. From the residual reaction small amounts of complex product mixtures were obtained which could not be separated by column chromatography.

## Reaction of E-2-chlorobut-2-enesulfen-3-yl chloride with silver hexafluorophosphate and cycloheptatriene:

To a solution of 5.40 g (34.4 mmol) of E-2-chlorobut-2-ene-sulfen-3-yl chloride (60) in 25 ml of dry methylene chloride was added at 0° a white suspension of 8.63 g (34.1 mmol) of dry silver fluorophosphate in 20 ml of methylene chloride followed by addition of 3.61 g (34.1 mmol) of cyclo-heptatriene. All operations were carried out in a nitrogen dry atmosphere (glove bag, P$_2$O$_5$). The reaction was allowed to warm to room temperature and was stirred for an additional 5 min.

The methylene chloride insoluble material was triturated with three 20 ml fractions of nitromethane to which was added 150 ml of methylene chloride. Cooling precipitated 1.65 g (20.4%) of white solid tropylium fluorophosphate: mp 250° (decomposition); nmr (CD$_3$NO$_2$) δ 9.30 (s); ir (KBr) 1480, 1390, 828 cm$^{-1}$.

The residual methylene chloride insoluble material was dissolved in ammonium hydroxide, and the silver chloride was

precipitated with nitric acid to afford 3.60 g (73.1%) of white solid.

Column chromatography of the methylene chloride soluble material on silica gel gave 0.072 g (6.9%) of elemental sulfur by elution with pentane: mp 110-113°; no nmr spectrum.

The methylene chloride soluble material was also investigated by vpc analysis. Two major products were identified, isolated by preparative vpc and found to be identical to authentic samples of chlorobutanones (62) as follows: 2-chloro-3-butanone (12.5% internal standard, anisole) was separated on a 10% 6-ft Apiezon L column, column temperature 120°, retention time = 3.8 min: nmr ($CCl_4$) δ 1.57 (d, 3H), 2.28 (s, 3H), 4.25 (s, 1H); ir ($CCl_4$) 1710 (s), 1440, 1350 cm$^{-1}$; mass spectrum (70 eV) m/e 106 M$^+$.

2,2-Dichloro-3-butanone (18.0%) was separated on an Apiezon L column, retention time = 5.0 min: nmr ($CCl_4$) δ 2.13 (s, 3H), 2.49 (s, 3H); ir ($CCl_4$) 1720 (s), 1355, 1080 cm$^{-1}$; mass spectrum (70 eV) m/e 142 M$^+$.

## Reaction of E-2-chlorobut-2-enesulfen-3-yl chloride with silver fluoroborate and cycloheptatriene:

To a solution of 4.64 g (30.3 mmol) of E-2-chlorobut-2-enesulfen-3-yl chloride (60) in 50 ml of nitromethane was added at 0° with mechanical stirring a solution of 5.90 g (30.3 mmol) of silver fluoroborate in nitromethane. A solution of 2.80 g (30.3 mmol) of cycloheptatriene in 25 ml of

nitromethane was then added over a period of 5 min. A nmr

yield of 48% tropylium fluoroborate was obtained by addition

of a known amount of authentic sample. Silver chloride was

isolated in the usual way with ammonium hydroxide and nitric

acid as a white solid 2.74 g (64%). Analysis by vpc also

showed 2-chloro-3-butanone (64) and 2,2-dichloro-3-butanone

(65) as described in the previous experiment with silver

fluorophosphate.

## Bis-E-2-chlorobut-2-en-3-yl disulfide (66):

To a solution of 0.360 g (2.29 mmol) of E-2-chlorobut-

2-enesulfen-3-yl chloride (60) in 5 ml of dry ether was added

0.445 g (2.29 mmol) of silver fluoroborate in 5 ml of dry

ether at 0° with brief stirring in a centrifuge tube. After

allowing the reaction to warm to room temperature the ether

insoluble material was removed by centrifugation. The solids

were dissolved in ammonium hydroxide, and the silver chloride

was precipitated with nitric acid to afford 0.240 g (75.0%)

of white solid.

The ether soluble material was chromatographed on silica

gel eluting with methylene chloride to afford 0.092 g (30.1%)

of the disulfude 66 as a yellow oil: nmr (CCl$_4$) δ 2.20 (q,

3H), 2.35 (q, 3H); ir (film) 1620, 1435, 1370, 1145, 1095,

1060 cm$^{-1}$ mass spectrum calculated for C$_8$H$_{12}$Cl$_2$S$_2$ m/e =

241.977577, found m/e = 241.975752.

## Low temperature nmr study of the reaction of E-2-chloro-but-2-enesulfen-3-yl chloride with silver tetrafluoroborate:

A nmr tube containing 0.037 g (0.236 mmol) of 2-chloro-but-2-enesulfen-3-yl chloride (60) in 0.3 ml of d$_3$-nitro-methane was cooled to -15°. A solution of 0.046 g (0.236 mmol) of silver fluoroborate in 0.3 ml of d$_3$-nitromethane was then cooled to -15° and added to the sulfenyl chloride solution. After stirring for one minute silver chloride was removed by centrifugation at -15° and the cold tube rapidly transferred to a nmr probe precooled to -15°. The nmr spectrum showed only one broad hump from δ 1.0 to 3.0. A cold solution of 0.022 g (0.238 mmol) of cycloheptatriene was then added, and the tropylium cation absorption was observed in the nmr spectrum: nmr (CD$_3$NO$_2$) δ 9.30 (s).

## Reaction of E-2-chlorobut-2-enesulfen-3-yl chloride with silver acetate:

A suspension of 1.00 g (6.37 mmol) of silver acetate in 5 ml dry methylene chloride was prepared in a centrifuge tube protected with a calcium sulfate drying tube. After cooling to 0°, a solution of 1.04 g (6.34 mmol) of E-2-chlorobut-2-enesulfen-3-yl chloride (60) in 5 ml of dry methylene chloride was added with magnetic stirring and allowed to warm to room temperature. Centrifugation removed silver chloride which was purified in the usual manner to afford 0.672 g (79.0%) of white solid.

Chromatography on 100 g of silica gel afforded 0.210 g (27.0%) of the bis-E-2-chlorobut-2-en-3-yl disulfide (66) characterized previously: nmr (CCl$_4$) δ 2.20 (q, 3H), 2.38 (q, 3H).

The methylene chloride soluble material was also investigated by vpc using a 6 ft x 1/4 in. 10% SE-30 column, column temperature = 80° and was found to contain 30.6% acetic anhydride. A preparative sample was collected by vpc and compared with an authentic sample of acetic anhydride: nmr (CCl$_4$) δ 2.18 (s); ir (film) 1830, 1755, 1370, 1125, 1000 cm$^{-1}$.

The experiment was repeated with the addition of cycloheptatriene as soon as silver chloride was precipitated. The products isolated were the same, and no tropylium cation signal was observed in the nmr spectrum.

The reaction of E-2-chlorobut-2-enesulfen-3-yl chloride with silver fluorophosphate and triphenylmethane:

To a suspension of 2.00 g (7.90 mmol) silver fluorophosphate in 15 ml dry methylene chloride was added a solution of 1.24 g (7.86 mmol) of E-2-chlorobut-2-enesulfen-3-yl chloride (60) in 5 ml methylene chloride at -10°. A solution of 1.93 g (7.90 mmol) of triphenylmethane in 5 ml methylene chloride was then added and allowed to warm to room temperature. The insoluble material was dissolved in ammonium hydroxide and acidified with nitric acid to afford 0.49 g

(44.1%) of silver chloride. From the methylene chloride was recovered 1.10 g (57.0%) of triphenylmethane: mp 89-91° [lit. (63) mp 94°].

Reaction of 2,4-dinitrobenzenesulfenyl chloride with silver fluorophosphate and cycloheptatriene:

To a suspension of 3.50 g (1.38 mmol) of silver fluoro-phosphate in 200 ml dry methylene chloride was added a solution of 3.26 g (1.39 mmol) of 2,4-dinitrobenzenesulfenyl chloride in 50 ml methylene chloride at -20° over a period of 10 min. Silver chloride was removed by filtration under nitrogen to afford 1.67 g (85.0%) of silver chloride.

The cold methylene chloride solution was filtrated into 1.28 g (1.39 mmol) of cycloheptatriene cooled to -20° in 50 ml of methylene chloride and allowed to warm to room temperature. A tan solid was removed by filtration and identified as tropylium fluorophosphate in a yield of 0.58 g (17.8%): nmr (CH$_3$NO$_2$) δ 9.38 (s).

From the residual black reaction mixture was isolated only small amounts of starting 2,4-dinitrobenzenesulfenyl chloride and cycloheptatriene.

Reaction of p-methoxybenzenesulfenyl chloride with silver fluorophosphate and cycloheptatriene:

To a suspension of 3.70 g (14.3 mmol) of silver hexa-fluorophosphate in 10 ml of methylene chloride was added a solution of 2.56 g (14.7 mmol) of p-methoxybenzenesulfenyl

chloride in 10 ml methylene chloride at 0°. Silver chloride formed immediately and was followed by addition of 1.32 g (14.3 mmol) of cycloheptatriene in 5 ml of methylene chloride.

After warming to room temperature the methylene chloride insoluble material was removed by centrifugation. The insoluble material was then triturated with 0.5 ml of $d_3$-nitromethane and found to contain tropylium hexafluorophosphate: nmr $(CD_3NO_2)$ δ 9.38 (s).

The nitromethane insoluble material was dissolved in ammonium hydroxide then acidified with nitric acid to precipitate silver chloride.

Chromatography of the methylene chloride soluble material on silica gel gave one major product cleanly by nmr which was identical to an authentic sample of bis-p-methoxybenzene sulfide (64): nmr $(CCl_4)$ δ 3.70 (s, 6H), 6.70 and 7.18 (centers AA'BB' aromatic, 8H).

Investigation of the crude reaction mixture revealed that no bis-p-methoxybenzene sulfide was present before chromatography, but rather a different species with the following nmr spectrum $(CH_2Cl_2)$ δ 3.89 (s, 6H) and 7.16 and 7.53 (centers AA'BB' aromatic, 8H). All attempts at purification or characterization of this unknown species by distillation or chromatography resulted in formation of bis-p-methoxybenzene sulfide and elemental sulfur, mp 118-120°.

Bis-p-methoxybenzene sulfide:

The title compound was prepared according to a literature procedure (64). Recrystallization from ethanol gave white prisms: mp 43-44°; nmr (CCl$_4$) δ 3.72 (s, 6H), 6.70 and 7.18 (centers AA'BB' aromatic 8H).

Bis-p-methoxybenzene sulfone:

To a solution of 1.62 g (8.00 mmol) of m-chloroperbenzoic acid in 15 ml of chloroform was added a solution of 0.92 g (3.76 mmol) of bis-p-methoxybenzene sulfide in 5 ml chloroform as the temperature increased to 50°. The mixture was cooled to 0° after 30 min and m-chlorobenzoic acid was removed by filtration. The chloroform filtrates were washed with 10% sodium carbonate, dried over magnesium sulfate and concentrated to a white solid. Recrystallization from chloroform--hexane afforded prisms, mp 139-140° [lit. (65) mp 139°].

2,4-Dimethoxybenzene thiol:

To a suspension of 4.00 g (0.10 mol) of lithium aluminum hydride in 200 ml dry ether was added a solution of 2,4-dimethoxybenzenesulfonyl chloride in 600 ml dry ether at a rate such that gentle reflux was obtained. After refluxing for 1.5 hr, 40 ml of 1.2 N HCl was added, and the mixture was stirred for an additional 30 min. The ether solution was dried over magnesium sulfate and rotary evaporated to 1.76 g (39.8%) of clear oil: nmr (CCl$_4$) δ 3.30 (s, 1H),

3.67 (s, 3H), 3.80 (s, 3H), and an aromatic ABX pattern with centers at 6.25 and 7.00 (3H).

### Bis-2,4-dimethoxybenzene disulfide:

A solution of 1.76 g (10.3 mmol) of 2,4-dimethoxybenzene thiol in 50 ml of ethanol was treated with 1.50 g (5.93 mmol) of iodine in portions with stirring. After 15 min at room temperature the crude disulfide was collected by filtration and recrystallized from absolute ethanol to afford 0.90 g (51.4%) of white needles: mp 111-112° [lit. (66) 109-112°]; nmr (CDCl$_3$) δ 3.78 (s, 12H), 6.30-6.50 (m, 4H), 7.35 (m, 2H).

### Attempted preparation of 2,4-dimethoxybenzenesulfenyl chloride:

A solution of 0.485 g (1.44 mmol) of 2,4-dimethoxybenzene disulfide in 2.0 ml of chloroform was cooled to -10° and treated with a solution of 0.194 g (1.44 mmol) of sulfuryl chloride in 2.0 ml of chloroform. After warming to room temperature a white solid was collected by filtration. This material did not melt at temperatures up to 250°, was insoluble in nitromethane, acetone, carbon tetrachloride, chloroform and ether and was assumed to be polymeric. The experiment was repeated with cyclohexene present in an attempt to trap the sulfenyl chloride at -10°, but the same insoluble white polymer and unreacted cyclohexene were isolated.

## Bis-octan-2-yl disulfide:

To a solution of 4.18 g (28.6 mmol) of 2-octanethiol in 50 ml of absolute ethanol was added iodine in small portions until the iodine color persisted at room temperature. The solution was stirred for 2 hr, concentrated to dryness and the residue dissolved in 50 ml of chloroform. Treatment with a 10% solution of sodium sulfite removed the iodine color. The organic layer was dried over anhydrous potassium carbonate, concentrated and distilled to collect 2.92 g (70.3%) of the desired disulfide: bp 106-108° (0.07 mm), [lit. (67) bp 115° (0.1 mm)]; nmr (CCl$_4$) δ 2.72 (d, 1H), 0.80 to 1.50 (m, 16H).

## Octanesulfen-2-yl chloride:

To a solution of 0.914 g (3.09 mmol) of bis-octan-2-yl disulfide in 10 ml of dry methylene chloride at -20° under nitrogen was added a solution of 0.47 g (3.48 mmol) of sulfuryl chloride in 2 ml of methylene chloride over a period of 5 min. The reaction was allowed to warm to room temperature for 30 min and concentrated to a yellow liquid. A trap to trap distillation afforded 0.880 g (77.5%) of the desired product: bp 80-85° (1.0 mm); nmr (CCl$_4$) δ 3.18 (m, 1H), 0.30-1.80 (m, 16H). The product was stored under nitrogen at 0° for use in further experiments.

## 2-Chlorocyclohexyloctane-2-yl sulfide:

To a solution of 0.237 g (1.31 mmol) of 2-octylsulfenyl chloride in 1.0 ml of dry methylene chloride was added 0.110 g (1.33 mmol) of cyclohexene in 2.0 ml of methylene chloride at room temperature. After 30 min the reaction was concentrated to a clear liquid by rotary evaporation. Distillation at 85-90° (0.1 mm) afforded 0.251 g (72.6%) of colorless liquid: nmr (CCl$_4$) δ 4.13 (m, 1H), 0.76-2.20 (m, 26H); ir (film) 2835, 2940, 1450, 1465 cm$^{-1}$.

Anal. Calcd for C$_{14}$H$_{27}$ClS: C, 63.97; H, 10.35; Cl, 13.49; S, 12.20. Found: C, 63.95; H, 10.23; Cl, 13.40; S, 12.02.

## Pyrolysis study of octanesulfen-2-yl chloride:

Pyrolysis studies were carried out at various temperatures using the following general method. The sulfenyl chloride was injected directly into a horizontal pyrolysis oven using a 12 in. Vycor tube packed with glass wool at 10$^{-4}$ mm. The products were trapped at liquid nitrogen temperature. Two of the products were analyzed by vpc by comparison with authentic samples using a 10% carbowax column, column temp = 130°. Retention time for 2-octene = 1.7 min and 2-octyl chloride = 5.2 min. The bis-octan-2-yl disulfide was determined by nmr spectroscopy.

At 450° an overall yield of 48.5% of the disulfide was obtained. Vpc analysis showed no 2-octyl chloride or 2-

octene.

At 480° an overall yield of 36.0% of products was obtained containing 92% 2-octene by nmr and vpc analysis.

At 510° the overall yield was 26.6% of products containing 79% 2-octene and 15% 2-octyl chloride.

## 1,3,4-H-1-Chloromethyl-4-chloro-2-benzothiopyran (76):

Solutions of o-divinylbenzene (6.90 g, 53 mmol) and freshly distilled sulfur dichloride (5.46 g, 53 mmol) in 125 ml of dry methylene chloride were simultaneously added to 125 ml of stirred methylene chloride. The addition was completed after 1 hr, and the solvent was removed in vacuo to afford 12.0 g (98.2%) of 76 as a yellow oil. Upon standing at room temperature the nmr spectrum revealed that rearrangement to a mixture of 76 and 78 had occurred, thus necessitating the immediate use of 76 in subsequent experiments: nmr (CDCl$_3$) δ 7.20 (m, 4H), 5.24-5.68 (m, 1H), and 2.80-4.22 (m, 5H); ir (film) 1490, 1445, 1300, 1255, 1025, 770 and 740 cm$^{-1}$; mass spectrum (70 eV) m/e 232 M$^+$.

## 1,3,4-H-1-Chloromethyl-4-chloro-2-benzothiopyran 2,2-dioxide (77):

To a solution of 76 (2.17 g, 9.3 mmol) in 5 ml of chloroform was added dropwise 3.77 g (18.6 mmol) of 85% m-chloroperbenzoic acid in 50 ml of chloroform over a period of 5 min. After 1 hr, m-chlorobenzoic acid was removed by fil-

tration and the filtrates washed with 10% sodium sulfite until
neutral to KI solution. Excess acid was removed by extrac-
tion with 5% sodium bicarbonate, and the chloroform layer was
dried over magnesium sulfate. Removal of solvent in vacuo
afforded 2.0 g (81.9%) of cis- and trans-77 as a colorless
oil which solidified upon standing. Repeated recrystalliza-
tion from chloroform--ether yielded a white solid: mp 98-
100°, as one pure isomer 77a : nmr (CDCl$_3$) δ 3.82 (d, 2H),
5.61 (t, 1H), 4.85 (dd, 1H), 4.19-4.34 (dd, 2H) and 7.50
(s, 4H); ir (KBr) 1140, 1330 cm$^{-1}$; mass spectrum (70 eV)
m/e (rel intensity) 264 (45) M$^+$, 266 (31), 118 (80), 200
(63) 165 (100).

Anal. Calcd for C$_{10}$H$_{10}$Cl$_2$O$_2$S: C, 45.30; H, 3.80; Cl,
26.74; S, 12.09. Found: C, 45.45; H, 3.99; Cl, 26.75;
S, 11.93.

### Rearrangement of 1,3,4-H-1-chloromethyl-4-chloro-2-benzo-thiopyran (76) to 1,3-dihydro-1,3-bis(chloromethyl)benzo[c]-thiophene (78):

Compound 76 (2.3 g) was chromatographed on a 3 x 40
cm column of silica gel with elution by 3 l. of hexane.
Concentration in vacuo left 1.47 g (63%) of a red liquid.
A small fraction was distilled at 80° (0.1 torr) to afford
a colorless liquid for an analytical sample. Both the crude
and purified samples had the same isomer ratio and were in
all respects identical by nmr. (The ratio of isomers was

approximately 70:30 by nmr, but severe overlap reduces the confidence level of this number.) The purified product darkens rather rapidly and must be stored under nitrogen at 0° in solution. The same conversion was found to occur on neutral alumina. An nmr spectrum of chromatographed material shows no evidence of $\underline{76}$: nmr (CDCl$_3$) δ 3.82 and 3.84 (2d, 4H), 4.60 and 4.80 (2t, 2H, $\underline{J}$ = 6 Hz) and 7.20 (sym m, 4H); ir (film) 450, 700, 750, 1435, 1455, 1480 cm$^{-1}$; mass spectrum (70 eV) $\underline{m/e}$ (rel intensity) 232 (6) M$^+$, 234 (4); 183 (100), 134 (39).

Anal. Calcd for C$_{10}$H$_{10}$Cl$_2$S: C, 51.55; H, 4.32; Cl, 30.41; S, 13.75. Found: C, 51.74; H, 4.45; Cl, 30.32; S, 13.56.

## 1,3-Dihydro-1,3-bis(chloromethyl)benzo[c]thiophene 2,2-dioxide (79):

The procedure employed was identical to the oxidation of $\underline{76}$ (vide supra). From 0.410 g (1.76 mmol) of $\underline{78}$ was obtained 0.390 g (85.0%) of yellow oil which was readily crystallized from methylene chloride--ether as a pale yellow solid, $\underline{79}$: mp 117-119°; nmr (CDCl$_3$) two doublets centered at δ 4.07 and 4.10 (4H), a triplet at 4.60 (2H) and a singlet at 7.49 (4H); ir (KBr) 1490, 1330, 1150, 1120, 730, 540 cm$^{-1}$; mass spectrum (70 eV) $\underline{m/e}$ (rel intensity) 264 (35) M$^+$, 266 (24), 200 (100).

1,3-Dihydro-1,3-dimethylbenzo[c]thiophene 2,2-dioxide (80):

To a solution of 79 (0.630 g, 2.4 mmol) in 50 ml of sodium-dried benzene was added 0.80 ml (2.8 mmol) of a 70% benzene solution of Vitride[1] [NaAlH$_2$(OCH$_2$CH$_2$OCH$_3$)$_2$] via syringe, and the solution was refluxed for 12 hr. The reaction was cooled to 0° and neutralized with 20% sulfuric acid.

The benzene layer was separated, washed with 10 ml of water, dried over potassium carbonate and concentrated to 0.350 g (72.9%) of 80 as a yellow oil: nmr (CDCl$_3$) δ 4.22 (q, 2H), 1.61 and 1.59 (two doublets, 6H, J = 7 Hz) and 7.3 (s, 4H); ir (film) 770, 1140, 1320 cm$^{-1}$; mass spectrum (70 eV) m/e (rel intensity) 196 (14) M$^+$, 132 (100); mass spectrum calculated for C$_{10}$H$_{12}$O$_2$S m/e = 196.055796, found m/e = 196.057587.

1,3-Bis(methylene)benzo[c]thiophene (81):

To a solution of 0.870 g (3.37 mmol) of 78 in 3 ml of acetonitrile was added 1.07 g (7.04 mmol) of 1,5-diazabicyclo-[5.4.0]undec-5-ene (DBU) in 3 ml of acetonitrile, and this solution was stirred for 5 min. The reaction mixture was concentrated to approximately 2 ml; 20 ml of chloroform was added, and the residual acetonitrile and the DBU salts were removed by washing with water. The chloroform layer was

[1]Eastman Chemical trademark.

dried over anhydrous potassium carbonate and concentrated under a nitrogen atmosphere. The structure assignment was based on the nmr spectrum since the instability of 81 precluded its purification despite numerous attempts. Oxidation of 81 with m-chloroperbenzoic acid in an attempt to obtain a stable sulfone derivative failed to afford an isolable product. The olefinic protons appeared as sharp peaks at δ 5.24 and 5.78 (each slightly split by geminal coupling, J = 1) and the aromatic protons as a symmetrical multiplet at δ 7.50.

### 1-Methylene-2-benzothiopyran (82):

The procedure was the same as described above for the reaction of 78 with DBU. The isomeric diolefin 82 was also unstable to isolation, and its structure was based on the appearance of four olefinic peaks at δ 5.15, 5.50, 6.42 and 6.48. The two olefinic peaks of 81 were also observable.

PART II.  THE SYNTHESIS AND REARRANGEMENTS OF
          ORGANOSILICON SYSTEMS

## HISTORICAL

## Silepin Synthesis

In contrast to cycloheptatriene, which was obtained by Ladenburg (68) from atropine in 1881, the unsubstituted organo-silicon analog, silepin 88, has not been reported in the literature.
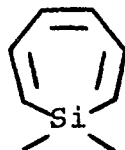
88

Extensive work has been invested in the carbon analog of silepin in the past 90 years as summarized in a recent review article by Maier (69). It has been established that cyclo-heptatriene itself exists in a boat conformation that is rapid-ly inverting. A coalescence temperature of -140° has been determined at which point the methylene protons show separate signals in the nmr spectrum. As substituents are added to the cycloheptatriene ring system, the inversion barrier in-creases. This is particularly true for benzo substituents which have been studied for both the carbocyclic and sila-cyclic systems. Although the geometry of cycloheptatrienes and silacycloheptatrienes are important questions in them-selves, there is a unique problem in the silacycloheptatriene ring system. The silicon atom possesses valence shell d orbitals, and as such this system might serve as a probe for

($\pi \rightarrow$d)$\pi$ bonding. The resulting cyclic delocalization of the

6$\pi$ electrons might be significant enough to stablize a planar

ring in silepin.

Birkofer and Kramer (70) reported the synthesis of 3,3-

diphenyl-3H-benzo[d]silepin (89) by dehydrohalogenation of

1,5-dibromo-3,3-diphenyl-1,2,4,5-tetrahydro-3H-benzo[d]-

silepin (90). Very low yields of the desired benzo[d]-

silepin 89 were obtained because of the known tendency of

the intermediate to undergo the β-halo silicon elimination.

The authors concluded that there was interaction between the

π electrons through the vacant d orbitals on silicon on

the basis of infrared double bond stretching frequencies.



| 90 | 89 R=Ph | 95 R=Cl |
| R=Ph | 94 R=Cl | |
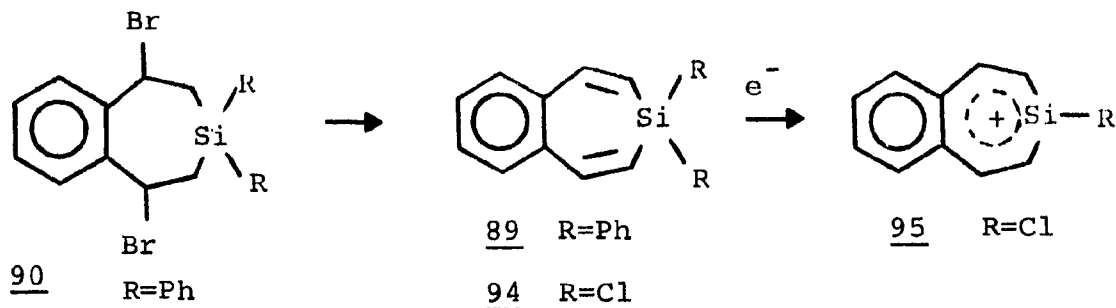
Three groups have independently reported the synthesis

of 5,5-dimethyl-5H-dibenzo[b,f]silepin (91) by dehalogenation

of the corresponding γ,γ' dibromide 92 (71), by dehydrohalo-

genation (72), and by dehydrogenation (73). Barton et al.

(71) have found that the silicon methyl groups of the

dibenzo[b,f]silepin 91 appeared as a singlet in the nmr

spectrum at room temperature, which suggested a rapidly inverting boat geometry, a planar geometry or a noninverting boat geometry with fortuitous nmr equivalence of silicon methyl groups. A low temperature nmr study showed no change on cooling until -80° when all lines started to broaden, presumably due to viscosity changes. This observation does not allow a decision to be made on the geometry of the system. The uv spectrum of dibenzo[b,f]silepin 91 was also examined and found to be extremely similar to the all-carbon analog, thus arguing against (π→d)π cyclic delocalization in this system. These authors also noted that the earlier ir spectrum of the benzo[d]silepin reported by Birkofer and Kramer was not significantly different from other vinyl silanes which do not have the possibility of (π→d)π cyclic delocalization.
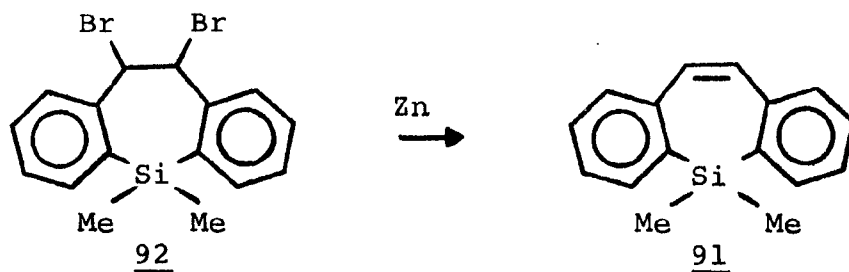
In 1972 Corey and Corey (74) reported investigations of 9,9-dimethyl-9H-tribenzo[b,d,f]silepin (93), and observed two signals in the nmr spectrum for the two methyl groups at room temperature. At 200° no line broadening was observed,

but a double resonance experiment showed some exchange of sites was occurring. An x-ray structure confirmed the proposed boat conformation of this silepin ring system. These authors pointed out that stereochemical rigidity has also been shown for tribenzo carbon analogs such as 9H-tribenzo[a,c,e]cycloheptene ($\Delta G^{\ddagger}$ = 24.0 kcal/mol at 202°), and that the barriers to rotation for the tribenzo[b,d,f] silepin 93 and the corresponding carbocycles are of the same magnitude.



93
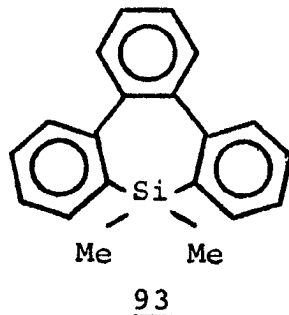
The silepin ring system is also of interest to the heterocyclic chemist as a potential precursor to the silicon analog of the tropylium cation. Surprisingly, there are no examples of the siliconium ion, a trivalent positively charged silicon species. Attempted synthesis of such a species and explanations of the absence of the siliconium ion have been very active areas of research in silicon chemistry. Birkofer et al. (75) have examined the mass spectrum of 3,3-dichloro-3H-benzo[d]silepin (94) and have found a very strong loss of Cl suggesting the formation of a benzosilepinium cation 95.

At present, there is no available evidence in support of through conjugation in the silepin system or evidence in support of a planar ring. However, it should be noted that benzosilepins might be poor models in which to look for through conjugation in view of the decreased stability of benzotropylium cations relative to the parent tropylium cation (76). Similar comments can be made on synthetic approaches to a silepinium cation; benzosilepinium cations are expected to be destabilized relative to the parent silepinium cation.

There are several examples of silepins that have tentative structure assignments. Gilman et al. (77) reported the reaction of hexaphenyl silole and dimethylacetylene dicarboxylate to form the silanorbornadiene 96. This adduct reacted with ethanol to form a yellow intermediate to which the silepin structure 97 or the norcaradiene structure 98 was tentatively assigned. Decomposition of this intermediate resulted in silylene loss and formation of the corresponding benzene derivative. The complete substitution on this possible silepin system made a positive assignment impossible without x-ray crystallography.

Witiak (78) has investigated the reaction of 2,3,4,5-tetraphenyl-1,1-dimethyl silole and perfluorobutyne. The silanorbornadiene 99 was proposed as an intermediate which
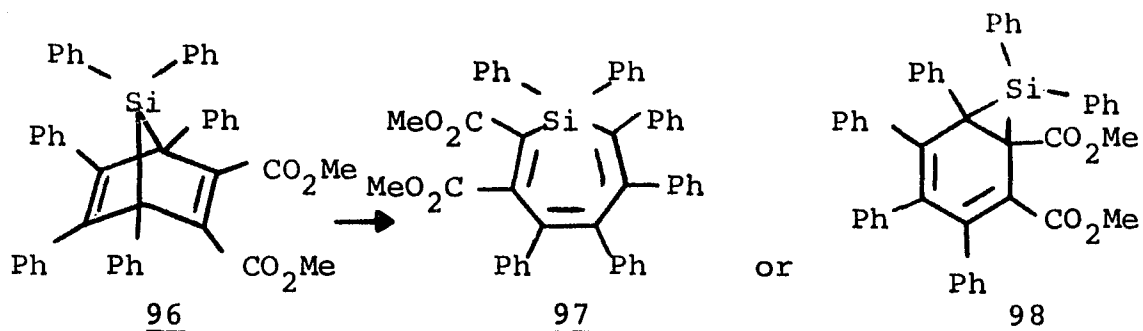
further rearranged to an isomer for which the silepin

structure 100 was tentatively assigned.
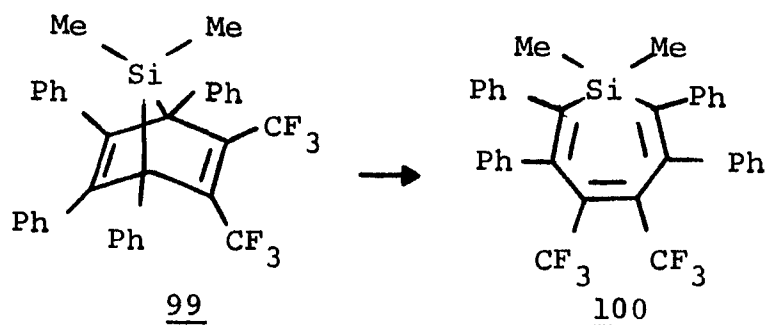


Silepin and Related Carbocyclic
Rearrangements

Much of the research effort in the carbocyclic analogs

of silepin has been directed toward a study of rearrange-

ments in order to develop better synthetic approaches by a

thorough understanding of the rearrangement process, and to

explore the implications of orbital symmetry. A brief summary

of these rearrangements and their relationship to the silepin

problem will be presented in the following section as sum-

marized in Scheme 8.

Scheme 8
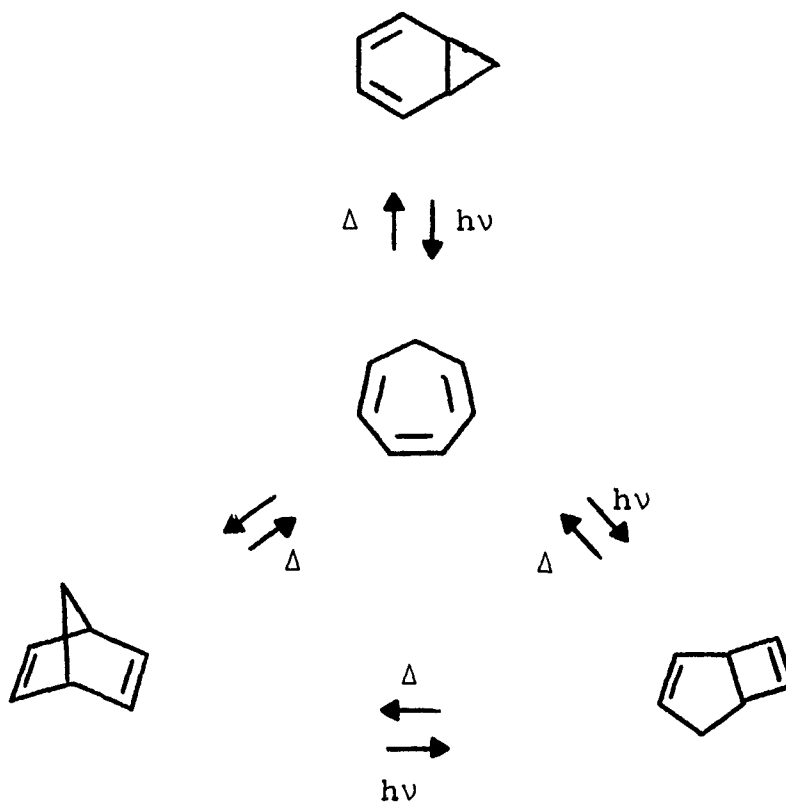


## Cycloheptatriene-norcaradiene isomerizations

The thermal isomerization of cycloheptatriene into nor-
caradiene can be viewed as a disrotatory electrocyclic ring
closure and therefore thermally allowed by the rules of Wood-
ward and Hoffmann (79). An important aspect of the silepin
problem is to consider the analogous equilibrium between
silepin 88 and the silanorcaradiene 101.

88          101
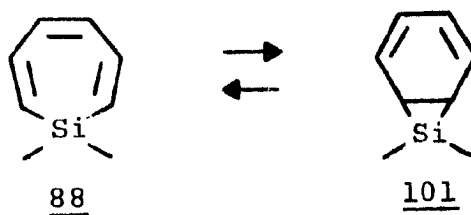
It has been found that simple cycloheptatrienes have
equilibria far on the mono-cyclic side, and the norcaradiene
structure can be obtained only with π-electron acceptors
or in unusual bridging situations (69). This equilibrium
is important in the chemistry of other heterocyclohepta-
trienes. The oxygen analog (oxepin) is known to exist in
equilibrium with the oxonorcaradiene, while the sulfur analog
(thiepin) equilibrium appears to be irreversible because the
thianorcaradiene readily extrudes sulfur to the related ben-
zene derivative (42). A tautomerization of silepin to sila-
norcaradiene would involve the formation of a silacyclo-
propane, which with one unusual exception (80) is unknown,
and might extrude a divalent silicon to form benzene.
Birkofer et al. (75) pyrolyzed the benzo[d]silepin 94 at
500° and isolated the corresponding hydrocarbon, napthalene,
without comment on the mechanism. Although all reported
silepins show no tendency to tautomerize to the silanorcara-
diene, it must be pointed out that benzene rings fused in the
b, d, or f positions lock the silepin double bonds in the sila-
cycloheptatriene isomer. This question must therefore remain

unanswered until nonannulated silepins can be synthesized.

Paquette and Leichter (81) found that pyrolysis of 1,1-dimethyl-2,5-diphenylcycloheptatriene (102) at 200° afforded 7,7-dimethyl-2,5-diphenylnorcaradiene (103). Photolysis of the norcaradiene through Pyrex resulted in a photo-1,5-sigmatropic carbon rearrangement back to the cycloheptatriene. Each of the individual paths have precedence in the literature, but this is the first example of a "closed loop reaction sequence" within the norcaradiene-cycloheptatriene series.
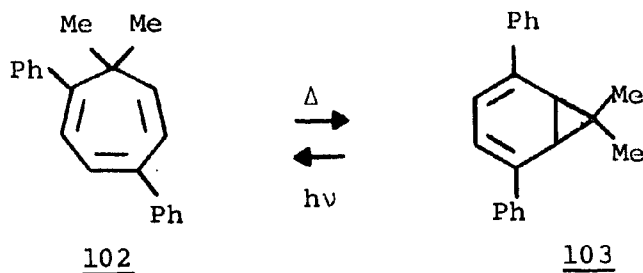


Cycloheptatriene-bicycloheptadiene isomerizations

The isomerization of cycloheptatriene to bicyclo[3.2.0]-heptadiene is a disrotatory 4 e⁻ electrocyclic ring closure and is therefore predicted to be photochemically allowed by the rules of Woodward and Hoffmann (79). In fact, photolysis of cycloheptatriene takes place, but very slowly. Similarly, thermolysis of bicyclo[3.2.0]heptadiene is a forbidden process and is not expected to proceed very readily. In spite of the orbital symmetry imposed barrier, successful pyrolysis of

bicyclo[3.2.0]heptadienes have been accomplished at high temperatures. Paquette and Leichter (81) reported that pyrolysis of bicyclo[3.2.0]heptadiene 104 at 170° afforded 1,1,2-trimethyl-7-phenylcycloheptatriene (105) which could be reversed very cleanly by photolysis through quartz.

170°
→
←
hν

Ph    Me
Me  Me Me

Ph    Me
Me  Me

104          105
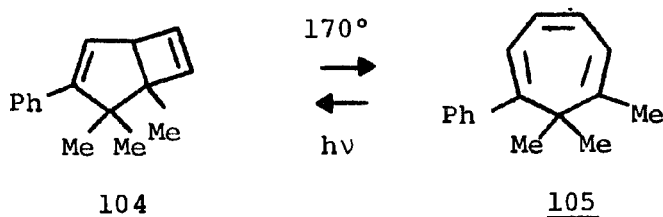
Similar routes have been employed in the synthesis of heterocyclic compounds. Both the synthesis of thiepins (42) and azepins (82) have been reported by pyrolysis of the appropriate hetero bicyclo[3.2.0]heptadiene.

Another convenient route to cycloheptatriene was reported by Dryden (83) in 1954. Solvolysis of bicyclo[3.2.0]-hept-2-ene-6-yl tosylate in acetic acid buffered with sodium acetate afforded cycloheptatriene in an overall yield of 50%. No mechanism was presented, but the allylcarbinyl ion was presumably formed, followed by elimination.

## Cycloheptatriene-norbornadiene isomerizations

The thermal rearrangement of 7,7-dimethyl-1,4-diphenyl-norbornadiene 106 was also reported as a route to 1,1-

dimethyl-2,5-diphenylcycloheptatriene <u>107</u>, presumably via a

1,3 shift with inversion at the migrating center followed

by isomerization of the intermediate (not isolated) nor-

caradiene. The cycloheptatriene <u>107</u>, however, was a kinetic

product and was difficult to isolate. A competing rearrange-

ment also occurred from which the more stable norcaradiene

<u>101</u> was isolated (81).
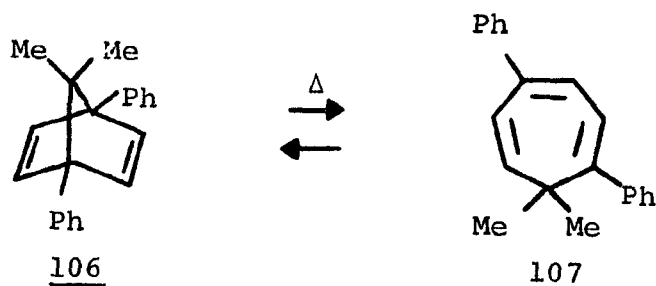


There is possibly a precedence for this type of re-

arrangement in organosilicon chemistry in the previously

mentioned work of Gilman <u>et al</u>. (77). 7-Silanorbornadiene

<u>96</u> was found to be unstable in methanol and rearranged to

silepin, presumably via the same mechanism as presented for

the carbon analog.

## Norbornadiene-bicycloheptatriene isomerizations

There is another potential relationship between the

cycloheptatriene isomers that also deserves to be mentioned.

Berson (84) has found that bicyclo[3.2.0]heptenes can be

converted to the appropriate norbornenes by a 1,3 shift with inversion at the migrating center. These findings are related to recent work reported by Russell and Schmitt (85) in which esr studies showed an isomerization between norbornadiene and bicyclo[3.2.0]heptadiene semidiones.

Vapor phase pyrolytic rearrangements of bicyclic systems have been reported by Schiess and Funfschilling (86) who prepared 2-methylbicyclo[3.2.0]hept-2-ene-7-one (108). Pyrolysis at 450° afforded products derived from the ketene 109 formed by a 2 + 2 cycloreversion. Another product isolated was the rearranged isomer, 1-methylbicyclo[2.2.1]hept-5-ene-2-one. The norbornene was cleanly converted to the bicyclo[3.2.0] 108 system by photolysis. No cycloreversion with fragmentation to ketene and methylcyclopentadiene was observed.



Products
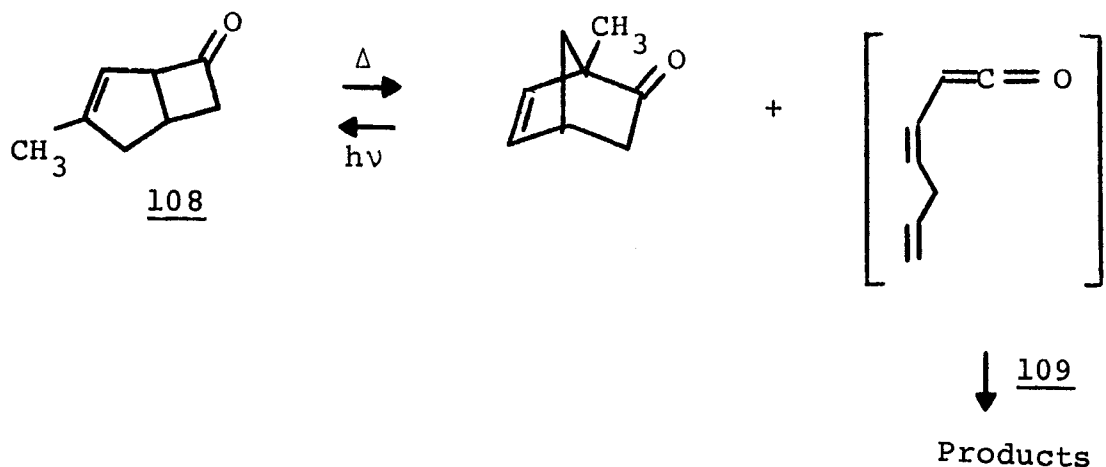
RESULTS AND DISCUSSION

The primary objective of this aspect of the research
program was to synthesize and investigate the properties of
a silepin, as discussed in the following section.  A
secondary and related goal in this investigation was to study
rearrangements in a bicyclic organosilicon system in view
of the limited information available in this area (87).

The previous exploratory work by Nelson (88) demonstrated
that an organosilicon bicyclic system might be a route to
silepin 88, although the silepin was not thoroughly purified
or characterized.  It was this work that formed the starting
point in the present investigations.

The basic starting material for the entire program was
1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-
5-one (110), the preparation of which had been outlined
previously (88).  Cyclization of dimethyldichlorosilane with
styrene and lithium afforded 1,1-dimethyl-2,5-diphenyl-
silacyclopentane (111) as a mixture of cis and trans iso-
mers.  Dehydrogenation of 111 with 2,3-dichloro-5,6-
dicyanoquinone (DDQ) gave good yields of 1,1-dimethyl-
2,5-diphenylsilacyclopenta-2,4-diene (112) using the method
developed by Barton and Gottsman (89).  A photocyclization
of 112 and 1,1-dimethoxyethylene using 1,1-dimethoxyethylene
as the solvent formed 1,1-dimethyl-2,7-diphenyl-5,5-

dimethoxy-l-silabicyclo[3.2.0]hept-2-ene (113) which was
hydrolyzed to 110.
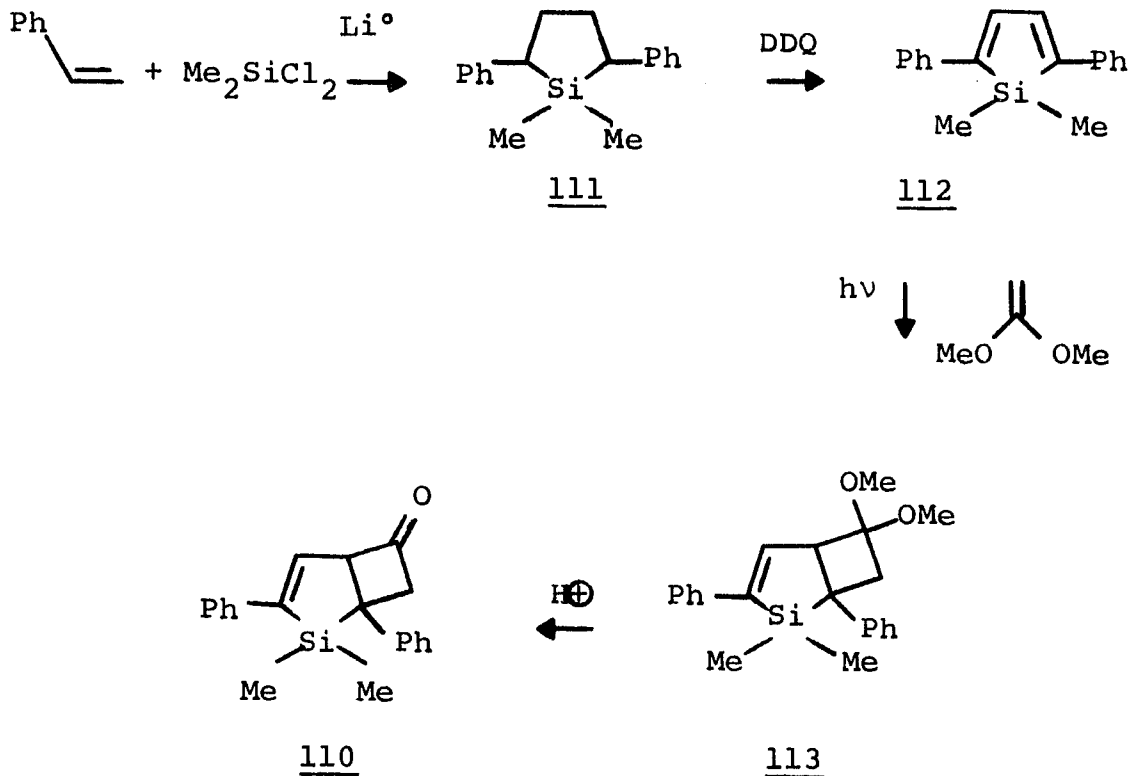


The diphenylbicyclo[3.2.0]ketone 110 was viewed as a good
precursor to a silepin through the intermediacy of a 7-
silanorbornene by direct analogy to the thermolysis of the
carbon analog reported by Schiess and Funfschilling (86).
Pyrolysis of the diphenylbicyclo[3.2.0] ketone 110 at 300°
afforded only 1,1-dimethyl-2,5-diphenyl-1-silacyclopenta-
2,4-diene (112) and (presumably) ketene. Although both the
carbocyclic and organosilicon bicyclic systems react by a

cycloreversion process, the reasons for the different
direction of ring opening and the failure to form a sila-
norbornene are not clearly understood.

These findings suggested that a more direct route to a
bicyclo[3.2.0] system might be possible which would avoid
the synthetically limiting photochemical reaction with 1,1-
dimethoxyethylene. The more reactive ketene, dichloroketene,
was generated at -20°, and silole 112 was added with warming
to room temperature. No reaction was observed, and the
starting silole was recovered almost quantitatively.
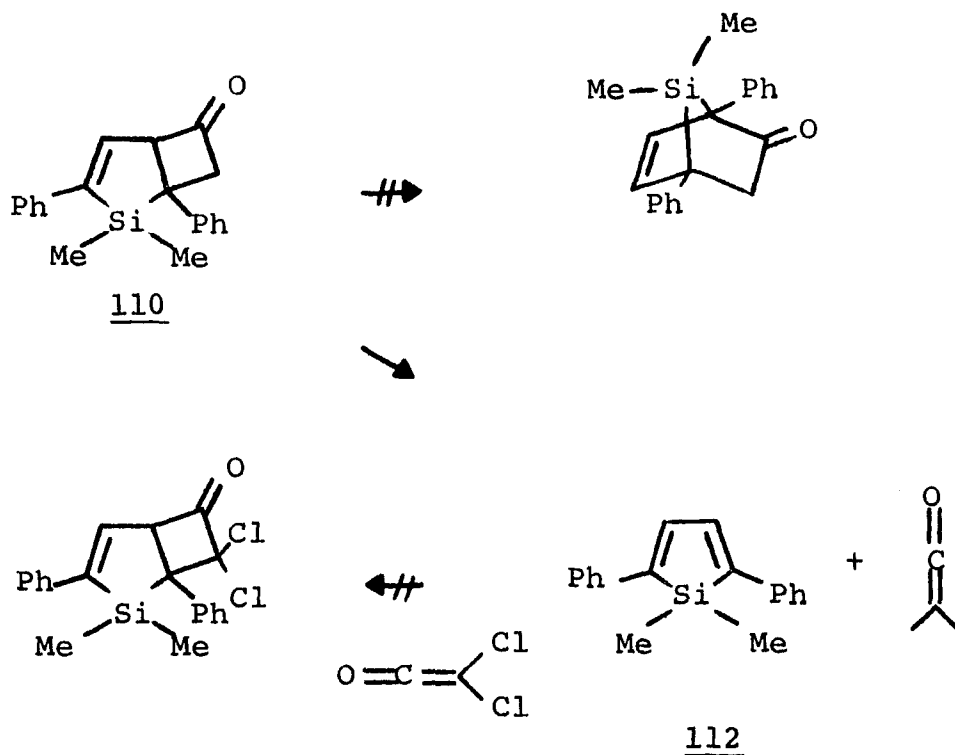
Our next approach to the problem was to investigate solvolytic reactions of bicyclic systems similar to those reported by Dryden (83) in carbocyclic systems. For this purpose a bicyclic[3.2.0] alcohol was a prerequisite for the necessary starting materials. Reduction of the diphenylbicyclo[3.2.0] ketone 110 with sodium borohydride in ethanol gave a 50:50 mixture of endo- and exo-1,1-dimethyl-2,5-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (114) and (115) respectively in contrast to the stereoselective reductions observed in the carbon analogs (90). The endo alcohol 114 was isolated as a white crystalline solid after column chromatography while the exo isomer was obtained only as a viscous oil. The 3,5-dinitrobenzoate derivatives of both the endo- and exo-diphenyl alcohols 116 and 117 were obtained as crystalline solids and were fully characterized.

An important aspect of this problem is the complete structure assignment of the endo-alcohol 114, which was facilitated by spin-decoupling experiments, shown in Figures 1 and 2 and summarized in Table 2. $H_C$ was assigned as the exo methylene proton because of the precedence of "W coupling" in cyclobutane rings where the interacting nuclei are in a cis arrangement (91). This is also consistent with the chemical shift of $H_B$ relative to $H_C$. The endo methylene proton $H_B$ is expected to lie in the shielding cone of the olefinic double bond and is therefore expected to be
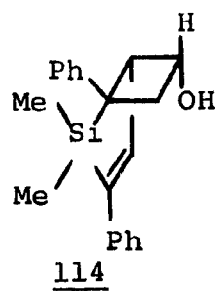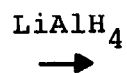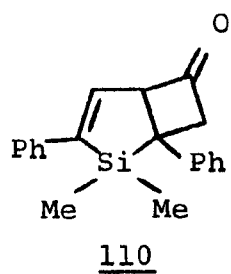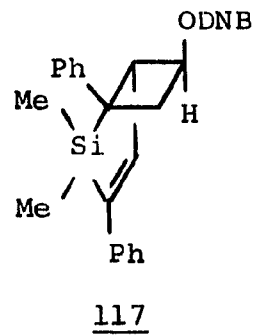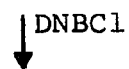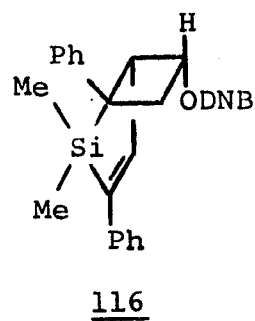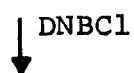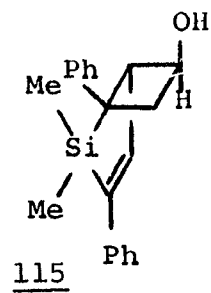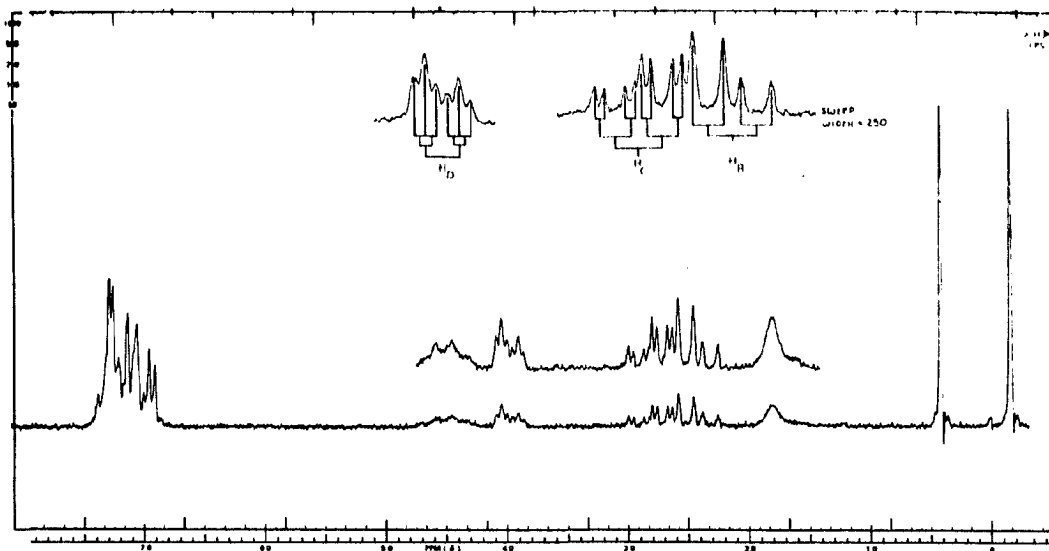
Figure 1.   60 MHz nmr spectrum of endo-1,1-dimethyl-2,7-
diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol
(114)
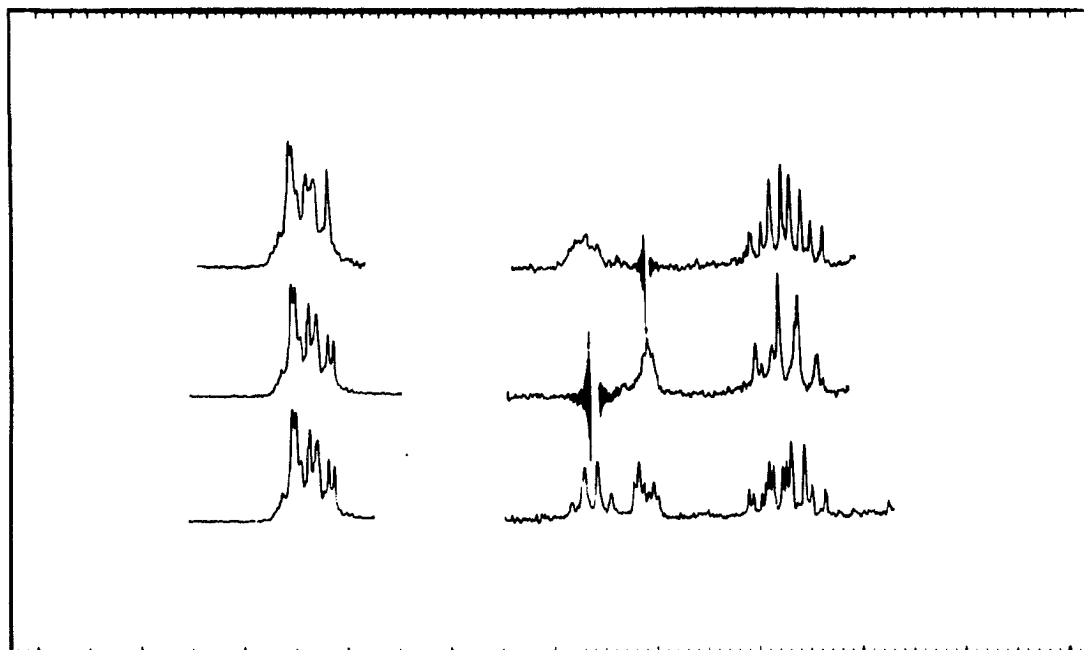


Figure 2.   60 MHz nmr spectrum of spin-decoupling of endo-
1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]
hept-2-ene-5-ol (114)

Table 2.  Results of spin-decoupling experiments on endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (114)
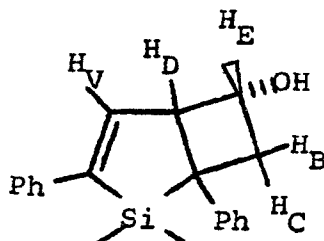


114

| Irradiation Frequency | $H_B$ $\delta$ 2.43 | $H_C$ $\delta$ 2.82 | $H_D$ $\delta$ 3.98 | $J_E$ $\delta$ 4.49 | $H_V$ $\delta$ 6.94 |
|---|---|---|---|---|---|
| no irradiation | d of d $J_{BC}$ = 12.0 Hz $J_{BE}$ = 7.5 Hz | d of d of d $J_{BC}$ = 12.0 Hz $J_{CD}$ = 2.5 Hz $J_{CE}$ = .7.5 Hz | d of t | m | d $J_{DV}$ = 3.0 Hz |
| $H_D$ 239 Hz | d of d $J_{BC}$ = 12.0 Hz $J_{BE}$ = 7.5 Hz | d of d $J_{BC}$ = 12.0 Hz $J_{CE}$ = 7.5 Hz | | | s |
| $H_E$ 270 Hz | d $J_{BC}$ = 12.0 Hz | d of d $J_{BC}$ = 12.0 Hz $J_{CD}$ = 2.5 Hz | | | d $J_{DV}$ = 3.0 Hz |

shielded and shifted upfield relative to the exo proton $H_C$.
This was found to be the case in that $H_B$ was 0.4 ppm up-
field from $H_C$.

Absolute assignment of the stereochemistry of the two
isomers was made by comparison of the nmr spectra of the endo-
and exo-3,5-dinitrobenzoates 116 and 117 respectively, shown
in Figures 4 and 3. The nmr spectrum of the endo-dinitro-
benzoate 116 derived from the crystalline endo-alcohol 114
has two striking features in comparison with the exo-
dinitrobenzoate 117 obtained from the exo-alcohol. The
olefinic proton $H_V$ of the endo-dinitrobenzoate 116 is shifted
upfield from the aromatic protons by approximately 0.3 ppm
in contrast to $H_V$ of the exo-dinitrobenzoate 117 which is
lost in the aromatic region. Inspection of the two isomers
shows that the olefinic proton of the endo isomer is directed
into the aromatic dinitrobenzoate shielding cone and there-
fore shifted upfield relative to the exo dinitrobenzoate.
An ideal model compound for this analogy is exo-1,1-dimethyl-
2,5,7-triphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (118,
page 102) in which the olefinic proton is also shielded, re-
sulting in an upfield shift of 0.7 ppm.

The other noticeable feature of the nmr spectrum of the
dinitrobenzoates is the hydroxy methine proton $H_E$ of the exo-
dinitrobenzoate 117 which is shifted approximately 0.6 ppm up-
field relative to the endo-dinitrobenzoate 116. An examination

Figure 3.  60 MHz nmr spectrum of exo-1,1-dimethyl-2,7-
diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-yl
3,5-dinitrobenzoate (117)
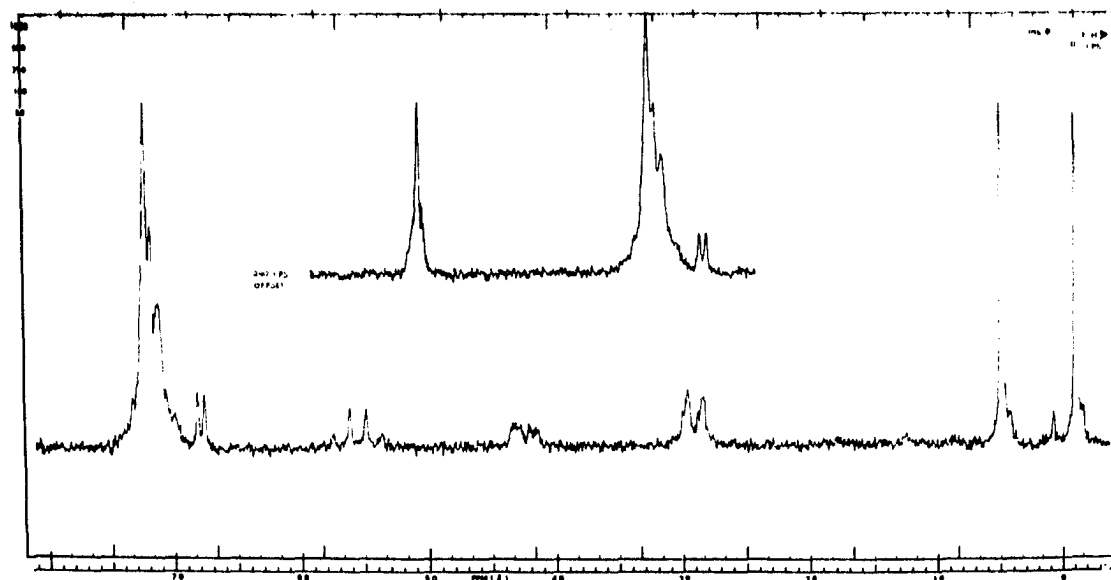


Figure 4.  60 MHz nmr spectrum of endo-1,1-dimethyl-2,7-
diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-yl
3,5-dinitrobenzoate (116)
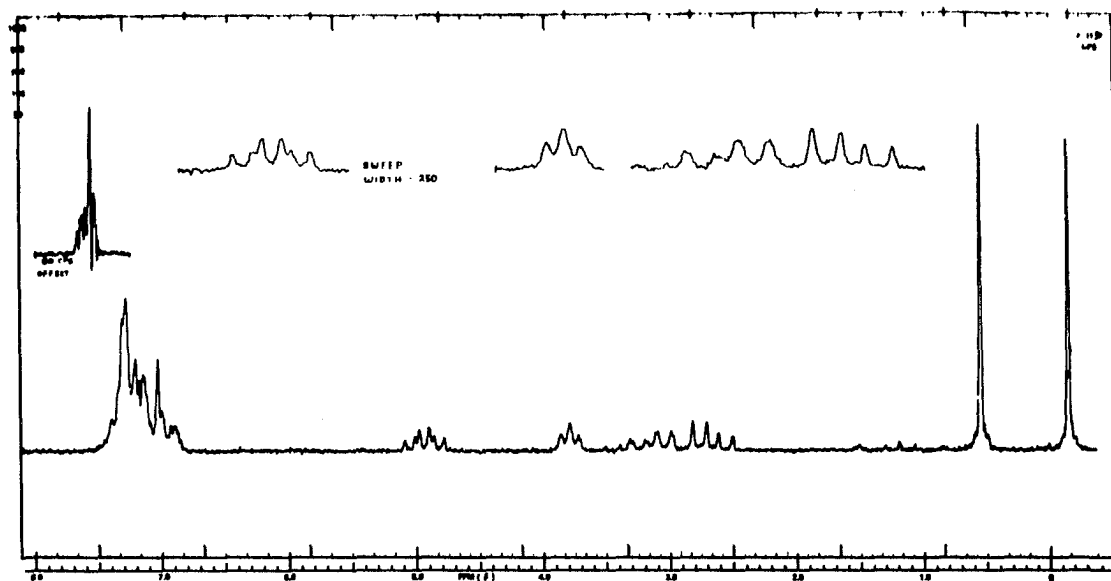
of models of the two systems again shows that the hydroxy methine proton $H_E$ of the exo dinitrobenzoate is directly in the shielding cone of the double bond and expected to appear at higher fields than the hydroxy methine proton of the endo dinitrobenzoate which is oriented away from the olefinic shielding cone.

Solvolysis of the endo-dinitrobenzoate 116 as a route to silepin was prompted by the report that solvolysis of bicyclo [3.2.0]hept-2-ene-6-yl tosylate in buffered acetic acid afforded cycloheptatriene in a 50% yield (83). The endo-dinitrobenzoate 116 was heated under reflux for 6 days in 90% aqueous ethanol containing a urea buffer. The ester was very resistant to solvolysis, and some starting material was present even after 6 days. The two main products of the reaction were identified as ethyl-3,5-dinitrobenzoate and the endo-alcohol 114. No product could be found in which the cyclobutane carbon-oxygen bond was broken in preference to acyl cleavage. This resistance to solvolysis in ethanol--water led to a second solvolysis attempt in which trifluoro-ethanol was used as a solvent. Trifluoroethanol has been promoted recently as a superior solvent with good ionizing ability and very low nucleophilicity in solvolysis reactions (92). After refluxing the endo-dinitrobenzoate 116 in neat trifluoroethanol for 24 hours, the starting material was re-covered unchanged.

Another solvolytic route to silepin was considered via
1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-
yl methane sulfonate (119). When the endo-alcohol 114 was
treated with methanesulfonyl chloride, followed by quenching
with water, a clear, impure oil was isolated by column
chromatography on silica gel. Further purification could not
be effected, and the product was found to be unstable on
silica gel. On the basis of the nmr spectrum the structure
was tentatively assigned as 1,1-dimethyl-2,7-diphenyl-1-
silabicyclo[4.1.0]hept-3-ene-2-ol (120). A comparison of
the nmr spectra of the rearranged bicyclo[4.1.0] alcohol 120
and an immediate nmr spectrum of the reaction mixture re-
vealed that the initially formed product (presumably 119) was
unstable and underwent further reaction over a period of four
hours.



MS = CH$_3$SO$_2^-$
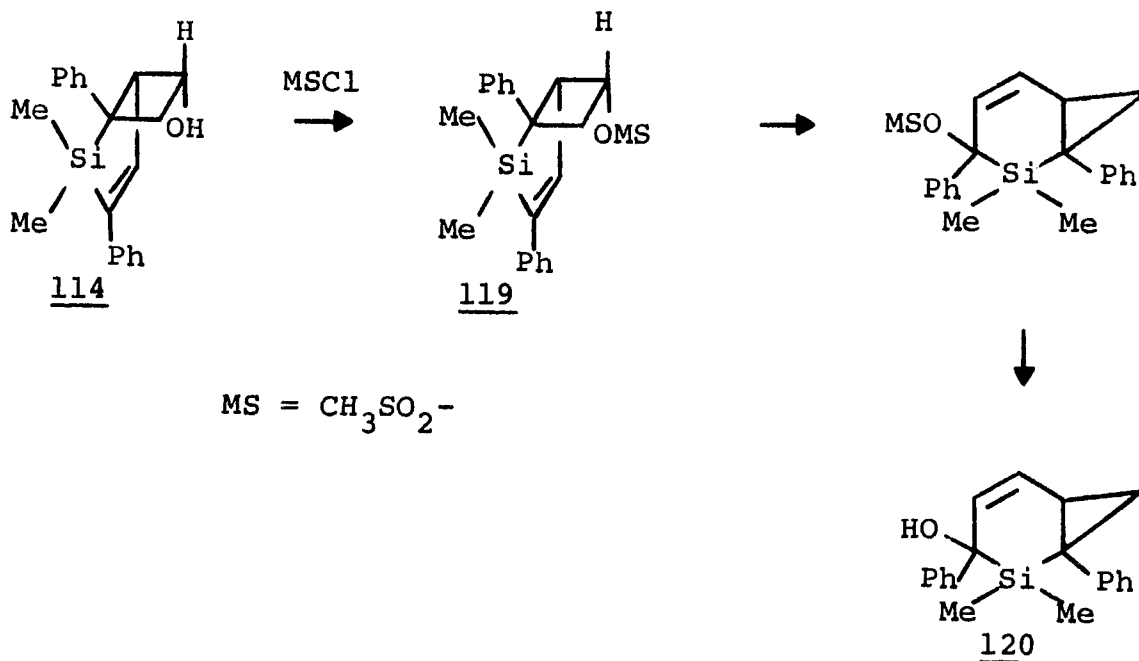
The failure of these solvolysis experiments suggested that a silabicyclo[3.2.0] cation might be generated more directly from the endo-diphenyl alcohol 114. The classical dehydration method of the early German chemists was attempted with a catalytic amount of p-toluenesulfonic acid in refluxing benzene. A recirculating Dean-Stark trap filled with molecular sieves was employed in the reaction to ensure complete removal of small amounts of water. The reaction was followed by tlc for 24 hours until no further change could be detected. A careful investigation of the reaction showed the formation of numerous products which were identified and isolated by several methods. Column chromatography on silica gel, eluting with hexane, separated an oil which had three components. Crystallization from hexane gave m-terphenyl (121) in an overall yield of 24% as identified by nmr and melting point comparison with an authentic sample. Liquid-liquid chromatography of the residual oil showed 3% of o-terphenyl (122) as identified by liquid-liquid chromatography retention times. Liquid-liquid chromatography showed that no p-terphenyl was formed in this reaction, even in trace amounts. The second component in the hexane chromatographed oil was isolated and purified by liquid-liquid chromatography and identified as 1,1-dimethyl-2,7-diphenyl silepin (123), 11% (nmr yield). The silicon methyl protons of the silepin appear as a singlet in the nmr spectrum, Figure 5, at $\delta$ 0.10 which
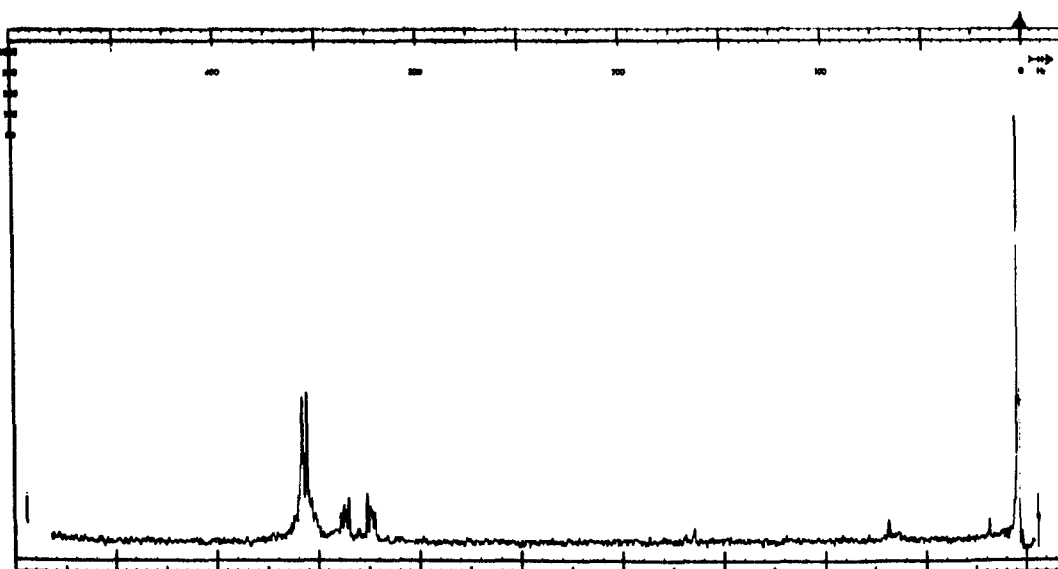
Figure 5.  100 MHz nmr spectrum of 1,1-dimethyl-2,7-
            diphenyl-silepin (123)

suggests either a rapidly inverting boat geometry, a planar

geometry or a noninverting boat geometry with fortuitous nmr

equivalence of silicon methyl groups.  A good model compound

for the silepin is 1,6,7-triphenyltropylidene, prepared by

a previously reported method (93).  The olefinic protons of

1,6,7-triphenyltropylidene appear as an AA'BB' eight-line

spectrum on an 100 MHz scale-expanded spectrum (lower field

protons further split) with centers at $\delta$ 6.40 and $\delta$ 6.71,

$J_{apparent}$ = 3.0,4.5 Hz.

    This can be compared with the olefinic protons of silepin

which also appear as an AA'BB' eight-line spectrum with

centers at δ 6.51 and δ 6.80, $J_{apparent}$ = 3.0,4.5 Hz. The

mass spectrum of 123 shows a strong parent ion at m/e 288

with methyl loss and dimethylsilylene loss as major fragmenta-

tions at 70 ev. At 24 ev the parent ion is the base peak.

Trapping experiments were attempted with a silepin-

terphenyl mixture and various dienophiles. Maleic anhydride

and the silepin did not react, even when heated to 130° for 12

hr. A more reactive dienophile, tetracyanoethylene, also

did not react at 60°. Increased heating to 150° resulted in

decomposition to a mixture of terphenyls.

Further elution with 50% ether--hexane removed the

fourth component of the reaction which was identified by nmr

comparison with an authentic sample as 1,1-dimethyl-cis-2,5-

diphenyl-1-silacyclopent-3-ene-2-ethanal (124), 12.2%.

Small amounts of the starting alcohol 114 were also observed

by nmr in the latter fractions of the 50% ether--hexane

elution.

It should be noted that the aldehyde 124 is isomeric

with the starting endo-diphenyl alcohol 114 and as such might

be a thermal rearrangement product of the starting alcohol,

because the reaction was carried out in refluxing benzene.

If this were the correct mechanism, it would be expected

that higher temperatures would result in higher yields of the

aldehyde 124. This was very clearly shown when the endo-

diphenyl alcohol 114 was pyrolyzed at 300° in a vertical
pyrolysis apparatus to afford 124, almost quantitatively, as
shown by the nmr spectrum in Figures 6 and 7.
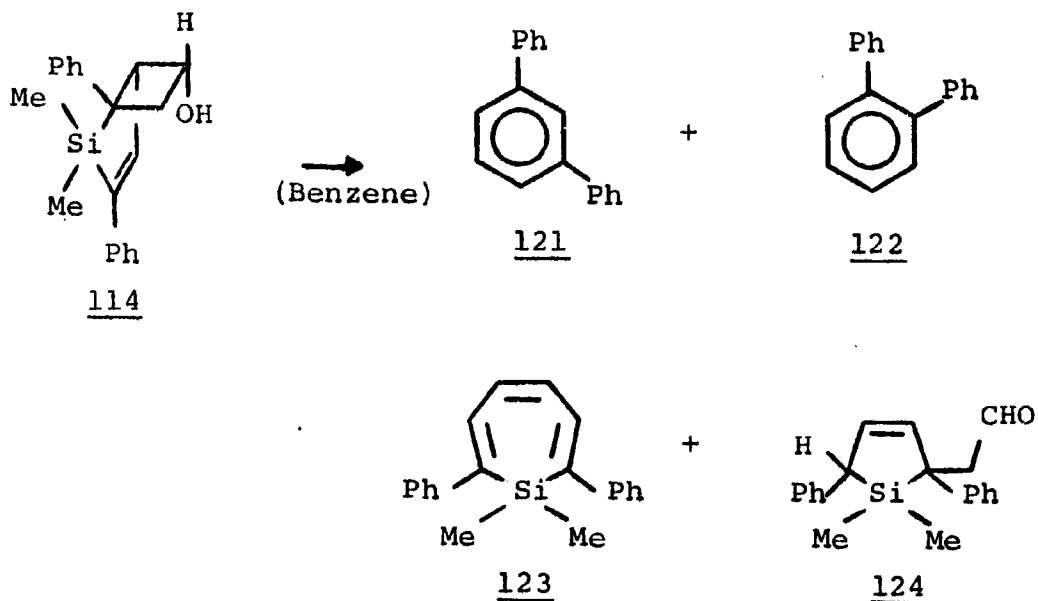
The structure of aldehyde 124 was assigned using the
spin-decoupling experiment shown in Figure 8 and summar-
ized in Table 3. An examination of stereochemical models
of the endo-diphenyl alcohol 114 revealed that the hydroxyl
proton is very proximate to the olefinic benzylic carbon
and suggested the 6e⁻ concerted mechanism for the forma-
tion of 124 shown in Scheme 9. An alternate mechanism
might involve a diradical process in which an initial
homolytic cleavage of the cyclobutane carbon bond could be
followed by hydrogen transfer and rearrangement to the same
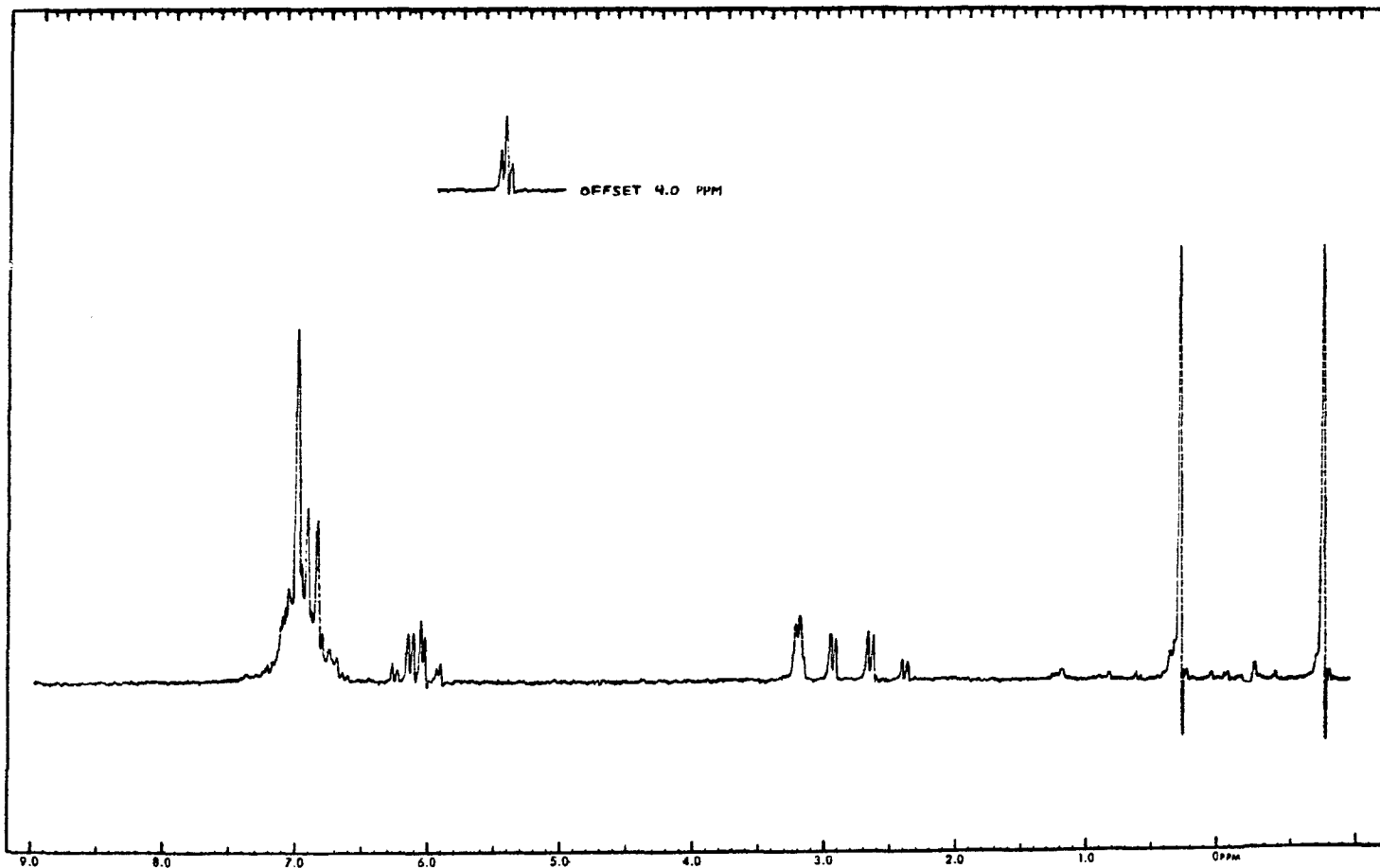
Figure 6. 60 MHz nmr spectrum of 1,1-dimethyl-cis-2,5-diphenyl-1-silacyclopent-3-ene-2-ethanal (124)
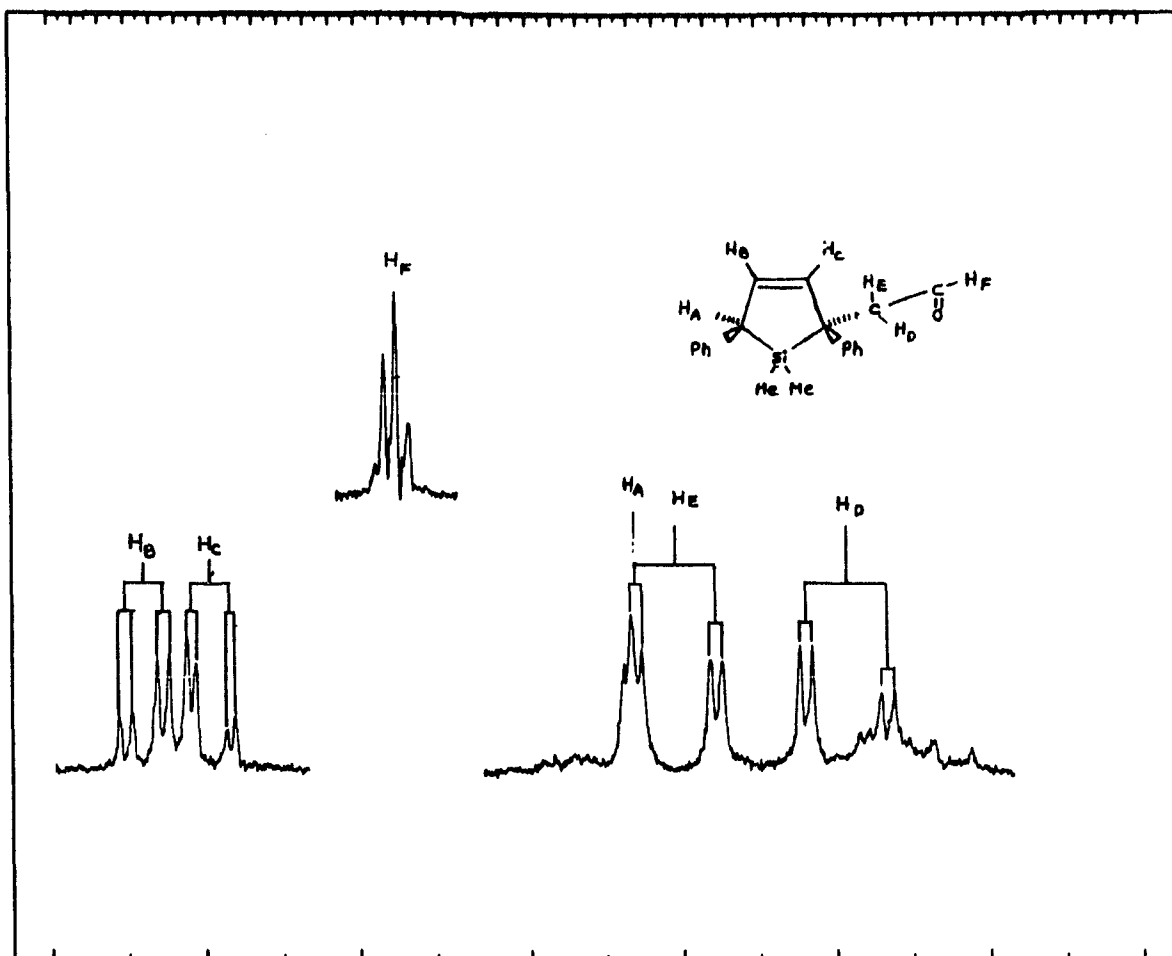
Figure 7.   60 MHz  nmr  spectrum of 1,1-dimethyl-cis-2,5-
diphenyl-1-silacyclopent-3-ene-2-ethanal (124)
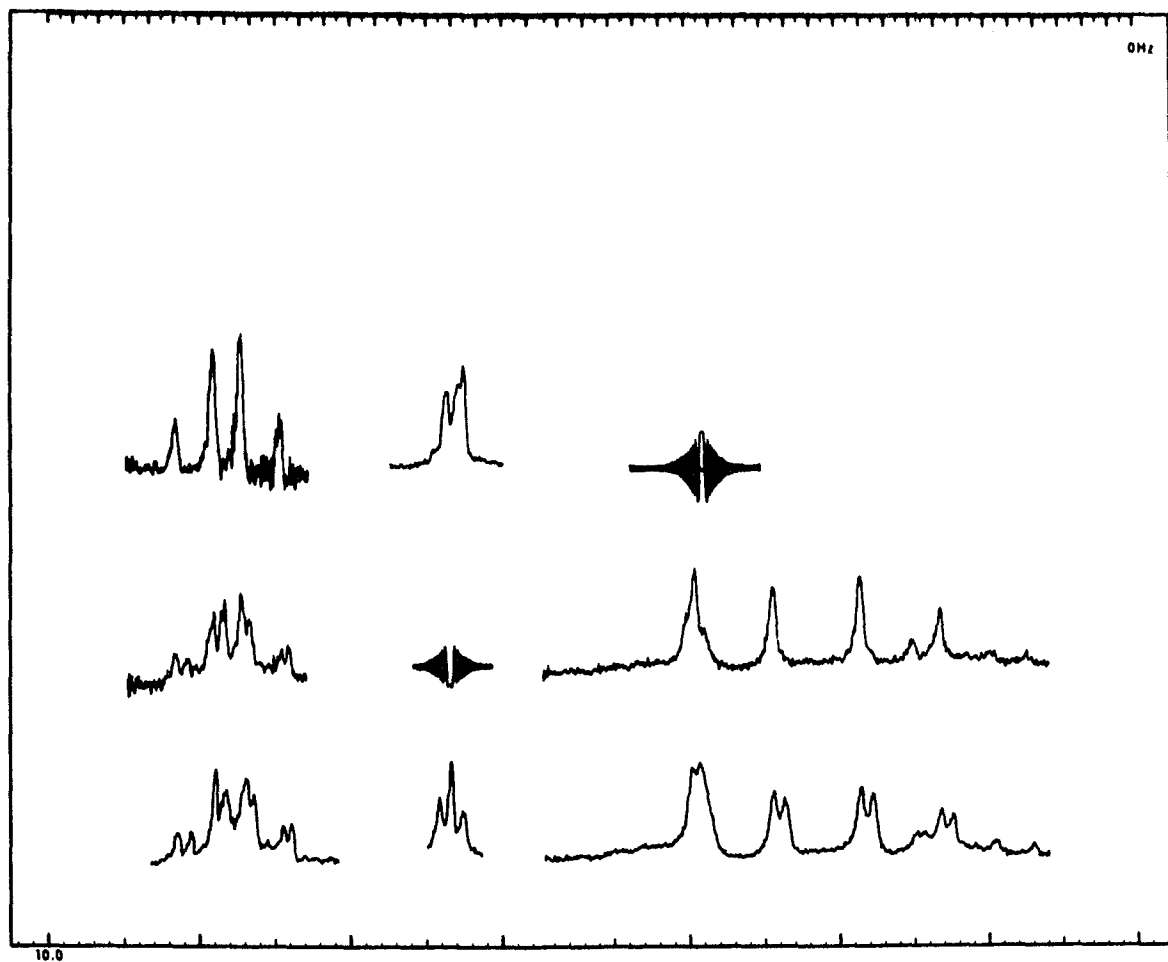
Figure 8.   60 MHz nmr spectrum of spin-decoupling of 1,1-
            dimethyl-cis-2,5-diphenyl-1-silacyclopent-3-
            ene-2-ethanal (124)

Table 3.  Results of spin-decoupling experiments on 1,1-dimethyl-cis-2,5-diphenyl-1-silacyclopent-3-ene-2-ethanal ($\underline{124}$)

| Irradiation Frequency | $H_A$ δ 2.43 | $H_B$ δ 6.00 | $H_C$ δ 6.21 | $H_D$ δ 2.51 | $H_E$ δ 3.04 | $H_F$ δ 9.44 |
|---|---|---|---|---|---|---|
| no irradiation | ? | d of d<br>$J_{BC}$ = 7.0 Hz<br>$J_{AB}$ = 3.0 Hz | d of d<br>$J_{BC}$ = 7.0 Hz<br>$J_{AC}$ = 2.0 Hz | d of d<br>$J_{DE}$ = 18.0 Hz<br>$J_{DF}$ = 3.0 Hz | d of d<br>$J_{DE}$ = 18.0 Hz<br>$J_{EF}$ = 2.0 Hz | t<br><br>t |
| $H_A$ 195 Hz | | d<br>$J_{BC}$ = 7.0 Hz | d<br>$J_{BC}$ = 7.0 Hz | | | |
| $H_F$ 566 Hz | | d of d<br>$J_{BC}$ = 7.0 Hz<br>$J_{AB}$ = 3.0 Hz | d of d<br>$J_{BC}$ = 7.0 Hz<br>$J_{AC}$ = 2.0 Hz | d<br>$J_{DE}$ = 18.0 Hz | d<br>$J_{DE}$ = 18.0 Hz | |

Scheme 9



114     124
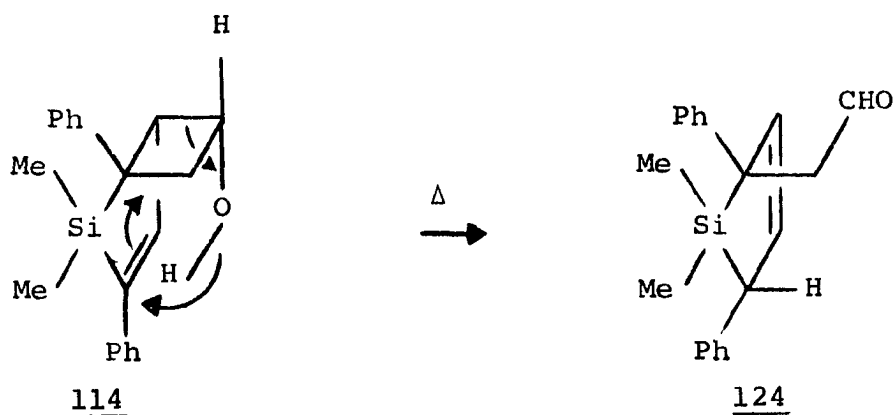
product. Such a process is not expected to be stereo-

selective and therefore not consistent with the finding

that only one isomer is formed. Pyrolysis of the exo alcohol

would be expected to form the same aldehyde product if the

diradical mechanism were operative. When the exo alcohol

pyrolysis was carried out, none of the aldehyde 124 was

formed, and only uncharacterized products were obtained.

This result is consistent with the concerted mechanism. The

stereochemistry is tentatively assigned as cis on the basis

of the expected geometry of the concerted mechanism.

Two possible mechanisms can be envisioned for the forma-

tion of silepin. Protonation of the endo-diphenyl alcohol

114 and dehydration would give rise to the cyclobutyl cation

125, which could rearrange to the allylcarbinyl ion 126 and

deprotonate to form 123. An alternate mechanism would be

the dehydration of <u>114</u> to afford 1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hepta-2,5-diene (<u>127</u>), followed by cyclobutene ring opening to <u>121</u>. It should be noted however that the latter pathway is not considered as likely because carbocyclic and heterocyclic bicyclo[3.2.0]heptadiene ring openings require higher temperatures (42, 81).
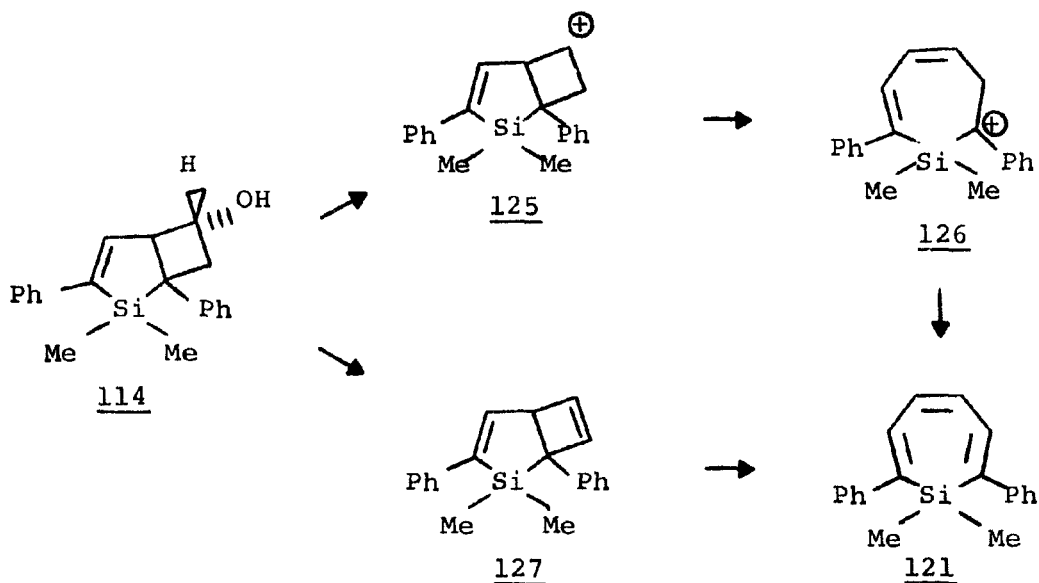


Although the finding of <u>m</u>-terphenyl in the reaction was surprising, a literature search revealed that similar isomerizations were not unprecedented. Seyferth <u>et al</u>. (94) found that a Diels-Alder reaction of α-pyrone and bis(trimethylsilyl)acetylene in bromobenzene at 140° afforded predominantly <u>m</u>-bis(trimethylsilyl)benzene (<u>128</u>) with only traces of the <u>o</u>- and <u>p</u>-isomers. It was proposed that a prismane

intermediate <u>129</u> was formed from the initial Diels-Alder adduct <u>130</u> by an unspecified mechanism. Cleavage of the cyclopropane ring between the two trimethylsilyl groups would form <u>128</u>. A reinvestigation (95) of this reaction, however, revealed that <u>128</u> was formed by acid catalyzed isomerization of <u>o</u>-bis(trimethylsilyl)benzene in the presence of small amounts of acid in the reaction mixture.
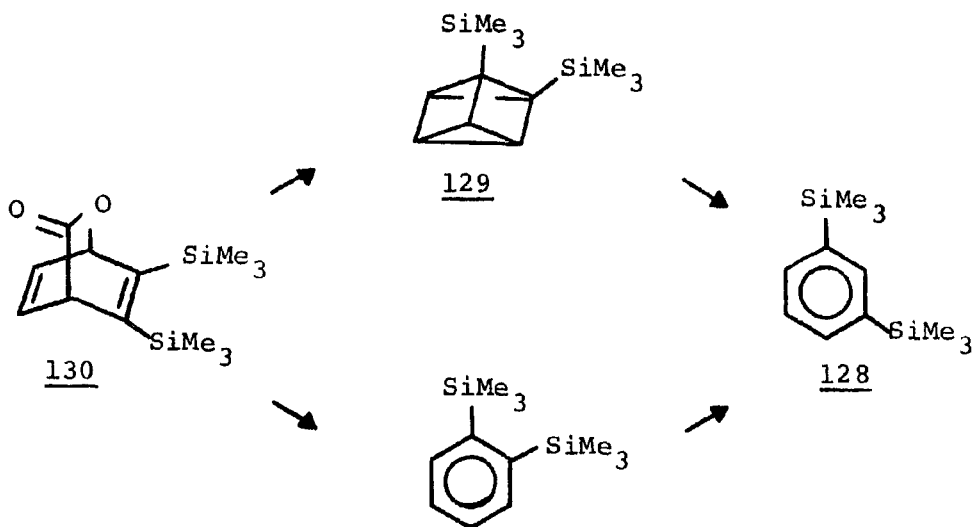


Prompted by the findings of Seyferth <u>et al.</u>, the stabilities of <u>o</u>-, <u>m</u>- and <u>p</u>-terphenyl were investigated in the presence of <u>p</u>-toluenesulfonic acid in refluxing benzene. No product isomerizations were observed, and this mechanism was eliminated from consideration in favor of the following. The initial ion <u>125</u> formed by protonation and dehydration of the

endo-diphenyl alcohol is a homoallylic ion and as such can
isomerize to the cyclopropylcarbinyl ion **131** which is also
a tertiary benzylic carbonium ion. This ion can deprotonate
and lose silylene to form the diphenyl prismane **132** with
both phenyls on the same cyclopropane ring. Although the
conversion of prismane to benzene is not a symmetry allowed
process according to Woodward and Hoffmann (79), cleavage
is expected to occur predominantly between the two phenyls
to form m-terphenyl by formation of the most stable diradical.
It should be noted that the prismane is never demanded as
an intermediate in the mechanism. Burgstahler and Chien
(96) have also proposed a prismane intermediate in a photo-
isomerization of o-di-t-butylbenzene to a mixture of meta and
para isomers.
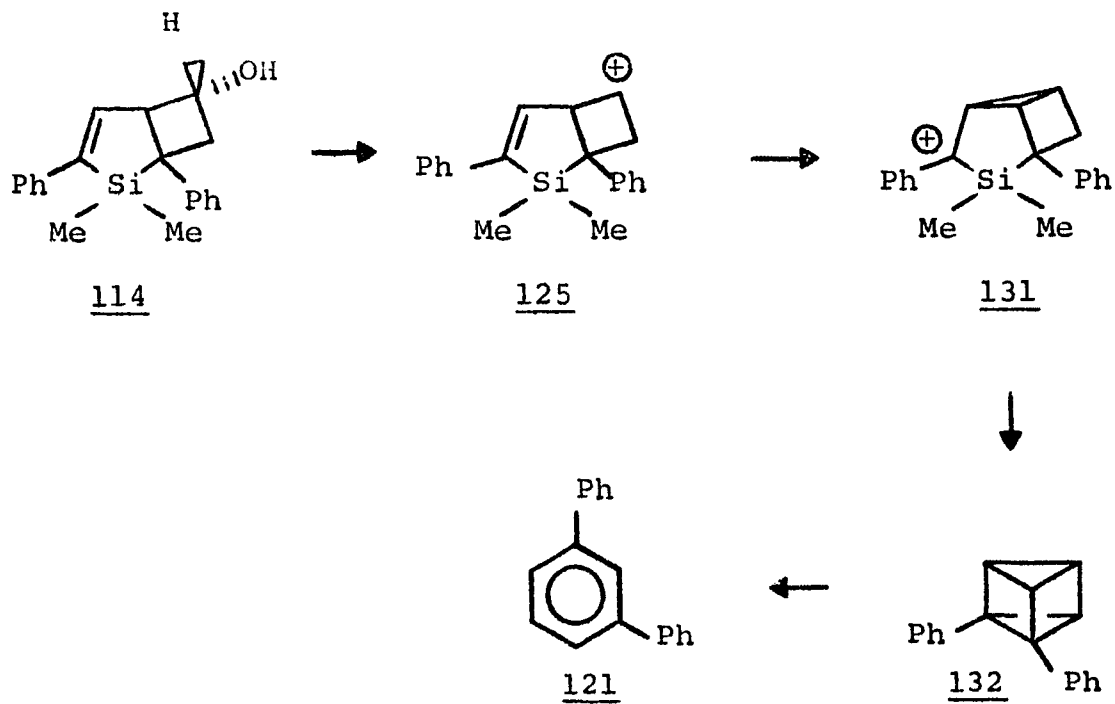
It seemed that it might be possible to reduce the thermal rearrangement to m-terphenyl, and therefore increase the amount of silepin by carrying out the reaction at a lower temperature. The endo-diphenyl alcohol 114 was therefore treated with trifluoroacetic acid at room temperature. Although the amount of m-terphenyl was reduced to zero by this process, only a 35% yield of o-terphenyl and no silepin was isolated. Presumably, the silepin could be formed and rearrange to o-terphenyl via a silanorcaradiene under the reaction conditions.
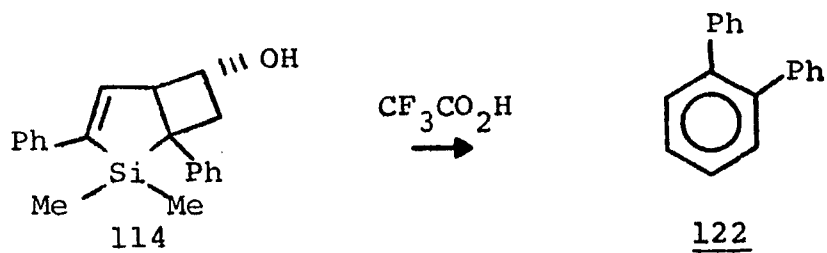


In order to consider the mechanism for silepin formation via a diene intermediate it was desired to prepare 1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hepta-2,5-diene (127). For this purpose the precursor endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-yl trifluoroacetate (133) was prepared from the corresponding alcohol. Pyrolysis of 133 at 250° did not form the desired diene 127 but rather a 19.9% yield of m-terphenyl.
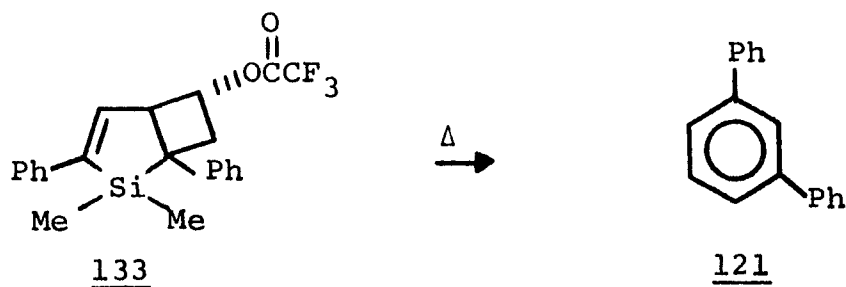
Another route to the diene intermediate 127 was sought that could be carried out at lower temperatures and possibly avoid the m-terphenyl formation. When the endo-alcohol 114 was treated with thionyl chloride in pyridine, a mixture of chlorides was obtained as determined by nmr spectroscopy. The major product was isolated and identified as 1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-yl chloride (134) in which the stereochemistry was assumed to be exo from the well established stereochemical route of this conversion in pyridine. Another product in the reaction mixture was 1,1-dimethyl-2,7-diphenyl-1-silabicyclo[4.1.0]hept-3-ene-2-yl chloride (135), presumably formed by a cyclobutyl cyclopropylcarbinyl rearrangement. These products are unstable to silica gel chromatography, but the nmr evidence is unambiguous. The rearranged isomer 135 showed a multiplet at δ 1.10 in the nmr spectrum for the geminal cyclopropyl protons $H_A$ and $H_B$ which can be compared to δ 1.50-1.54 for the geminal cyclopropyl protons $H_a$ and $H_b$ in the model compound 136. The cyclopropylallyl proton $H_C$, at δ 1.90 can be compared with $H_C$ at δ 2.36 in the model compound 136 (97).
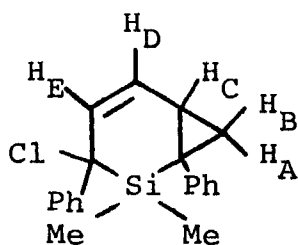
135
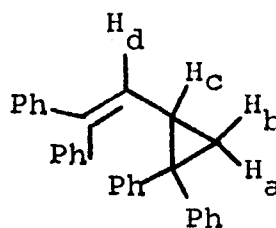
136

A solution of 134 and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in acetonitrile did not undergo reaction at room temperature but required heating to 60°. The desired dehydrohalogenation product 127 was not obtained but instead a small amount of p-terphenyl was isolated. A mechanism for the formation of p-terphenyl (137) which can be written for this reaction is one in which dehydrohalogenation formed 127 followed by a 1,3-sigmatropic rearrangement with inversion to form 2,5-diphenyl-7,7-dimethyl-7-silanorbornadiene (138). The precedented elimination of silylene from silanorbornadiene systems (78) would then explain the formation of p-terphenyl.

A different 1,3 rearrangement of the diphenyl[3.2.0] system can be visualized in which a carbon-silicon bond is broken and migrated to a cationic center to form the tertiary benzylic carbonium ion 139. Proton loss and rearrangement would lead to 1,1-dimethyl-2,5-diphenylsilepin (140). By
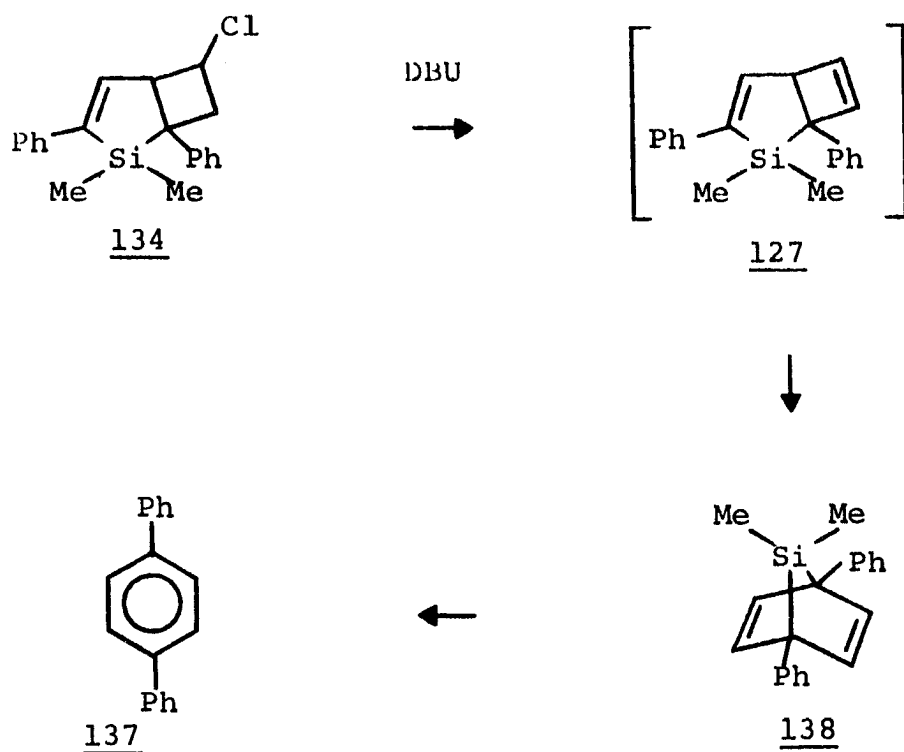
analogy to the carbocyclic diphenyl cycloheptatriene 102, an

isomerization of 140 to the silanorcaradiene followed by

silylene loss could form p-terphenyl (137). This mechanism

would explain p-terphenyl formation, but a study (98) of

1,3 substituted cyclobutanes showed no enhancement in

solvolysis reactions and argued against 1,3 rearrangements.

At present there is no means of distinguishing between a

mechanism involving the silanorbornadiene 138 and the di-

phenylsilepin 140.

The failure to synthesize 1,1-dimethyl-2,7-diphenyl-1-

silabicyclo[3.2.0]hepta-2,5-diene and the competing re-

arrangements prompted the preparation of a system in which
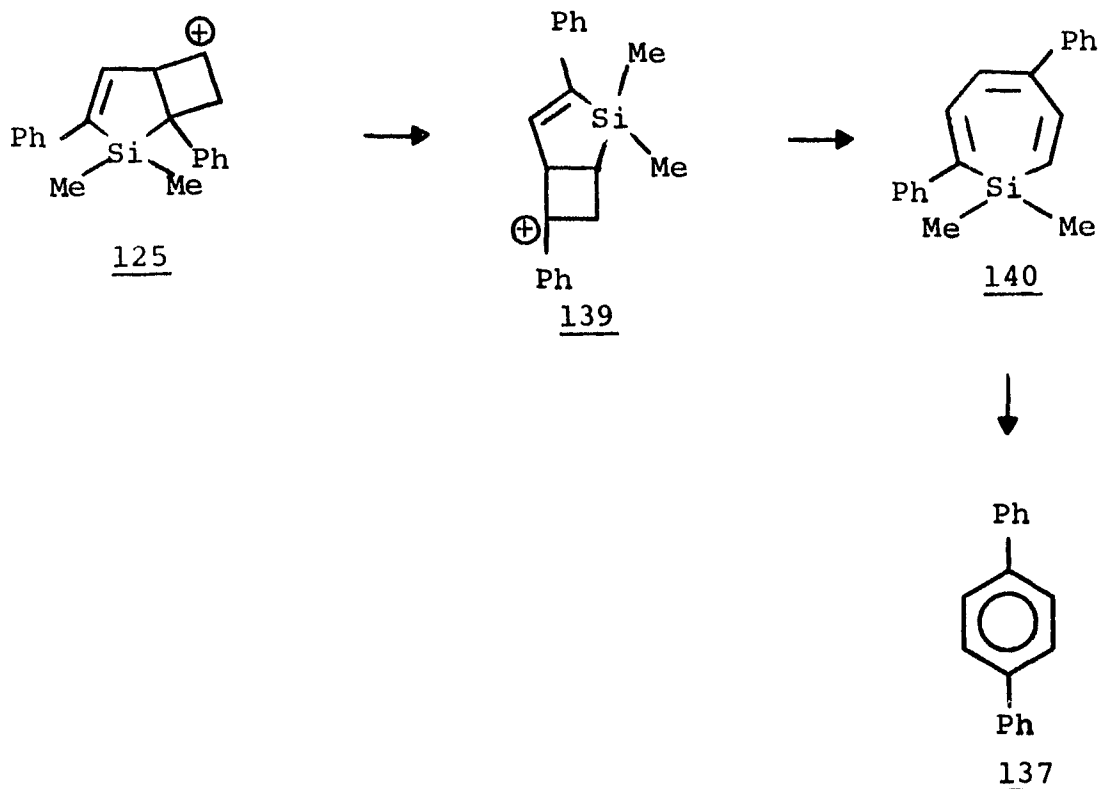
the 5 position of the bicyclo[3.2.0] skeleton would be substi-
tuted with an aromatic substuent to stabilize the resulting
carbonium ion. Phenyl magnesium bromide was added to 1,1-
dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-one
to form a 50:50 mixture of endo- and exo-1,1-dimethyl-
2,5,7-triphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (141) and
(118) respectively. The isomers were separated by chromatog-
raphy and fractional crystallization, and the structures of the
separated isomers were established with the aid of spin-

decoupling experiments, shown in Figure 11 and summarized in Table 4.
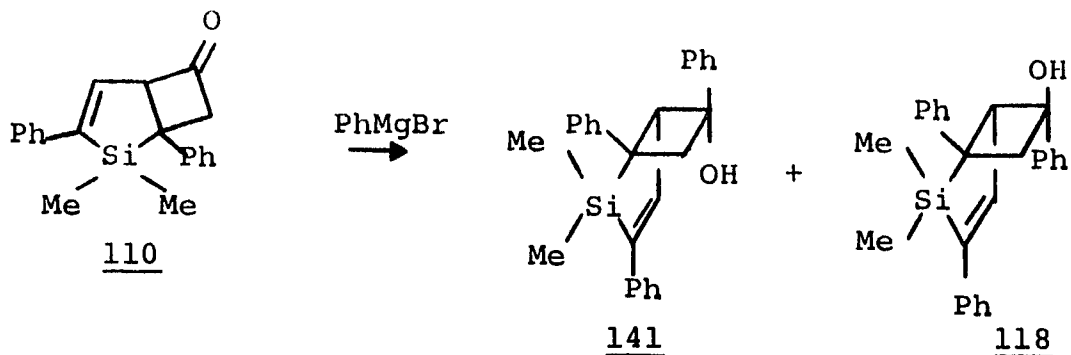


The nmr spectrum of the endo-alcohol 137, shown in Figure 10, was fortuitously simple. The olefinic proton was covered by the aromatic multiplet. The corresponding olefinic proton of the exo-alcohol 118 was directly in the shielding cone of the endo phenyl group and was accordingly shifted upfield to δ 6.15.

The direct p-toluenesulfonic acid catalysis method was again employed in the dehydration of the triphenyl alcohol 118. It was expected that the initially formed cyclobutyl cation 142, as a tertiary benzylic carbonium ion, might be of greater or comparable stability compared to the strained cyclopropylcarbinyl ion 143 and as such proceed via path b instead of path a, shown in Scheme 10. It should be noted that the additional phenyl substituent provided a new label to distinguish between path a and path b, because the final products of these two pathways are 1,2,4-triphenylbenzene
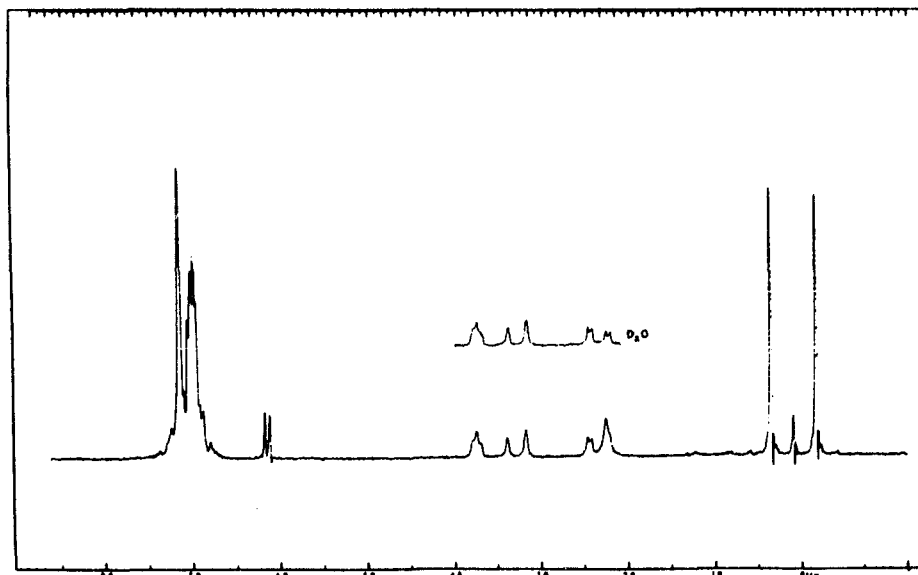
Figure 9. 60 MHz nmr spectrum of exo-1,1-dimethyl-2,5,7-triphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (118)
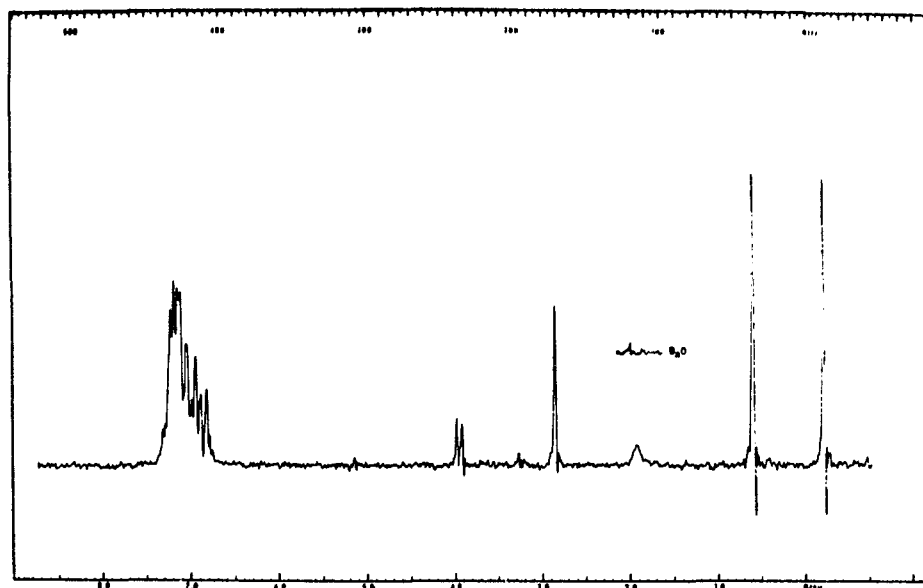


Figure 10. 60 MHz nmr spectrum of endo-1,1-dimethyl-2,5,7-triphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (141)
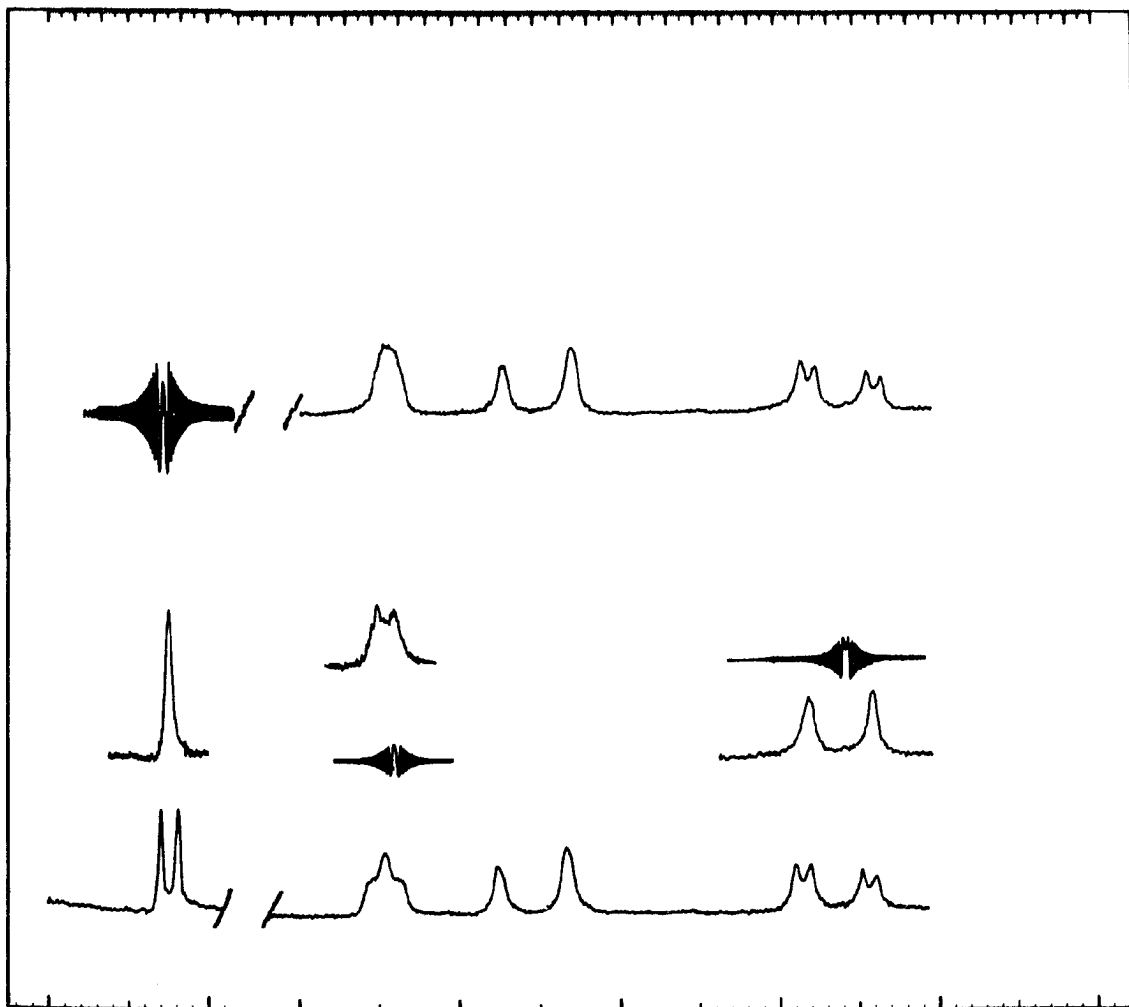
Figure 11. 60 MHz nmr spectrum of spin-decoupling of exo-
1,1-dimethyl-2,5,7-triphenyl-1-silabicyclo
[3.2.0]hept-2-ene-5-ol (118)

Table 4. Results of spin-decoupling experiments on exo-1,1-dimethyl-2,5,7-triphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol ($\underline{118}$)

$H_C$  OH
$H_D$  Ph
Ph  $H_A$
Ph  $H_B$
Si
Me  Me  $\underline{118}$
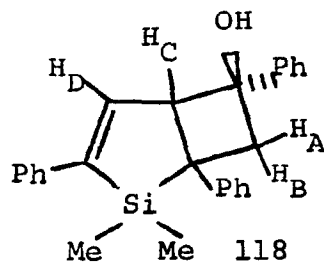
| Irradiation Frequency | $H_A$ δ 3.28 | $H_B$ δ 2.33 | $H_C$ δ 3.37 | $H_D$ δ 6.15 |
|---|---|---|---|---|
| no irradiation | d<br>$J_{AB}$ = 12.0 Hz | d of d<br>$J_{AB}$ = 12.0 Hz<br>$J_{BC}$ = 3.0 Hz | t<br>$J_{CD}$ = 3.0 Hz<br>$J_{BC}$ = 3.0 Hz | d<br>$J_{CD}$ = 3.0 Hz |
| $H_B$ 140 Hz | | | d (b)<br>$J_{CD}$ = 3.0 Hz | |
| $H_C$ 224 Hz | | d<br>$J_{AB}$ = 12.0 Hz | | s |
| $H_D$ 369 Hz | d<br>$J_{AB}$ = 12.0 Hz | d of d<br>$J_{AB}$ = 12.0 Hz<br>$J_{BC}$ = 3.0 Hz | d (b)<br>$J_{BC}$ = 3.0 Hz | |

(144) and 1,3,5-triphenylbenzene (145) respectively. After
heating the triphenyl alcohol 118 for 12 hr in refluxing
benzene with p-toluenesulfonic acid, a 57% yield of 1,2,4-
triphenylbenzene was obtained and argued against path a
involving the prismane intermediate 146 for this particular
alcohol.

To distinguish between an ionic mechanism such as
path b and a mechanism involving 1,1-dimethyl-2,5,7-tri-
phenyl-1-silabicyclo[3.2.0]hepta-2,5-diene (147), by path c,
the triphenyldiene was synthesized by chlorination of the
alcohol 118 followed by elimination with 1,5-diazabicyclo-
[5.4.0]undec-5-ene (DBU). A good model compound for nmr
comparison with triphenyl diene 147 is 1,2,2-trimethyl-3-
phenylbicyclo[3.2.0]hepta-3,6-diene (104). In both compounds
the highest upfield olefinic proton is the cyclobutenyl
proton at δ 5.80 in 104 and at δ 6.70 in 147. The bridge-
head proton was reported at δ 3.20 in the nmr spectrum of
104 while the bridgehead proton of 147 is δ 4.15. The down-
field shifts of the bridgehead and olefinic protons of 147
are consistent with the effects of the additional two β
phenyl substituents.

After heating the triphenyl diene 147 in refluxing ben-
zene for 18 hr, the starting material was recovered unchanged,
and thereby eliminated path c from consideration. However
the possibility remains that the triphenyl diene 147 is a

Scheme 10



118

142

Path c

Path b

Path a

147

143

145

146

144
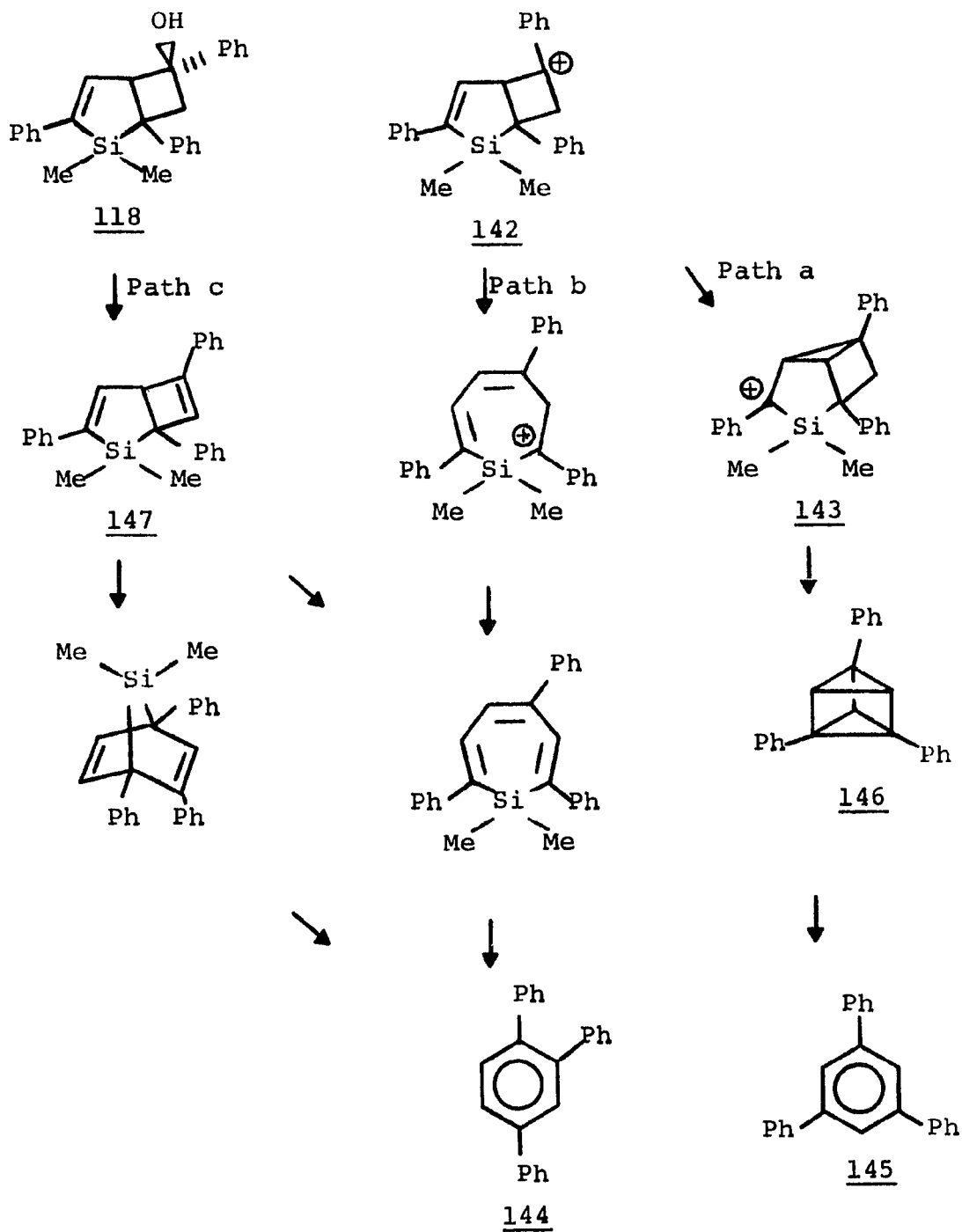
transient intermediate that is rapidly protonated to an ion

such as <u>142</u> under the reaction conditions.

EXPERIMENTAL

Infrared spectra (ir) were recorded on a Beckman 12 spectrophotometer. Routine nmr spectra were determined on a Varian model A-60 or a Hitachi R20-B spectrometer, and chemical shifts were reported as parts per million (δ scale) from tetramethyl silane as an internal standard. Decoupling and low temperature studies were recorded on the Hitachi R20-B spectrometer. The Varian HA-100 spectrometer was used to record all 100 MHz spectra. Routine mass spectra were obtained on an Atlas CH-4 spectrometer. High resolution mass spectra were recorded on a MS-902 mass spectrometer manufactured by AEI. Ultraviolet spectra (uv) were recorded using a Cary model 14 spectrophotometer. All melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Ilse Beetz Mikronanlytisches Laboratorium, Kronach, West Germany.

1,1-Dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-one (110):

The procedure of Nelson (88) was used to prepare this compound as a yellow oil. Crystallization from hexane or methanol gave white shiny crystals, mp 72-73°.

Anal. Calcd for $C_{20}H_{20}OSi$: C, 78.90; H, 6.62. Found: C, 79.03; H, 6.49.

## endo- and exo-1,1-Dimethyl-2,7-diphenyl-1-silabicyclo-[3.2.0]hept-2-ene-5-ol (114) and (115):

To a solution of 13.02 g (42.8 mmol) of silabicyclo-[3.2.0] ketone 110 in 600 ml of absolute ethanol was added 0.548 g (14.5 mmol) of sodium borohydride in 200 ml of absolute ethanol. After 50 min ethanol was removed by rotary evaporation, and the yellow oil was purified by chromatography on a 6 x 37 cm column of silica gel. Silole dimer and other impurities were removed by eluting with 5% ether--hexane. The mixture of endo- and exo-alcohols was removed from the column with 50% ether--hexane, collecting 50 ml aliquots. Fractions 52-74 containing both alcohols were combined and concentrated to a clear oil. Multiple crystallization and recrystallization from hexane allowed isolation of 2.10 g (16.2%) of the pure endo-isomer 114 as a white solid: mp 115-116°; nmr (CDCl$_3$) $\delta$ -0.17 (s, 3H), 0.42 (s, 3H), 1.82 (b, 1H, exchanges with D$_2$0), 2.43 center (d of d, 1H, $J_{BE}$ = 7.5 Hz, $J_{BC}$ = 12.0 Hz), 2.82 center (d of d of d, 1H, $J_{BC}$ = 12.0 Hz, $J_{CD}$ = 2.5 Hz), 3.98 center (apparent d of t, 1H, bridgehead, $J_{DV}$ = 3 Hz, $J_{DE}$ = 8.5 Hz), 4.49 (b, 1H, hydroxy methine), 6.94 (d, 1H, vinyl), 6.98-7.50 (m, 10H), (couplings were assigned using spin decoupling experiments, Figure 2); ir (KBr) 3300, 3090, 3065, 3040, 2980, 2910, 1980, 1580, 1500, 1255, 1100 cm$^{-1}$; mass spectrum (70 eV) m/e (rel intensity) 307 (1), 306 (6) M$^+$, 262 (100).

<u>Anal</u>. Calcd for $C_{20}H_{22}OSi$:  C, 78.38; H, 7.23;  Found:
C, 78.37; H, 7.37.

The residual filtrates contained the <u>exo</u>-alcohol <u>115</u>
which was isolated as an oil and could not be further
purified by column chromatography, although a crystalline
derivative <u>117</u> was prepared and characterized in the follow-
ing experimental.  Integration of the silicon methyl peaks in
the crude reaction by nmr shows that the <u>endo</u>- <u>114</u> and <u>exo</u>-
<u>115</u> alcohols are formed in a 1:1 ratio and thereby places
the yield of exo alcohol at 16.2% based on the isolated pure
endo alcohol.

<u>endo-1,1-Dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-
2-ene-5-yl 3,5-dinitrobenzoate (116)</u>:

A solution of 0.140 g (0.46 mmol) of the <u>endo</u>-alcohol
<u>114</u> in 5 ml of dry pyridine was treated with 0.115 g (0.50
mmol) of freshly recrystallized 3,5-dinitrobenzoyl chloride
with ice bath cooling, stirred for one hour at 0° and placed
in the freezer overnight.  The solution was poured over 10 g
of ice and extracted with 50 ml of methylene chloride.  After
drying over anhydrous magnesium sulfate, the methylene
chloride solution was rotary evaporated to a white solid which
was recrystallized from methylene chloride--hexane to obtain
0.152 g (66.3%) of crystalline endo dinitrobenzoate <u>116</u>.  An
analytical sample was prepared by chromatography on silica gel:
mp 162-164°; nmr (CDCl$_3$) δ -0.11 (s, 3H), 0.45 (s, 3H), 2.92

(m, 2H), 4.25 (m, 1H), 5.57 (d of d, 1H), 6.80 (d of d, 1H, vinyl), 6.90-7.37 (m, 10H), 9.07 (s, 3H); ir (KBr) 1740, 1600, 1550, 1500, 1350, 1280, 1170 and 1075 $cm^{-1}$; mass spectrum (70 eV) $\underline{m/e}$ (rel intensity) 500 (< 1), 262 (100).

$\underline{Anal}$. Calcd for $C_{27}H_{24}N_2O_6Si$: C, 64.78; H, 4.83; N, 5.60. Found: C, 64.71; H, 4.79; N, 5.49.

### exo-1,1-Dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-yl 3,5-dinitrobenzoate (117):

The procedure followed was identical to that described above for the preparation of the endo dinitrobenzoate. A small amount of dinitrobenzoic acid was removed by chromatography on silica gel. Recrystallization of the product from methylene chloride--ether afforded 20.3% of large white prisms of 117: mp 165-166°; nmr ($CDCl_3$) δ -0.16 (s, 3H), 0.53 (s, 3H), 2.67 (d of d, 1H), 3.16 (d of d, 1H), 3.80 (apparent triplet, 1H, bridgehead), 4.98 (apparent triplet of doublets, 1H), 6.80-7.50 (m, 11H), 9.08 (m, 3H); ir (KBr) 1738, 1550, 1347, 1270 and 1160 $cm^{-1}$; mass spectrum (70 eV) $\underline{m/e}$ (rel intensity) 500 (< 1), 262 (100).

$\underline{Anal}$. Calcd for $C_{27}H_{24}N_2O_6Si$: C, 64.78; H, 4.83; N, 5.60. Found: C, 64.85; H, 4.98; N, 5.55.

### Pyrolysis of 1,1-dimethyl-2,7-diphenyl-1-silabicyclo-[3.2.0]hept-2-ene-5-one (110):

A solution of 0.100 g of the title compound in 4.0 ml of benzene was added dropwise over a period of 5 min into

a 1/2 in. x 12 in. pyrolysis tube, packed with Vycor chips, at 300° under nitrogen. Collection of the yellow oil at Dry Ice--isopropanol temperature afforded 0.079 g (79% recovery) of a yellow liquid.

Chromatography on 10 ml of silica gel, eluting with hexane, gave 0.041 g (36.1%) of 1,1-dimethyl-2,5-diphenyl-1-silacyclopenta-2,4-diene (112): mp 126-128° [lit. (99) 131-133°]; nmr (CDCl$_3$) δ 0.05 (s, 6H), 7.10-7.30 (m, 12H).

Attempted cyclization of 1,1-dimethyl-2,5-diphenyl-1-silacyclopenta-2,4-diene (112) and dichloroketene:

A solution of 0.262 g (1.00 mmol) of silole 112 and 0.111 g (1.10 mmol) of triethylamine in 50 ml of ether were cooled to -40°. A solution of 0.147 g (1.00 mmol) of dichloroacetyl chloride in 2 ml of ether was added dropwise under nitrogen, and the reaction was allowed to warm to room temperature. Triethylamine hydrochloride was removed by filtration, and the residual solution was concentrated to dryness. Recrystallization from methylene chloride--hexane afforded 0.20 g (76.2%) of starting silole 112 as yellow crystals, mp 131-133° [lit. (99) mp 131-133°]. The nmr spectrum of the crude reaction showed that silole was the only proton containing species present: nmr (CDCl$_3$) δ 0.55 (s, 6H), 7.2 (m, 12H).

## Solvolysis of endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo-[3.2.0]hept-2-ene-5-yl 3,5-dinitrobenzoate (116) in aqueous ethanol:

A solution of 0.073 g (0.145 mmol) of the title compound in 200 ml of 90% aqueous ethanol and 100 mg of urea buffer was heated under reflux for 6 days. Ethanol was removed by rotary evaporation; the residue was dissolved in 50 ml of methylene chloride, and washed with 20 ml of water. The methylene chloride layer was dried over anhydrous magnesium sulfate and concentrated to 0.043 g of dark oil. The residue was applied to a 20 x 20 x 0.1 cm preparative silica gel plate and eluted with 50% ether--hexane to afford two major components.

The first component, $R_f$ = 0.24, was identified as ethyl 3,5-dinitrobenzoate, 0.011 g (31.5%). Recrystallization from ethanol gave crystals: mp 90-91° [lit. (100) mp 92°]; nmr (CDCl$_3$) δ 1.43 (t, 3H), 4.45 (q, 2H), 7.19 (s, 10H), 9.09 (s, 3H); ir (KBr) 3100, 1735, 1630, 1530, 1350, 1285 cm$^{-1}$.

The second component, $R_f$ = 0.14, was identified as endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (114), 0.010 g (13.7%), mp 113-114° (previous mp 115-116° of 114 obtained by reduction of ketone 110.

A small amount of residual starting material was also present by tlc comparison with authentic samples.

Attempted solvolysis of endo-1,1-dimethyl-2,7-diphenyl-1-
silabicyclo[3.2.0]hept-2-ene-5-yl 3,5-dinitrobenzoate (116)
in trifluoroethanol:

A solution of 0.082 g of the title compound in 10 ml of

distilled trifluoroethanol was heated under reflux for 24 hr.

Removal of the solvent by rotary evaporation afforded the

starting dinitrobenzoate unchanged, mp 168-170°.

Attempted preparation of 1,1-dimethyl-2,7-diphenyl-1-
silabicyclo[3.2.0]hept-2-ene-5-yl methane sulfonate (119):

To a solution of 0.280 g (0.92 mmol) of alcohol 114 at

0° in 5 ml of pyridine was added 0.193 g (1.69 mmol) of

methanesulfonyl chloride in 2.5 ml of dry pyridine. After

12 hr at freezer temperature the reaction was poured into 10

ml of water and 5 g of ice. The organic products were

extracted with two 25 ml portions of ethyl ether and then

washed with 25 ml of 1 $\underline{N}$ hydrochloric acid. After drying over

anhydrous magnesium sulfate, the solvent was removed by

rotary evaporation, and the residual oil was purified by

column chromatography on silica gel. The major product

was removed from the column with 50:50 ether--hexane to af-

ford 0.102 g of colorless oil. The product was impure and

repetitive chromatography revealed decomposition on silica

gel. Some spectral data were obtained, however, and the re-

arranged structure, 1,1-dimethyl-2,7-diphenyl-1-sila-

bicyclo[4.1.0]hept-3-ene-2-ol (120), was tentatively proposed:

nmr (CDCl$_3$) δ 0.10 (s, 3H), 0.23 (s, 3H), 1.10 (m, 2H), 1.80

(m, 2H, 1H exchanges with $D_2O$), 4.77 (d of d, 1H, $\underline{J}$ = 3,6 Hz), 6.55 (d of d, 1H, $\underline{J}$ = 1,6 Hz), (irradiation at $\delta$ 6.55 collapsed the absorption pattern at $\delta$ 4.77 to a simple doublet); ir (film) 3350 (broad) $cm^{-1}$; mass spectrum (70 eV) m/e 306.

The same reaction was studied by nmr. As soon as the reaction was quenched and allowed to warm above 0° in the nmr probe, a rearrangement of an initially formed product (presumably a bicyclo[3.2.0]mesylate 119) was observed in which signals of 120 increased over a period of 4 hr.

### Pyrolysis of endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo-[3.2.0]hept-2-ene-5-ol (114):

A solution of 0.313 g (1.02 mmol) of the title compound in 2 ml of benzene was added dropwise over a period of 5 min into a 1/2 in. by 12 in. pyrolysis tube, packed with Vycor chips, at 300° under nitrogen. Collection of the yellow oil at Dry Ice--isopropanol temperature afforded 0.303 g (96.8%) of 1,1-dimethyl-cis-2,5-diphenyl-1-sila-cyclopent-3-ene-2-ethanal (124). The aldehyde was very unstable and could not be purified by chromatography on silica gel, although the reaction appears to contain only one component by nmr spectroscopy. Some purification was achieved by rapid chromatography through a 10 ml column of Florisil[1], eluting with 50:50 ether--hexane: nmr ($CCl_4$) $\delta$ -0.78

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(s, 3H), 0.26 (s, 3H), 2.51 (d of d, 1H $J_{DE}$ = 18 Hz $J_{DF}$ =

3 Hz), 3.04 (d of d, 1H, $J_{DE}$ = 18 Hz, $J_{EF}$ = 2 Hz), 3.24 (b,

1H), 6.00 (d of d, 1H, $J_{BC}$ = 7 Hz, $J_{AC}$ = 2 Hz), 6.21 (d of

d, 1H, $J_{BC}$ = 7 Hz, $J_{AB}$ = 3 Hz), 6.80-7.40 (m, 10H), 9.44

(m, 1H); coupling constants were assigned using spin de-

coupling experiments; ir (film) 3060, 3020, 2960, 2730, 1727

(s), 1680, 1600, 1495, 1295, 1250, 790 cm$^{-1}$; mass spectrum

(70 eV) m/e 304; mass spectrum calculated for $C_{20}H_{22}SiO$ m/e

= 306.1439. Found: m/e = 306.1432 $\pm$ .004.

Carbon and hydrogen values were found to be nonrepro-

ducible and all were below the calculated values. A chemical

characterization was therefore carried out using the Tollen's

test. A sample of the aldehyde in tetrahydrofuran solution

was added to a suspension of excess aqueous silver oxide

with stirring for 2 hr, resulting in the formation of a

bright silver mirror.

### Pyrolysis of exo-1,1-dimethyl-2,7-diphenyl-1·silabicyclo-[3.2.0]hept-2-ene-5-ol (115):

A solution of 0.060 g of the title compound in 1.0 ml of

benzene was pyrolyzed as described in the previous experiment.

Temperatures were investigated from 275-325°, but none of the

aldehyde 124 characterized in the previous experiment could

be detected by nmr spectroscopy. The reaction contains

numerous products as indicated by the large number of peaks

in the silicon methyl region of the nmr.

Acid catalyzed dehydration of endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (114):

A solution of 0.206 g (0.677 mmol) of the title compound and 0.009 g of p-toluenesulfonic acid in 25 ml of dry benzene were heated under reflux for 24 hr using a recirculating Dean-Stark trap filled with molecular sieves. Benzene was removed by rotary evaporation, and the resulting yellow oil was purified by chromatography on a 1.2 x 16 cm column of silica gel, collecting 50 ml fractions.

Fractions 1-4 were eluted with hexane to afford 0.070 g of a yellow oil, which was found to contain three components. The major component was identified as m-terphenyl (121) in an overall yield of 23% (nmr yield). Crystallization from pentane afforded pure m-terphenyl as white needles, mp 86-87° [lit. (101) mp 87°]. The nmr spectrum shows a multiplet at δ 7.20-7.75 that is identical to an authentic sample.

The second component was separated by liquid-liquid chromatography using a 6 ft by 1/8 in. bondapak $C_{18}$/porasil B column and acetonitrile--water as carrier solvent and identified as 1,1-dimethyl-2,7-diphenylsilepin (123 , 11% (nmr yield). Crystallization from methanol gave needles: mp 60-61°; nmr ($CCl_4$) δ 0.10 (s, 6H), centers 6.51 and 6.80 (AA'BB' pattern, 4H), 7.10 (d, 10H); ir ($CCl_4$) 3010, 2990, 1600, 1490, 1440, and 1160 cm$^{-1}$; mass spectrum (70 eV) m/e (rel intensity) 288 (95), 273 (85), 230 (100), (24 eV) (rel intensity) 288 (100), 273 (10), 230 (10); uv ($CH_2Cl_2$)$\lambda_{max}$

$(\varepsilon \times 10^{-4})$, 234 nm (1.95), 320 nm (1.10); high resolution mass spectrum calculated for $C_{20}H_{20}$: $\underline{m/e} = 288.1328$ (corrected for $C^{13}C_{19}^{12}H_{19}Si$ contribution). Found $\underline{m/e} = 288.1315 \pm .002$.

<u>Anal</u>. Calcd for $C_{20}H_{20}Si$: C, 83.28; H, 6.99; Si, 9.74. Found: C, 83.25; H, 6.91; Si, 9.96.

The third component was identified as <u>o</u>-terphenyl by comparison with authentic samples on liquid-liquid chromatography (3% overall yield by liquid-liquid).

Fractions 5-8 were combined and concentrated to afford 0.025 g (12.2%) of yellow oil, which was identified as 1,1-dimethyl-<u>cis</u>-2,5-diphenyl-1-silacyclopent-3-ene-2-ethanal (<u>124</u>), by nmr comparison with the sample prepared previously by pyrolysis of the alcohol <u>114</u>: nmr $(CCl_4)$ $\delta$ -0.78 (s, 3H), 0.26 (s, 3H), 2.51 (d of d, 1H), 3.04 (d of d, 1H), 3.24 (b, 1H), 6.00 (d of d, 1H), 6.21 (d of d, 1H), 6.80-7.40 (m, 10H), 9.44 (m, 1H).

## <u>Thermal stabilities of o-, m- and p-terphenyl (122), (121) and (137)</u>:

A check on product stabilities was carried out by refluxing three individual samples (300 mg) of <u>o</u>-, <u>m</u>-, and <u>p</u>-terphenyl in 25 ml of dry benzene and 0.06 g of <u>p</u>-toluene sulfonic acid. Gas chromatography and melting points revealed that all terphenyls were stable to the reaction conditions under which the bicyclo[3.2.0]alcohol <u>114</u> was dehydrated.

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Reaction of endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo-
[3.2.0]hept-2-ene-5-ol (114) with trifluoroacetic acid:

To a solution of 0.056 g (0.183 mmol) of the title com-
pound in 0.50 ml of deutero chloroform was added trifluoro-
acetic acid dropwise until the nmr spectrum showed no addi-
tional change (20 drops). The reaction mixture was diluted
with 2 ml of chloroform and washed with a small amount of
10% sodium bicarbonate. The organic layer was dried over
anhydrous potassium carbonate and concentrated to a yellow
oil. Preparative thin layer chromatography on a 20 x 20 x
0.1 cm plate of silica gel, eluting with 40% ether--hexane
afforded 0.015 g (35.4%) of o-terphenyl (122) which was
identified by nmr and gc comparison with an authentic sample:
nmr (CCl$_4$) δ 7.05 and 7.30 (s); gc retention time = 2.9
min, 10% SE-30, 1/4 in. by 3 ft column, column temperature =
225°. The reaction mixture shows no trace of m- or p-ter-
phenyl by gc comparison with authentic samples.

endo-1,1-Dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-
ene-5-yl trifluoroacetate (133):

To a solution of 0.300 g (0.980 mmol) of the endo-
diphenyl alcohol 114 in 10 ml of methylene chloride at 0°
was added 0.2 ml of trifluoroacetic anhydride and 0.4 ml of
trifluoroacetic acid. The reaction mixture was washed with
cold sodium bicarbonate solution and cold water. The organic
layer was dried over magnesium sulfate and concentrated to a

yellow oil. Residual trifluoroacetic acid was removed by high vacuum pumping to afford 0.386 g (98.0%) of the title compound. The product was used without further purification in subsequent experiments because it was unstable to silica gel chromatography and distillation: nmr ($CCl_4$) δ -0.13 (s, 3H), 0.40 (s, 3H), 2.50 (m, 2H), 4.15 (d of d, 1H, bridgehead), 5.42 (d of d, 1H, hydroxy methine), 6.72 (d, 1H), 7.00-7.50 (m, 10H); ir (film) 3020,300°,1790 (s), 1605, 1500, 1230, 1160 $cm^{-1}$; mass spectrum (70 eV) (rel intensity) 402 (1) $M^+$, 288 (1), 262 (100) cleavage to silole; high resolution mass spectrum calculated for $C_{22}H_{21}F_3O_2Si$ $\underline{m/e}$ = 402.126266. Found: $\underline{m/e}$ = 402.124878.

## Pyrolysis of endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo-[3.2.0]hept-2-ene-5-yl trifluoroacetate (133):

A sample of 0.268 g (0.668 mmol) of the title compound was placed in a vertical Kugelrohr apparatus (0.1 mm) preheated to 250°. The pyrolysis was carried out by successively lowering more bulbs as distillate collected in the outer bulb until three bulbs were inside the oven. The total collected distillate (0.150 g) contained 71.7% (nmr yield) starting material by nmr comparison with an authentic sample. The major product was m-terphenyl (121) (19.9% gc yield) as determined by nmr and gc comparison with authentic samples: nmr ($CCl_4$) δ 7.50-7.80 (m); gc retention time = 6.4 min, 10% SE-30, 1/4 in. by 3 ft column, column temperature = 225°,

flow rate = 1.7 ml/min. Small amounts (< 5%) of o- and p-
terphenyl were also detected by gc, although gc analysis of
the starting trifluoroacetate shows m- and p-terphenyl
(< 2%).

### 1,1-Dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-yl chloride (134):

To a solution of 0.085 g (0.280 mmol) of the endo-
diphenyl alcohol 114 in 0.25 ml of deutero chloroform was
added 0.037 g (0.460 mmol) of pyridine and 0.054 g (0.450
mmol) of thionyl chloride in 0.25 ml of deutero chloroform.
The reaction was followed by nmr for 2 hr until no further
change could be detected at room temperature. The product
was not stable on silica gel or alumina and could be puri-
fied only by a rapid column chromatography on 5 ml of silica
gel to afford 0.031 g (34.4%) of the title compound as a
yellow oil on elution with 5% ether--hexane: nmr (CCl$_4$) δ
-0.11 (s, 3H), 0.40 (s, 3H), 2.80 (m, 2H), 4.05 (m, 1H),
4.72 (d of d, 1H, $J$ = 7,8 Hz), 6.80-7.30 (m, 11H); ir (film)
3000, 1600, 1490, 1450, 1250 cm$^{-1}$; mass spectrum (70 eV)
m/e 324 M$^+$.

A small amount of impurity was removed by dissolving
the above oil in hexane and allowing to stand at freezer
temperature. The precipitated product was obtained as a tan
solid softening 101-103° and was tentatively identified as a
rearranged chloride isomer, 1,1-dimethyl-2,7-diphenyl-1-

silabicyclo[4.1.0]hept-3-ene-2-yl chloride (<u>135</u>): nmr

(CDCl$_3$) δ 0.13 (s, 3H), 0.30 (s, 3H), 1.10 (m, 2H), 1.90

(m, 1H), 5.05 (d of d, 1H, <u>J</u> = 3,8 Hz), 6.35 (d of d, 1H, <u>J</u> =

2,8 Hz), 7.25 (m, 11H); ir (KBr) 1600, 1495, 1255, 830,

705 cm$^{-1}$; mass spectrum (70 eV) (rel intensity) <u>m/e</u> 326

(11), 324 (30) M$^+$, 288 (81), 273 (100); mass spectrum calcu-

lated for C$_{20}$H$_{21}$ClS; <u>m/e</u> = 324.1101. Found: <u>m/e</u> = 324.1098 ±

.003.

### Dehydrohalogenation of 1,1-dimethyl-2,7-diphenyl-1-sila-bicyclo[3.2.0]hept-2-ene-5-yl chloride (134):

A solution of 0.099 g (0.335 mmol) of the title compound

and 0.057 g (0.335 mmol) of 1,5-diazabicyclo[5.4.0]undec-5-

ene (DBU) in 4 ml of acetonitrile was heated at 60° for

12 hr. Solvent was removed by rotary evaporation, and the

residual oil was purified by column chromatography on 10 ml

of silica gel. Elution with 100% hexane afforded 0.008

g (11.4%) of white solid identified as <u>p</u>-terphenyl by gc and

ir comparison with an authentic sample: gc retention time =

6.0 min, 10% SE-30, 1/4 in. by 3 ft column, column tempera-

ture = 225°, flow rate = 1.7 ml/min; ir (KBr) 1600, 1500,

1450, 830, 740, 700 cm$^{-1}$. There was no evidence for <u>o</u>-

or <u>m</u>-terphenyl by gc analysis.

### Low temperature nmr studies of endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (114) in strong acid media:

A solution of fluorosulfonic acid and sulfuryl chloride

fluoride (1:4 v/v) in d$_2$-methylene chloride was prepared at

liquid nitrogen--ether temperatures. A solution of 0.030 g

(0.10 mmol) of the title compound in $d_2$-methylene chloride was added and briefly stirred keeping the solution below -120°. The resulting purple solution was stored for several weeks at liquid nitrogen temperatures before spectra were obtained.

The sample was rapidly transferred to a probe pre-cooled to -120° of the Varian HA-100 nmr, but only broad line spectra of the aromatic region could be obtained. On warming to -90° the following nmr spectrum was obtained using fluoro-sulfonic acid as an internal standard: nmr δ 0.58 (s, 3H), 0.72 (s, 3H), 2.50 (b, 1H), 3.50-3.70 (b, 2H), 6.90-8.20 (m, 11H), 9.62 (b, 1H ?).

On warming to -70° the intensity of the silicon methyl signals decreased while a new signal increased at δ 0.92. Continued warming resulted in complete sample decomposition.

## endo- and exo-1,1-Dimethyl-2,5,7-triphenyl-1-silabicyclo-[3.2.0]hept-2-ene-5-ol (141) and (118):

A solution of 7.5 ml of 1.0 M phenyl magnesium bromide in ether was added to a solution of 1.52 g (5.0 mmol) of the sila-ketone 110 in 100 ml of ether under nitrogen and refluxed for 12 hr.

Saturated ammonium chloride was added to the reaction mixture at 0° until a sticky white precipitate had formed. The ether solution was dried over anhydrous magnesium sulfate and concentrated to a yellow oil. Chromatography on a 4 x 45

cm column (100 g) of silica gel separated two major components on elution with 5% ether--hexane. Fractions 27-37 (50 ml fractions) were collected and found to contain a mixture of endo and exo isomers of the title compound. A small amount of the endo-alcohol 141 was obtained for characterization by careful recrystallizations from methanol as white prisms: mp 106-108°; nmr (CCl$_4$) δ -0.20 (s, 3H), 0.64 (s, 3H), 2.12 (s, 1H, exchange with D$_2$O), 3.05 (s, 2H), 4.14 (d, 1H, $J$ = 5 Hz, bridgehead), 6.98-7.60 (m, 16H, aromatic and olefinic); ir (KBr) 3600, 3500, 1600, 1495, 1450, 1255 cm$^{-1}$; mass spectrum (70 eV) (rel intensity) m/e 382 (4) M$^+$, 262 (100).

Anal. Calcd for C$_{26}$H$_{26}$OSi: C, 81.63; H, 6.85. Found: C, 81.51; H, 6.99.

Fractions 38-60 were combined and concentrated to afford 0.824 g (43.4%) of a sticky white solid. Recrystallization from methanol gave fine white needles: mp 125-128°; nmr (CCl$_4$) δ -0.18 (s, 3H), 0.36 (s, 3H), 2.20 (b, 1H, exchanges with D$_2$O), 2.33 (d of d, 1H, $J_{AB}$ = 12 Hz, $J_{BC}$ = 3.0 Hz), 3.28 (d, 1H, $J_{AB}$ = 12 Hz), 3.73 (apparent t, 1H, $J_{BC}$ = 3.0 Hz, $J_{CD}$ = 12 Hz, bridgehead), 6.15 (d, 1H, $J_{CD}$ = 12 Hz), 6.88-7.30 (m, 15H) (coupling constants were assigned using spin-decoupling experiments summarized in Table 4); ir (KBr) 3520, 2460, 1600, 1590, 1500, 1450 cm$^{-1}$; mass spectrum (70 eV) m/e (rel intensity) 382 (4) M$^+$, 262 (100).

Anal. Calcd for $C_{26}H_{26}OSi$:  C, 81.63; H, 6.85.  Found:
C, 81.75; H, 6.94.

## Acid catalyzed dehydration of exo-1,1-dimethyl-2,5,7-triphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (118):

A solution of 0.164 g (0.428 mmol) of the title compound
and 0.025 g of p-toluenesulfonic acid in 25 ml of dry benzene
was refluxed for 12 hr using a recirculating Dean-Stark trap
filled with 4A molecular sieves.  Solvent was removed by
rotary evaporation, and the residual yellow oil was chroma-
tographed on 10 ml of silica gel eluting with 5% ether--
hexane.  Crystallization from methanol gave 0.076 g (57.6%)
of white crystals identified as 1,2,4-triphenylbenzene:
mp 94-96° [lit. (102) mp 98-100°]; nmr (CDCl$_3$) δ 7.06
(s), 7.06-7.50 (m); uv (methylcyclohexane) $\lambda_{max}$ = 250 nm,
log ε = 4.39 [lit. (102) $\lambda_{max}$ = 248 nm, log ε = 4.54]; mass
spectrum (70 eV) m/e (rel intensity) 306 (69) M$^+$, 77 (100).

## 1,1-Dimethyl-2,5,7-triphenyl-1-silabicyclo[3.2.0]hepta-2,5-diene (147):

To a solution of 0.238 g (0.625 mmol) of exo alcohol in
10 ml of methylene chloride was added 0.083 g (1.05 mmol) of
pyridine in 1 ml of methylene chloride followed by 0.120 g
(0.985 mmol) of thionyl chloride in 1 ml of methylene chloride.
The reaction was refluxed for 4 hr; the solvent was removed
by rotary evaporation, and the crude chlorides dehydro-
halogenated without further purification.

The residual oil was dissolved in 2 ml of deutero acetonitrile, treated with 0.190 g (1.25 mmol) of 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in 0.5 ml of deutero acetonitrile, and heated at 50° for 4 hr until the nmr spectrum showed no further reaction. Column chromatography on 6 ml of Florisil[1] separated 0.098 g (59.2%) of the title compound on elution with 10% ether--hexane as a yellow oil. Crystallization from methanol afforded needles: mp. 106-9°; nmr (CCl$_4$) δ 0.00 (s, 3H), 0.36 (s, 3H), 4.15 (d, 1H, $\underline{J}$ = 4 Hz), 6.70 (s, 1H), 6.90-7.40 (m, 16H); mass spectrum (70 eV) $\underline{m/e}$ (rel intensity) 364 (100) M$^+$, 349 (74), 306 (50).

Anal. Calcd for C$_{26}$H$_{24}$Si: C, 85.66; H, 6.64; Si, 7.70. Found: C, 85.70; H, 6.66; Si, 7.67.

Thermolysis of 1,1-dimethyl-2,5,7-triphenyl-1-silabicyclo-[3.2.0]hepta-2,5-diene (147):

A solution of 0.031 g of the title compound in 0.5 ml of deuterobenzene was heated in a closed nmr tube at 80° for 18 hr. The nmr spectrum shows no change from the starting material.

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[1] J. T. Baker trademark for activated magnesium silicate.

LITERATURE CITED

1. E. D. Hughes, C. K. Ingold, and C. S. Patel, _J. Chem. Soc._, 526 (1933).

2. E. D. Hughes, _Quart. Rev._, 5, 245 (1951).

3. W. von E. Doering and L. H. Knox, _J. Amer. Chem. Soc._, 76, 3203 (1954).

4. P. G. Gassman, _Accounts Chem. Res._, 3, 26 (1970).

5. O. Foss, _Acta Chem. Scand._, 1, 307 (1947).

6. N. Kharasch, S. J. Potempa, and H. L. Wehrmeister, _Chem. Rev._, 39, 269 (1946).

7. S. Archer and C. M. Suter, _J. Amer. Chem. Soc._, 74, 4296 (1952).

8. J. L. Franklin and H. E. Lumpkin, _J. Amer. Chem. Soc._, 74, 1023 (1952).

9. N. Kharasch, C. M. Buess, and W. King, _J. Amer. Chem. Soc._, 75, 6035 (1953).

10. N. Kharasch in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, New York, N.Y., 1961, Chapter 32.

11. R. E. Benesch and R. Benesch, _J. Amer. Chem. Soc._, 80, 1666, (1958).

12. G. K. Helmkamp and D. C. Owsley, _Quarterly Reports in Sulfur Chemistry_, 2, 303 (1967).

13. G. A. Olah, B. M. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., _J. Amer. Chem. Soc._, 87, 2997 (1965).

14. G. A. Olah, D. H. O'Brian, and C. U. Pittman, Jr., _J. Amer. Chem. Soc._, 89, 2996 (1967).

15. D. C. Owsley and G. K. Helmkamp, _J. Amer. Chem. Soc._, 89, 4558 (1967).

16. P. D. Bartlett and C. G. Swain, _J. Amer. Chem. Soc._, 71, 1406 (1949).

17. R. C. Fuson, C. C. Price, and D. M. Burness, J. Org. Chem., 11, 475 (1956).

18. N. Kharasch, Quarterly Reports in Sulfur Chemistry, 1, 93, (1966).

19. D. J. Cram, J. Amer. Chem. Soc., 71, 3383 (1949).

20. C. Brown and D. R. Hogg, Chem. Commun., 357 (1965).

21. W. H. Mueller, Angew. Chem., Int. Ed. Engl., 8, 482 (1969).

22. W. H. Mueller and P. E. Butler, J. Amer. Chem. Soc., 88, 2866 (1966).

23. C. M. Buess and N. Kharasch, J. Amer. Chem. Soc., 72, 3529 (1950).

24. G. H. Schmid, V. M. Csizmadia, V. J. Nowlan, and D. G. Garrat, Canad. J. Chem., 50, 2457 (1972).

25. K. Yates. University of Toronto, Toronto, Ontario. Unpublished communication.

26. G. H. Schmid and V. M. Csizmadia, Canad. J. Chem., 50, 2465 (1972).

27. E. Kuhle, Synthesis, 572 (1970).

28. T. J. Barton and R. G. Zika, Tetrahedron Lett., 1193 (1970).

29. F. Lautenschlager, J. Org. Chem., 31, 1679 (1966).

30. E. J. Corey and E. Block, J. Org. Chem., 31, 1663 (1966).

31. E. D. Weil, K. J. Smith and R. J. Gruber, J. Org. Chem., 31, 1669 (1966).

32. F. Lautenschlager, J. Org. Chem., 33, 2620 (1968).

33. G. Modena and G. Scorrano, Mechanisms of Reactions of Sulfur Compounds, 3, 115 (1968).

34. N. Kharasch and S. J. Assony, J. Amer. Chem. Soc., 75, 1081 (1953).

35. V. Calo, G. Melloni, G. Modena, and G. Scorrano, Tetrahedron Lett., 4399 (1965).

36. G. H. Schmid and M. Heinola, J. Amer. Chem. Soc., 90, 3466 (1968).

37. A. S. Denes, I. G. Csizmadia and G. Modena, J. Chem. Soc., Chem. Commun., 9 (1972).

38. G. Capozzi, G. Modena, G. Scarrano and U. Tonellato, Mechanisms of Reactions of Sulfur Compounds, 5, 213 (1970).

39. L. Brandsma and J. F. Arens, Rec. Trav. Chim. Pays-Bas, 80, 237 (1961).

40. T. J. Barton and R. G. Zika, J. Org. Chem., 35, 1729 (1970).

41. N. Kharasch and C. N. Yiannios, J. Org. Chem., 29, 1190 (1964).

42. A. Rosowsky in "Seven-Membered Heterocyclic Compounds Containing Oxygen and Sulfur", The Chemistry of Heterocyclic Compounds, Vol. 26, Wiley-Interscience, New York, N.Y., 1972.

43. M. J. S. Dewar and N. Trinajstic, J. Amer. Chem. Soc., 92, 1453 (1970).

44. J. M. Hoffman, Jr., and R. H. Schlessinger, J. Amer. Chem. Soc., 92, 5263 (1970).

45. D. C. Neckers, J. H. Dopper, and H. Wynberg, Tetrahedron Lett., 2913 (1969).

46. H. Hofmann and B. Meyer, Tetrahedron Lett., 4597 (1972).

47. W. L. Mock, J. Amer. Chem. Soc., 89, 1281 (1967).

48. H. L. Ammon, P. H. Watts, Jr., J. M. Stewart, and W. L. Mock, J. Amer. Chem. Soc., 90, 4501 (1968).

49. F. A. L. Anet, C. H. Bradley, M. A. Brown, W. L. Mock, and J. H. McCausland, J. Amer. Chem. Soc., 91, 7782 (1969).

50. T. J. Barton, M. D. Martz, and R. G. Zika, *J. Org. Chem.*, **37**, 552 (1972).

51. R. Helder and H. Wynberg, *Tetrahedron Lett.*, 605 (1972).

52. H. Wynberg and R. Helder, *Tetrahedron Lett.*, 3647 (1972).

53. D. N. Reinhoudt and G. G. Kouwenhouven, *J. Chem. Soc., Chem. Commun.*, 1233 (1972).

54. D. N. Reinhoudt, H. C. Volger, C. G. Kouwenhouven, H. Wynberg, and R. Helder, *Tetrahedron Lett.*, 5269 (1972).

55. J. Font, E. L. Dedio, P. Kebarle, H. E. Gunning, and O. P. Strausz, *J. Amer. Chem. Soc.*, **89**, 4805 (1967).

56. F. W. Stacy and J. F. Harris, Jr., *J. Amer. Chem. Soc.*, **85**, 963 (1963).

57. R. Mayer, J. Morgenstern, and J. Fabian, *Angew. Chem., Int. Ed. Engl.*, **3**, 277 (1964).

58. R. Mayer and H. Frey, *Angew Chem.*, **76**, 861 (1964).

59. I. B. Douglass, R. V. Norton, R. L. Weichman, and R. B. Clarkson, *J. Org. Chem.*, **34**, 1803 (1969).

60. W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **90**, 2075 (1968).

61. K. Conrow, *Organic Synthesis*, **43**, 101 (1963).

62. E. M. Kosower, W. J. Cole, G. S. Wu, D. E. Cardy, and G. Meisters, *J. Org. Chem.*, **28**, 630 (1963).

63. D. C. Sayles and M. S. Kharasch, *J. Org. Chem.*, **26**, 4210 (1961).

64. T. Fujisawa, *Tetrahedron Lett.*, 4533 (1968).

65. Z. S. Ariyan and L. A. Wiles, *J. Chem. Soc.*, 4709 (1962).

66. E. Miller, F. S. Crossley, and M. L. Moore, *J. Amer. Chem. Soc.*, **64**, 2322 (1942).

67. B. B. Brown, A. S. Dreiding, D. W. Goheen, D. W. McCready, and W. Vaughan, J. Chem. Eng. Data, 6, 52 (1961).

68. A. Ladenburg, Chem. Ber., 14, 2126 (1881).

69. G. Maier, Angew. Chem., Int. Ed. Engl., 6, 402 (1967).

70. L. Birkofer and E. Kramer, Chem. Ber., 102, 427 (1969).

71. T. J. Barton, W. E. Volz, and J. L. Johnson, J. Org. Chem., 36, 3365 (1971).

72. J. Y. Corey, M. Deuber, and B. Bichlmeir, J. Organometal. Chem., 26, 167 (1971).

73. F. K. Cartledge and P. D. Mollere, J. Organometal. Chem., 26, 175 (1971).

74. J. Y. Corey and E. R. Corey, Tetrahedron Lett., 4669 (1972).

75. L. Birkofer, H. Haddad, and H. Zamarlik, J. Organometal. Chem., 25, C57 (1970).

76. G. Berti and A. Da Settimo, Ann. Chim. (Rome), 49, 1237 (1959).

77. H. Gilman, S. G. Cottis, and W. H. Atwell, J. Amer. Chem. Soc., 86, 5584 (1964).

78. J. Witiak, M. S. Thesis, Iowa State University, 1972.

79. R. B. Woodward and R. Hoffmann, J. Amer. Chem. Soc., 87, 2511 (1965).

80. R. L. Lambert, Jr., and D. Seyferth, J. Amer. Chem. Soc., 94, 9246 (1972).

81. L. A. Paquette and L. M. Leichter, J. Amer. Chem. Soc., 93, 5128 (1971).

82. L. A. Paquette and J. A. Barrett, J. Amer. Chem. Soc., 88, 1718 (1966).

83. H. L. Dryden, J. Amer. Chem. Soc., 76, 2841 (1954).

84. J. A. Berson, Accounts Chem. Res., 5, 406 (1972).

85. G. A. Russell and K. Schmitt, J. Amer. Chem. Soc., 94, 8918 (1972).

86. P. Schiess and P. Funfschilling, Tetrahedron Lett., 5194 (1972).

87. C. Eaborn and R. W. Bottin, in "Organometallic Compounds of the Group IV Elements", Vol. 1, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N.Y., 1968, pp. 443-450.

88. A. J. Nelson, Ph.D. Thesis, Iowa State University, 1972.

89. T. J. Barton and E. E. Gottsman, Synthesis in In-organic and Metal-Organic Chemistry, 3, 201 (1973).

90. V. M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, Helv. Chim. Acta, 53, 417 (1970).

91. L. M. Jackman and S. Sternhell in "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", International Series of Monographs in Organic Chemistry, Vol. 5, Pergamon Press, New York, N.Y., 1969, p. 334.

92. V. J. Shiner, Jr., W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, J. Amer. Chem. Soc., 91, 4838 (1969).

93. T. J. Barton, Ph.D. Thesis, University of Florida, 1967.

94. D. Seyferth, D. R. Blank, and A. B. Eunin, J. Amer. Chem. Soc., 89, 4793 (1967).

95. D. Seyferth and D. L. White, J. Amer. Chem. Soc., 94, 3132 (1972).

96. A. Burgstahler and P. L. Chien, J. Amer. Chem. Soc., 86, 2940 (1964).

97. H. E. Zimmerman and J. A. Pincock, J. Amer. Chem. Soc., 95, 2957 (1973).

98. C. J. Michejda and R. W. Comnick, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April, 1969.

99. W. H. Atwell, D. R. Weyenberg, and H. Gilman, _J. Org. Chem._, __32__, 885 (1967).

100. H. C. Brill, _J. Amer. Chem. Soc._, __43__, 1323 (1921).

101. H. France, I. Heilbron, and D. Hey, _J. Chem. Soc._, 1288 (1939).

102. C. G. Overberger and J. M. Whelan, _J. Org. Chem._, __24__, 1155 (1959).

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