

Spring 1964

NORBORNYL AND NORTRICYCLYL  
DERIVATIVES: I PREPARATION AND SOME  
PROPERTIES OF SILANES II REDUCTION  
OF HALIDES BY ORGANOTIN HYDRIDES

CHARLES ROCKWELL WARNER

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NORBORNYL AND NORTRICYCLYL DERIVATIVES:  
I. PREPARATION AND SOME PROPERTIES OF  
SILANES. II. REDUCTION OF HALIDES BY  
ORGANOTIN HYDRIDES.

University of New Hampshire, Ph.D., 1964  
Chemistry, organic

University Microfilms, Inc., Ann Arbor, Michigan

NORBORNYL AND NORTRICYCLYL DERIVATIVES

- I. PREPARATION AND SOME PROPERTIES OF SILANES
- II. REDUCTION OF HALIDES BY ORGANOTIN HYDRIDES

BY

CHARLES ROCKWELL WARNER

B.S., Union College, 1958

M.S., New York State University at Albany, 1960

A THESIS

Submitted to the University of New Hampshire

In Partial Fulfillment of

The Requirements for the Degree of

Doctor of Philosophy

Graduate School

Department of Chemistry

April, 1964

This thesis has been examined and approved.

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April 13, 1964

Date

## ACKNOWLEDGEMENTS

This research was carried out under the supervision of Dr. Henry G. Kuivila. It is a pleasure to acknowledge the unlimited assistance and encouragement offered by Dr. Kuivila.

I would like to thank the other members of the Chemistry Department for the cooperation and aid offered me.

This investigation was supported in part by a Public Health Service Fellowship 4-F1-GM-19, 157-02 from the National Institute of General Medical Sciences.

I would also like to thank my wife, Jean, for her assistance.

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**NORBORNYL AND NORTRICYCLYL DERIVATIVES**

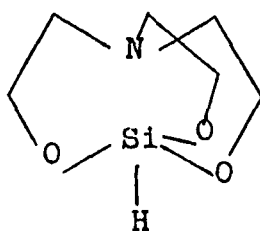
**PART I**

**PREPARATION AND SOME PROPERTIES OF SILANES**

## A INTRODUCTION

Doubtlessly, much of the current interest in organo-silane chemistry is a result of the great commercial value of these compounds. They have found wide use as lubricants, surfactants, cosmetics and plastics.

In addition, the electropositive character of silicon relative to carbon, as well as the availability of the low-lying  $d$ -orbitals, provides a fruitful area for the extension and modification of the current theories of physical organic chemistry. The results of many studies are most readily interpreted by involving the use of one or more of these orbitals. Recently, Frye, Vogel and Hall<sup>(1)</sup> concluded that the silicon atom of 4,6,11,1,5-trioxazasilolane-5-hydrotricyclo-(3.3.3.0<sup>1,5</sup>)-undecane (hereafter designated triptychsiloazolidine) participates in transannular dative bonding with the nitrogen atom. The electron rich character of the sili-



con atom in this molecule is apparent from the anomalously low Si-H stretching frequency in the infrared. The hybridization of the silicon atom in the triptych-siloxazolidines is probably of the  $sp^3d$  type. The available evidence strongly suggests that the racemization of an optically active fluoro-

silane involves the formation of a complex of the silicon atom with methoxide ion. The resulting intermediate is pictured with the four groups which were originally bonded to the silicon, lying in one plane. Subsequent removal of the methoxide ion leads to racemization.

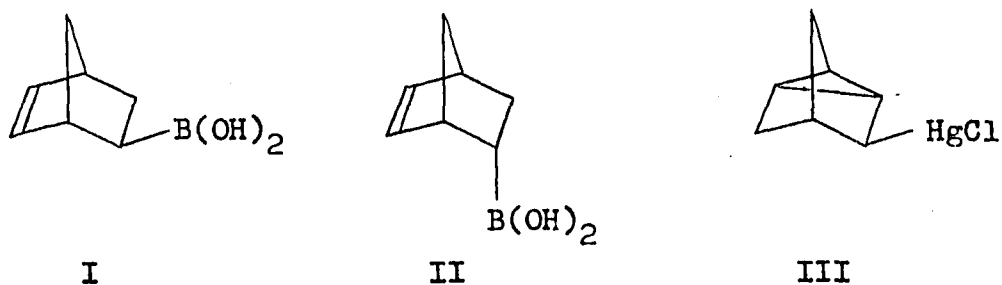
The postulate that silicon can undergo  $d_{\pi}-p_{\pi}$  bonding now seems to be generally accepted. Eaborn<sup>(3)</sup> has thoroughly reviewed the literature concerned with the subject prior to 1960. The example cited illustrate the capacity of silicon for delocalizing adjacent electrons through the use of its  $d$ -orbitals. Trisilylamine,  $(\text{H}_3\text{Si})_3\text{N}$ , which might be expected to be a stronger base than trimethylamine because of the electropositive character of silicon relative to carbon, is, in fact, a much weaker base than the carbon analogue. Eaborn<sup>(4)</sup> also notes that dipole moment, as well as other studies, suggest that the  $\pi$ -electrons of the aromatic ring can enter the  $d$ -orbitals of a silicon atom bonded to the ring. Recently, silyl methyl ether  $(\text{SiH}_3\text{OCH}_3)$  has been prepared<sup>(5)</sup> and appears to be a weaker Lewis base than dimethyl ether. Again it is apparent that the back donation of electrons from the oxygen to the  $d$ -orbitals of silicon more than compensates for any increased electron density at the oxygen resulting from the fact that silicon is more electropositive than carbon. West, Whatley and Lake<sup>(6)</sup> reached the same conclusion from studies concerned with the relative basicities of ethers, alkoxysilanes and siloxanes. These authors concluded that oxygen forms a strong  $\pi$  bond to silicon using only one of its two  $p$  orbitals, which over-

laps one 3d orbital of silicon. While it is possible to draw many parallels between carbon and silicon chemistry, the differences in electronic structure cause many changes in reactivity. Study of the mechanisms of organosilane reactions provides interesting opportunities to learn more about silicon, as well as carbon, chemistry.

It is true that nucleophilic attack at the saturated carbon atom is well understood; however, the nature of electrophilic attack at the saturated carbon atom is the subject of much speculation. Dewar<sup>(7)</sup> postulated that such attack would proceed with inversion. Winstein, Traylor and Garner<sup>(8)</sup> point out that the electron repulsion -- one of the major reasons why backside attack is preferred in  $\text{Sn}_2$  reactions -- would be of much less consequence in electrophilic attack at a saturated carbon atom. Indeed, the transition state of such an attack may be regarded as electron deficient and, perhaps, some stabilization is derived from bonding between the leaving group and the incoming electrophile. These arguments have been substantiated in later experimental work<sup>(9)</sup>.

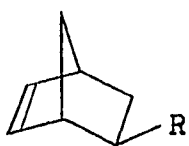
Organomercurials have proven to be ideally suited for studies investigating the nature of the attack of electrophiles on the saturated carbon atom. In a comprehensive review, Reutov<sup>(10)</sup> reports that the electrophilic cleavages of all of the organomercurials studied proceeded with retention of configuration. Retention of configuration was suggested as a general rule for electrophilic cleavages of carbon-metal bonds.

Studies concerned with the alkaneboronic acids have introduced complications into an otherwise tidy picture. Although Brown<sup>(11)</sup> found that the oxidation of organoboron compounds with hydrogen peroxide results in retention of configuration, Matteson and Waldbillig<sup>(12)</sup> have described reactions which indicate that cleavage of the carbon-boron bond can proceed preferentially with inversion of configuration. The bicyclic alkaneboronic acids I and II were subjected to electrophilic attack by mercuric chloride.

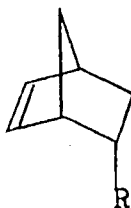


Matteson and Waldbillig<sup>(12)</sup> found that the exo isomer I reacted hundreds of times faster than the endo isomer II. The evidence indicates that pi-complex formation with  $\text{HgCl}^+$ , followed by transannular displacement of the boron functional group, takes place with the formation of III.

The purpose of the work described in this thesis was to prepare and to study the electrophilic reactions of compounds of the types IV, V and VI.



IV



V



VI

a, R = SiCl<sub>3</sub>

b, R = SiCH<sub>3</sub>Cl<sub>2</sub>

c, R = Si(CH<sub>3</sub>)<sub>3</sub>

d, R = Si(OEt)<sub>3</sub>

e, R = SiF<sub>3</sub>

While detailed and careful work has been carried out by Eaborn and co-workers on the electrophilic cleavage of aryl-silicon bonds<sup>(13)</sup>, presently available information about the cleavage of saturated carbon-silicon bonds is fragmentary. Organosilanes have been known to undergo eliminations of the E1 type. The treatment of beta-chloroethyl trimethylsilane with aluminum chloride<sup>(14)</sup> generates ethylene in high yield. The same olefin results from the solvolysis of this silane<sup>(15)</sup>. A reaction, which formally involves the electrophilic cleavage of the carbon-silicon bond, results from the treatment of gamma-bromopropyl trimethylsilane with aluminum chloride. Apparently, the initially formed carbonium ion attacks the carbon-silicon bond. The net result is the formation of cyclopropane in nearly quantitative yields. In somewhat less definitive studies<sup>(16)</sup>, allyltrimethylsilane was subjected to cleavage using concentrated sulfuric acid, hydrogen chloride and bromine.

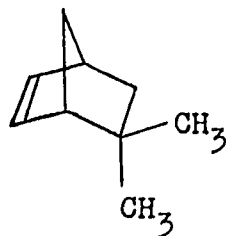
Other studies yielded information regarding the ef-



facts of silicon substituents on the ease of carbon-silicon bond cleavage. It was found that allyltrichlorosilane cleaves much less readily than the corresponding trimethyl and triethoxy compounds<sup>(17)</sup>. Bailey and Pepe<sup>(18)</sup> reported that arylfluorosilanes can be nitrated in excellent yield by conventional nitration procedures without aryl-silicon cleavage. In contrast, the aryltrialkylsilanes and arylchlorosilanes do undergo cleavage under these reaction conditions.

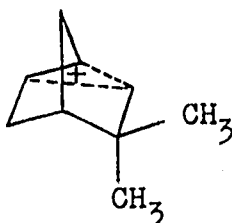
The literature concerned with the addition of electrophilic reagents to the carbon-carbon double bond of bicyclo(2.2.1)heptene derivatives is voluminous. However, for the purposes of this introduction, only the publications will be reviewed which evaluate the influence of remote substituents on the rate of addition.

Kwart and Miller<sup>(19)</sup> studied the electrophilic addition of 2,4-dinitrobenzenesulfonyl chloride to norbornene derivatives. The results showed quite clearly that substituents on the 5 and 6 positions of the norbornene carbon skeleton can have a profound effect upon the rate of electrophilic addition to the double bond. For example, cis-exo-5,6-dicarboxynorbornene undergoes addition almost seventy-five times faster than the corresponding endo compound. These results strongly imply the operation of a transannular field effect. Apparently, the substituent need not undergo any chemical change itself to influence strongly the reactivity of the double bond. McGreer<sup>(20)</sup> investigated the acetates formed by the addition of acetic acid to 5,5-dimethylnorbornene (VII). Due to the asymmetric character of this

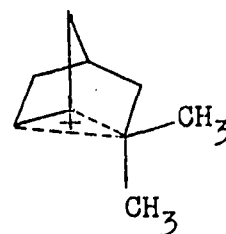


VII

compound, two possible non-classical carbonium ions VIII and IX are conceivable, depending upon the mode of addition

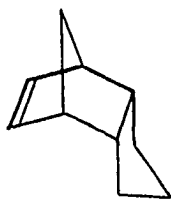


VIII

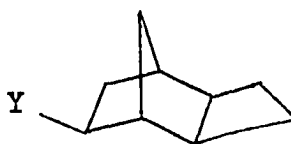


IX

of the proton to the double bond. It might be argued that IX would be the most stable ion due to the electropositive character of the methyl groups. However, the acetates that were isolated showed that addition to the double bond had been completely random. The methyl groups exert no directive influence. Electrophilic additions to norbornene often proceed with rearrangement. Cristol<sup>(21)</sup> has recently shown that the acid-catalyzed additions of acetic acid, formic acid and water to endo-dihydrodicyclopentadiene X as well as to the exo-isomer, lead almost exclusively to derivatives of XI.

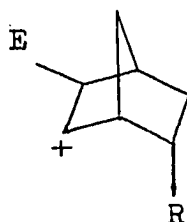


X

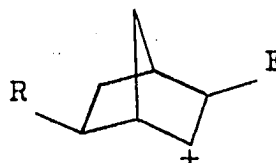


XI

The study of the reaction of electrophilic reagents with compounds of the types IV and V seemed of interest for a number of reasons. Addition of an electrophile,  $E^+$ , to the double bond could lead to carbonium ions XII and XIII.

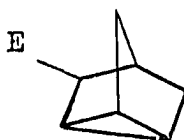


XII



XIII

Should the carbonium ion attack the carbon-silicon bond, the resulting product would be a 3-substituted nortricyclene XIV.



XIV

The relative ease of electrophilic cleavage of the two compounds would reveal the energetically most favorable path. In the event that cleavage with inversion is the most facile, then the exo isomer IV would react faster than the endo iso-

mer V. The results of cleavage studies of I and II have been rationalized in just this fashion by Matteson and Waldbillig<sup>(12)</sup>. This reasoning neglects other factors such as solvation and steric differences involving the leaving group. Also, the formation of a non-classical carbonium ion would introduce an interesting complication. If the attacking electrophile is a proton ( $E = H$ ), then classical carbonium ions XII and XIII represent canonical forms of the same non-classical carbonium ion. In the event of initial formation of a non-classical carbonium ion, the exo and endo isomers should cleave at approximately the same rate. However, an additional factor must be considered.

Kwart and Miller<sup>(19)</sup> noted that 2,4-dinitrobenzenesulfonyl chloride reacts with 5-exo-methyl bicyclo(2.2.1)hept-2-ene 1.3 times faster than with the corresponding endo isomer. Apparently, the field effect of the methyl group in the endo position retards electrophilic addition to the double bond. In view of the effect of this rather subtle structural change, the influence of the stereochemistry of the boronic acid functional group on the rate of addition of the mercurium ion would be interesting to investigate. Matteson and Waldbillig<sup>(12)</sup> noted an isotope effect upon varying the isotopic composition of the boron. This fact indicates that breaking of the carbon-boron bond is involved in the rate-determining step. An alternate mechanism to the one suggested by Matteson and Waldbillig<sup>(12)</sup>, and one which is consistent with the data, involves direct attack of the mercurium ion on the carbon-boron bond. While it is true

that a norbornenyl organomercury compound would be produced initially, these compounds are known to isomerize readily to III<sup>12</sup>. Because of the inert character of ordinary alkane boronic acids under these reaction conditions, it would be necessary to evolve a unique type of transannular interaction between the C5 position and the double bond.

Certainly, the homoenolization observed by Nickon<sup>(22)</sup> suggests that such interaction is possible. This worker found that a carbonyl in the 2 position of a bicyclo(2.2.1)-heptane molecule causes the hydrogens at the 6 position -beta to the carbonyl-carbon to be unusually susceptible to exchange in strongly basic media. The conclusions of Matteson and Waldbillig<sup>(12)</sup> cannot have unqualified acceptance until the direct cleavage mechanism has been tested.

The study of electrophilic addition to the double bond of compounds of the types IV and V was undertaken. It was suspected, and later confirmed by experimentation, that the carbon-silicon bond in these compounds would demonstrate a reactivity much greater than that shown in ordinary tetra-alkyl silanes. However, the carbon-silicon bond in these systems proved to be stable enough to permit a study of the effect of the stereochemistry of the silane function on the rate of addition of electrophilic reagents to the double bond without cleavage of the carbon-silicon bond.

## B RESULTS AND DISCUSSION

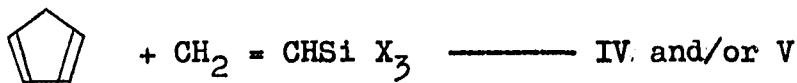
### 1. Preparative Methods

For the preparation of the desired compounds, two obvious routes were available: (1) the much studied hydrosilation of double bonds, i.e., the addition of silicon hydrides to carbon-carbon unsaturation; and (2) the Diels-Alder reaction between vinyl silanes and cyclopentadiene<sup>(24)</sup>. The reaction of various silicon hydrides with bicycloheptadiene XV has been reported previously; however, no attempt was made to



XV

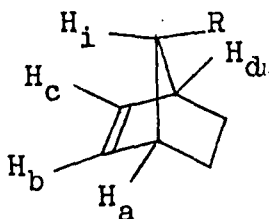
determine the stereochemistry of the resulting norbornenyl products. Wagner and co-workers<sup>(24)</sup> have carried out reactions of a variety of vinyl silanes with cyclopentadiene.



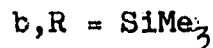
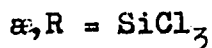
The authors were noncommittal about the stereochemistry of the products.

To the writer's knowledge, the free radical cata-

lyzed addition of trichlorosilane to bicycloheptadiene XV was carried out for the first time in these laboratories. The hope that the reaction would yield the exo isomer IVa was realized. However, the results were extraordinary for three reasons: (1) the relatively high yield of norbornenyl product places trichlorosilane among thiophenols<sup>(26)</sup> and diethyldithiophosphoric<sup>(27)</sup> acid as the only free radical addends which add to XV to give norbornenyl products along with the more usual nortricyclic products; (2) the formation of the 7-anti-trichloro bicyclo(2.2.1)hept-2-ene (XVIa) -- a product of a formal free radical Wagner-Meerwein rear-

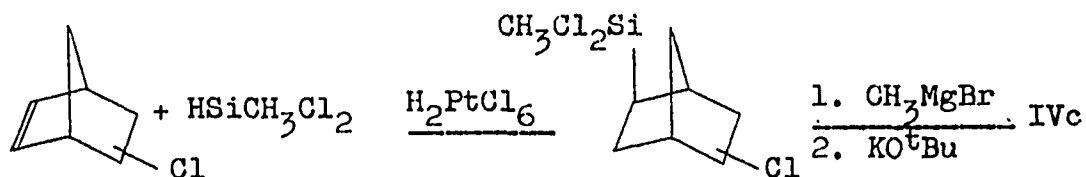


XVI



angement -- is surprising in view of the reported difficulty with which such rearrangements occur<sup>(28,29)</sup>; (3) the isolation of Va establishes the first documented case of endo free radical addition to bicycloheptadiene XV resulting in the formation of norbornenyl product. Similar results were obtained with either benzoyl or acetyl peroxide.

A wide variety of synthetic approaches was attempted before the one represented by the following equation led to the successful preparation of IVc.



This reaction scheme served as an unequivocal synthesis of IVc. The hydrosilation step would be expected to proceed from the exo side where there is less steric hindrance. The rule of exo addition in norbornenyl systems is well established by precedent<sup>(30)</sup>, and is reasonable on steric grounds. The isomeric purity of the product formed depended greatly on the composition of the 5-chloro bicyclo(2.2.1)hept-2-ene used. Thus, the use of the pure exo isomer resulted in the formation of a mixture of 73% of IVc and 27% of Vc. However, a 50:50 mixture of the two chlorides resulted in the formation of IVc which was more than 90% pure. This suggests that the chloride in the exo position could be creating some steric hindrance to exo approach to the double bond through the operation of a buttressing effect upon the methylene bridge. This would make endo addition more competitive with exo addition. As can be seen by reference to Table I, a sample of Vc could be obtained in greater than the 90% purity by the methylation and fractional distillation of the reaction mixture derived from chloroplatinic acid, methyl-dichlorosilane and bicycloheptadiene XV.

In order to verify the structural assignments made on the basis of synthetic and spectral data, it was desired



TABLE I

Data on Preparation of Silylnorbornenes and -nortricyclenes

<u>Silane</u>	<u>Temp.</u> ° C	<u>Catalyst</u>	<u>Yield</u> %	<u>Product</u> <u>Distribution, %</u>		
				<u>IV</u>	<u>V</u>	<u>VI</u>
HSiMeCl <sub>2</sub> <sup>a</sup>	50-60	H <sub>2</sub> PtCl <sub>6</sub>	80	6	64	30
HSiMeCl <sub>2</sub> <sup>a</sup>	50-60	Pt/C	77		6	94
HSiCl <sub>3</sub> <sup>a</sup>	35-50	Pt/C	25			100
HSiCl <sub>3</sub> <sup>a</sup>	80-100	AIBN	80 <sup>b</sup>	28	7	53
HSiMe <sub>3</sub> <sup>a</sup>	175-200	H <sub>2</sub> PtCl <sub>6</sub>	45	23	56	21
HSiMe <sub>3</sub> <sup>a</sup>	175-200	Pt/C	55	35	53	12
ViSiCl <sub>3</sub> <sup>c</sup>	50-60		68	20	80	
ViSiCl <sub>3</sub> <sup>c,d</sup>	175-200		73	50	50	
ViSiMeCl <sub>2</sub> <sup>c</sup>	50-60		40	27	73	
viSiMeCl <sub>2</sub> <sup>c,d</sup>	175-200		58	55	45	
ViSi(OET) <sub>3</sub> <sup>c,d</sup>	175-200		15	65	35	

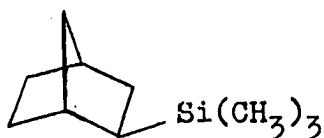
<sup>a</sup> Reaction was carried out with bicycloheptadiene.

<sup>b</sup> Another olefinic silane constituted 13% of this reaction mixture. It was identified as 7-anti-trichlorosilyl bicyclo(2.2.1)hept-2-ene.

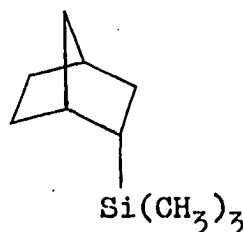
<sup>c</sup> Reaction was carried out with cyclopentadiene; Vi denotes vinyl.

<sup>d</sup> The cyclopentadiene was generated in situ from the dimer.

to synthesize 2-exo-trimethylsilyl bicyclo(2.2.1) heptane (XVII) and 2-endo-trimethylsilyl bicyclo(2.2.1)heptane (XVIII) by unequivocal routes. These compounds could then



XVII



XVIII

be compared with the hydrogenated norbornenyl compounds encountered in this work. The operation of Bredt's Rule limits the double bond to two positions.

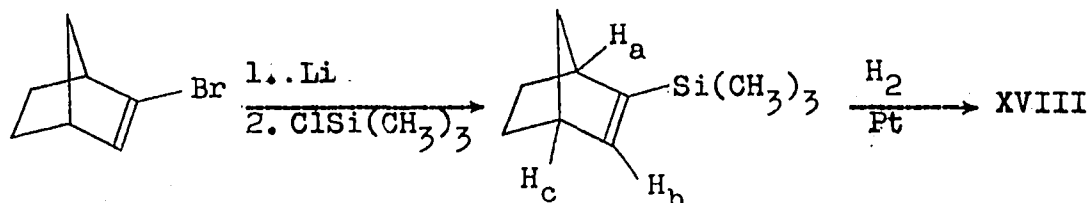
The rule of exo addition was applied in the synthetic schemes for XVII and XVIII. The reaction of norbornene (XIX)



XIX

and methyldichlorosilane with platinum catalysis, followed by methylation would be expected to yield XVII in high purity. In fact, the resulting reaction mixture consisted of 97% XVII and 3% XVIII.

An unequivocal synthesis of 2-endo-trimethylsilyl bicyclo(2.2.1)heptane (XVIII) was carried out as depicted in the following reaction scheme:



Catalytic hydrogenation of norbornenyl derivatives has been shown to proceed by exo addition<sup>(31)</sup>. The postulate<sup>(32)</sup> that platinum-catalyzed hydrosilation and hydrogenation proceed by analogous mechanisms with the catalyst polarizing the bond involving the hydrogen has received supporting evidence in the cis-hydrosilation of acetylene<sup>(33,34)</sup>.

## 2. Infrared Spectral Data

The distinction between the 3-substituted nortricyclene and the isomeric 5-substituted bicyclo(2.2.1)hept-2-ene is easily made because of characteristic differences in the infrared spectra. Nortricyclene derivatives are known to absorb at  $3070 \text{ cm.}^{-1}$  due to the C-H stretching of the cyclopropyl hydrogens and to have a highly characteristic band in the  $800 \text{ cm.}^{-1}$  region<sup>(35,36)</sup>. Hart and Martin<sup>(37)</sup> have found that nortricyclenes substituted on the cyclopropyl ring absorb near  $860 \text{ cm.}^{-1}$  and  $780 \text{ cm.}^{-1}$ . Norbornenes character-

istically absorb in the 1580 to 1565  $\text{cm}^{-1}$  region<sup>(36,38,39,40)</sup>.

The compounds VIa-c, IVa-c and Va-c show a band of medium intensity in the region near 3060  $\text{cm}^{-1}$ . The  $\beta$ -trichlorosilyl tricyclo(2.2.1.0<sup>2,6</sup>)heptane (VIa) absorbs very strongly at 800  $\text{cm}^{-1}$  in contrast to the bicyclo(2.2.1)hept-2-ene compounds IVa and Va which have no absorbance at 800  $\text{cm}^{-1}$ . All three of these compounds absorb at 820  $\text{cm}^{-1}$ , and IVa and Va absorb at 810  $\text{cm}^{-1}$ . However, the peak at 810  $\text{cm}^{-1}$  in the spectrum of VIa is obscured by a strong absorption at 800  $\text{cm}^{-1}$ . The Si-Cl bond absorbs in the 810  $\text{cm}^{-1}$  region<sup>(41)</sup>; therefore, the strong absorption at 800  $\text{cm}^{-1}$  should be taken as indicative of the nortricyclic structure of VIa. The carbon-carbon double bond stretching frequency of the bicyclo(2.2.1)heptene olefinic bond at 1570  $\text{cm}^{-1}$  appeared in the spectra of IVa-d and Va-d. This band was totally absent in the spectra of compound VIa-c. The sharp absorbance at 1333  $\text{cm}^{-1}$  due to the cis-substituted double bond C-H stretch is absent or very weak in VIa-c but appears strongly in IVa-d and Va-d. Of the two main categories of structural types under consideration, only the norbornenyl compounds give a weak, broad absorbance in the 1620 to 1640  $\text{cm}^{-1}$  region. The 800  $\text{cm}^{-1}$  region is obscured by an absorption band due to the methyldichlorosilyl function group in IVb, Vb and VIb. However, it is interesting to note that the 825 to 890  $\text{cm}^{-1}$  region is clear in the spectrum of VIb; thus indicating that this compound is not a 1-substituted nortricy-

clene derivative<sup>(37)</sup>. Both IVc and Vc absorb weakly between 800  $\text{cm}^{-1}$  and 803  $\text{cm}^{-1}$ ; however, VIc has a strong absorbance at 795  $\text{cm}^{-1}$  with a shoulder at 802  $\text{cm}^{-1}$ . It was also noticed that the norbornenyl compounds, IV and V, have a weak absorbance at 3140  $\text{cm}^{-1}$  which is completely absent in VI.

There are subtle differences in the infrared spectra among the exo and endo isomers. The spectra of the saturated isomers XVII and XVIII are shown in Figure 1; and the spectra of the unsaturated isomers IVc and Vc are shown in Figure 2. The three peaks in the 1250  $\text{cm}^{-1}$ , 840  $\text{cm}^{-1}$  and 755  $\text{cm}^{-1}$  regions which are characteristic of the trimethylsilyl group are clearly visible<sup>(42)</sup>. The major spectral differences among the isomers are presented in Table II. The

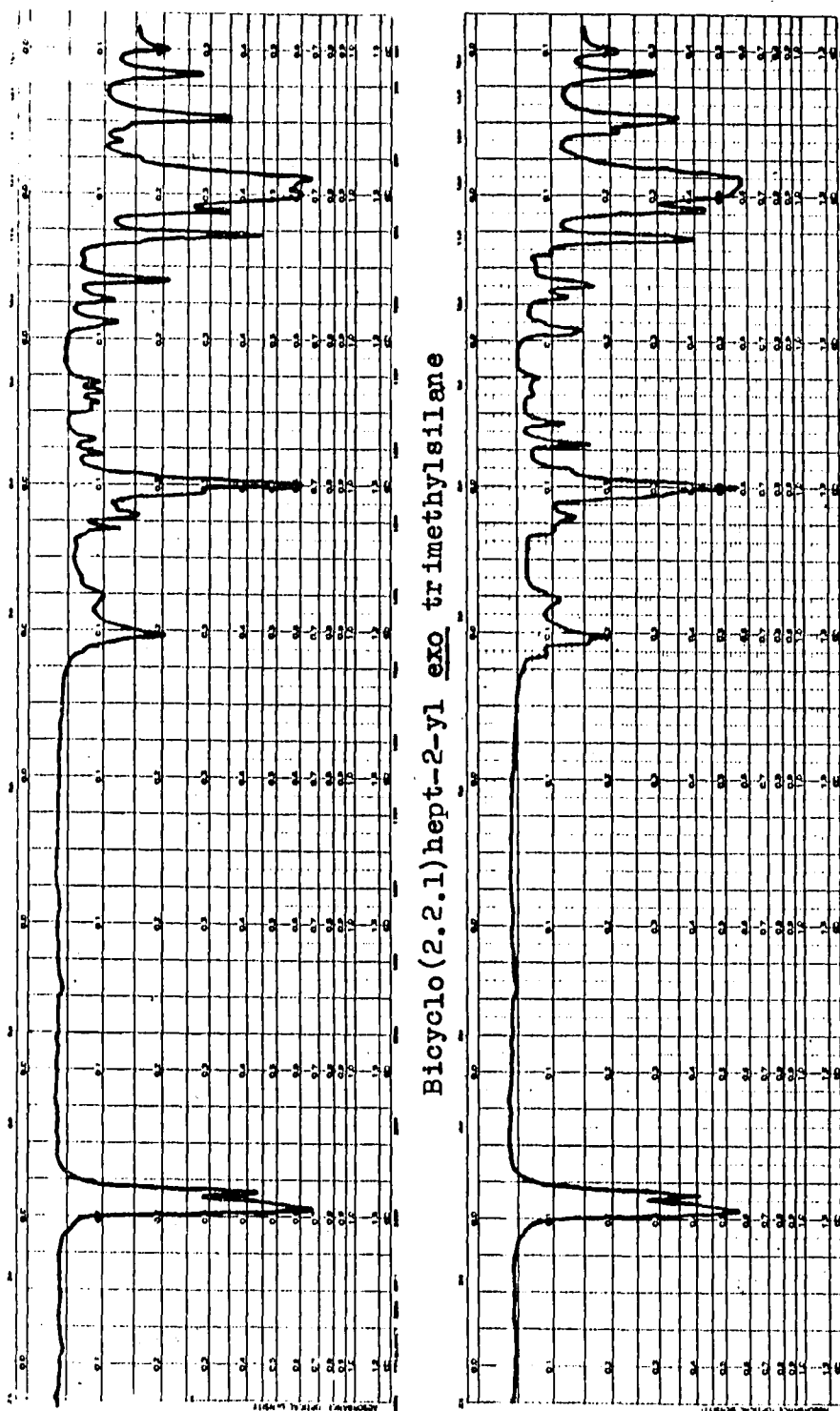
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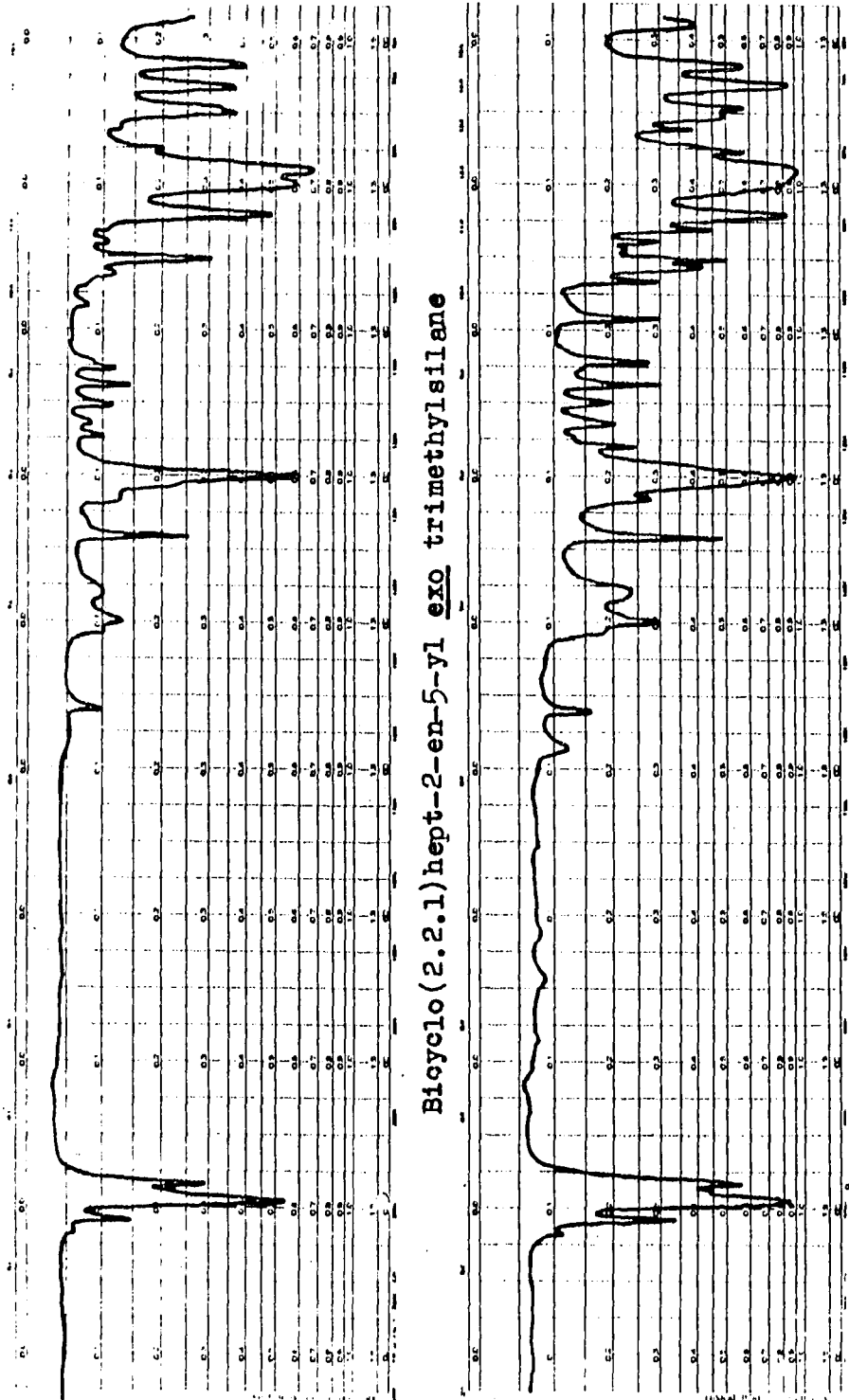
TABLE II  
Major Infrared Spectral Differences<sup>a</sup>  
Between Endo and Exo Isomers

	<u>IV</u>	<u>V</u>	<u>XVII</u>	<u>XVIII</u>
SiMe <sub>3</sub>	1196	1210	1209	1191
	1103	1092	1187	1163
	1016	1035	1147	763
	975	982	1137	
		962		
		910		
SiCl <sub>3</sub>	1105	1095		
	1200			
SiCH <sub>3</sub> Cl <sub>2</sub>	1105	1045		
	1200			

<sup>a</sup> In reciprocal centimeters; taken as film.

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Bicyclo(2.2.1)hept-2-en-5-yl exo trimethylsilane

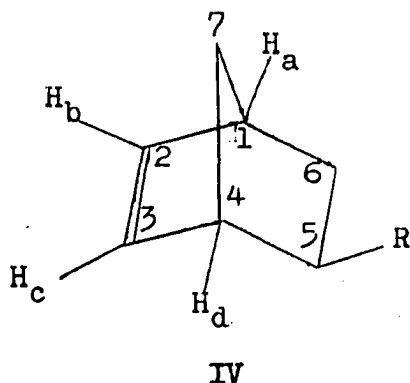
Bicyclo(2.2.1)hept-2-en-5-yl endo trimethylsilane

Figure 2

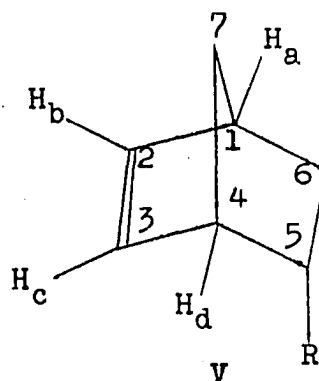
assignment of characteristic bands to the isomers IVa-b and Va-b is more difficult because these compounds have not been obtained in a pure state. However, it has been possible to obtain known mixtures of various compositions. Thus, the bands shown in Table II could be assigned with a great deal of confidence.

### 3. Proton Magnetic Resonance Data

a. Interpretation of vinyl region. Many studies directed toward the interpretation of the n.m.r. spectra of bicyclic compounds have appeared recently. These reports have made it possible to prove that the spectra observed for IV and V are consistent with the proposed structures.



- a, R = SiCl<sub>3</sub>  
 b, R = SiCH<sub>3</sub>Cl<sub>2</sub>  
 c, R = Si(CH<sub>3</sub>)<sub>3</sub>



- d, R = Si(OET)<sub>3</sub>  
 e, R = SiF<sub>3</sub>

The relationship between the dihedral angle and the coupling constant established by Karplus<sup>(43)</sup> suggests that all cis-disubstituted olefins should have vinyl proton coup-



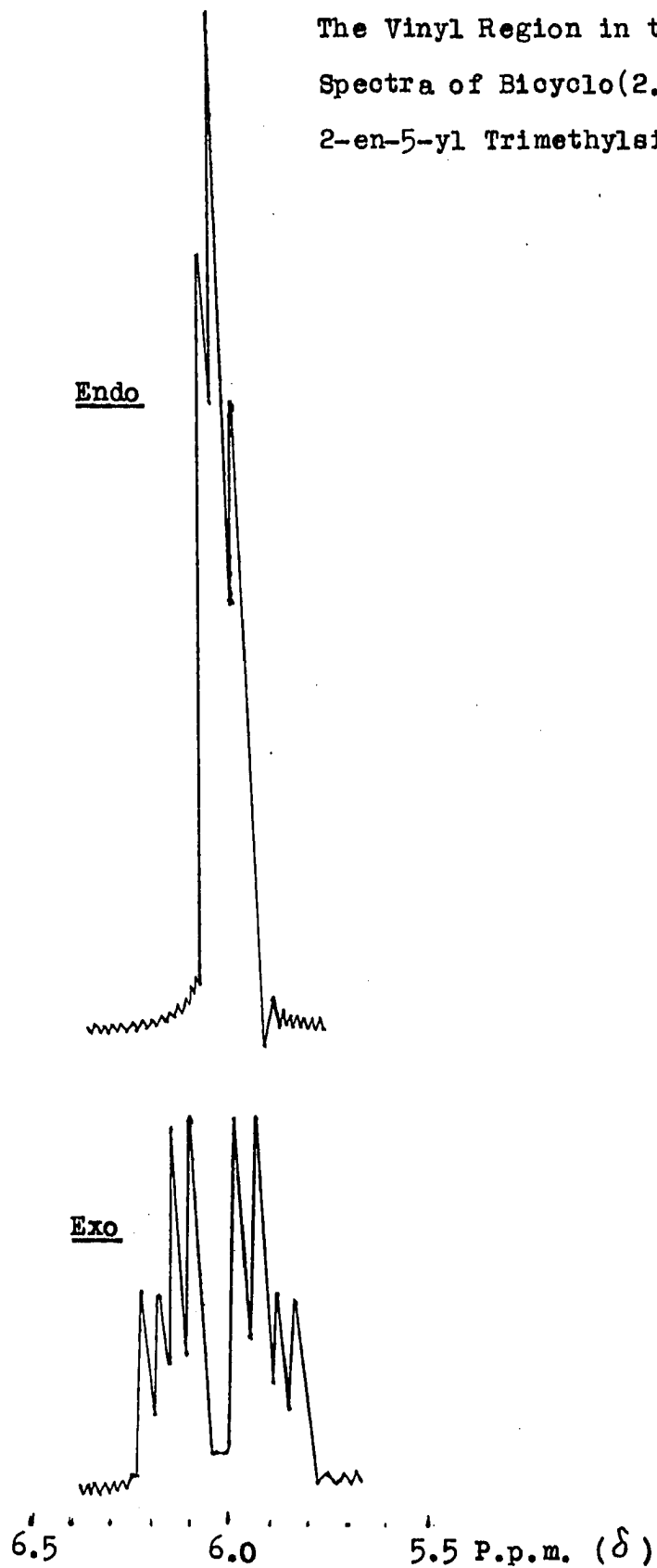
lings of 6.1 c.p.s., whereas trans-disubstituted olefins should show vinyl proton coupling constants of 11.9 c.p.s.<sup>(44)</sup> Experimentally, the ratio  $J_{\text{cis}}/J_{\text{trans}}$  gives good agreement with theory<sup>(45)</sup>. However, a consideration of other factors is necessary if the predicted absolute values are to be correlated with the observed values<sup>(46)</sup>. Chapman<sup>(44)</sup> and others<sup>(47,48)</sup> found that the absolute magnitude of the vinyl proton coupling constant in cis-cyclic olefins is not constant but depends on the size of the ring. A wide variety of norbornene derivatives have been studied<sup>(44,48)</sup> and the vinyl proton coupling constant is always of the magnitude 5.1-6.0 c.p.s. The spin-spin interactions between the vinyl protons and the adjacent bridgehead proton demonstrate values between 2.2 c.p.s. and 3.3 c.p.s., the exact value depending upon the nature of the substituents in the molecule. This information strongly suggests that, in the absence of unexpected effects, the coupling constants observed in the series IV and V should fall within a rather narrow range:

$$J_{bc} \cong 6 \text{ c.p.s.} \quad \text{and} \quad J_{ab} = J_{cd} \cong 3 \text{ c.p.s.}$$

The vinyl region of the n.m.r. spectrum of 5-exo-trimethylsilyl-2-norbornene (IVc) is shown in Figure 3. This is an easily recognizable AB type spectrum with a small perturbation of 3.0 c.p.s. caused by the coupling of the bridgehead protons with the adjacent vinyl protons. Using the normal AB analysis<sup>(19)</sup>, one finds that  $J_{bc} = 5.5$  c.p.s. with  $\delta_{bc} = 15$  c.p.s.

Figure 3

The Vinyl Region in the N.m.r. Spectra of Bicyclo(2.2.1)hept-2-en-5-yl Trimethylsilane.



Interestingly, the olefinic proton splitting pattern for 5-endo-trimethylsilyl-2-norbornene (Vc), which is shown in Figure 3, has little superficial resemblance to the same spectral region for IVc. The spectrum involving the vinyl and bridgehead protons could be classified as an ABXY system. Ordinarily, such a system would give a complex spectrum. However, at times a "deceptively simple spectrum"<sup>(49)</sup> is observed. One of the consequences of such a spectrum is that the line separations in each group of the spectrum are equal to the average of two or more of the coupling constants involved. The result is that explicit values for the coupling constants cannot be derived from a consideration of the spectrum alone. A commonly employed method for converting these "deceptively simple spectra" into more complex, and hence more informative spectra, is based upon the increasing of the chemical shift differences between some or all of the protons involved. It is hoped that these changes can be carried out without appreciably altering the values of the coupling constants involved. Often, variation of the substituents in the molecule will give the desired result. While it can be assumed with some confidence that a new spectrum is the consequence of the same coupling constants, the values obtained should be checked by analysis to see if the "deceptively simple spectra" could be the result of such coupling constants. Another method consists of varying the solvent in which the spectrum is determined with the purpose of finding specific solute-solvent interactions. Frequently

these interactions will increase the chemical shift differences. Certainly, the most satisfactory technique would be to determine the spectrum using a magnet of greater strength. This will increase the chemical shift difference between the protons as the chemical shift is directly proportional to the strength of the applied field. Abraham and Bernstein<sup>(49)</sup> have illustrated all of these techniques.

A survey of the literature<sup>(44,48,50,51)</sup> reveals that rather drastic changes in the stereochemistry, number and nature of the substituents on the 5-, 6- and 7-positions of the norbornene carbon skeleton cause little change in the coupling constants among the vinyl and bridgehead protons. By comparison, the change of the stereochemistry of the 5-trimethylsilyl functional group from exo to endo is a very minor one indeed. Thus, the vinyl coupling constant  $J_{bc}$  is probably about the same in both IVc and Vc. The analysis which follows will lend strong support to this assumption. Also, it is reasonable to assume that  $J_{cd} = J_{ab}$  and  $J_{ac} = J_{db}$ .

With this information, a fruitful discussion of the vinyl proton n.m.r. spectrum of Vc is possible. The bridgehead protons in Vc appear as a broad peak which is an unresolved multiplet. This is apparently the result of coupling with many protons. Therefore, it will be possible to consider in detail only the vinyl region of the spectrum. Abraham and Bernstein<sup>(49)</sup> have derived the conditions under which an ABXY system will give a simple spectrum of two trip-

let groups. Applied to the case under consideration, the equation for the vinyl protons would be:

$$(1) \quad \left\{ \delta_{bc} + \frac{1}{2} (J_{ab} - J_{ac} + J_{db} - J_{cd}) \right\}^2 / 2 J_{bc} \langle \Delta \nu \rangle_{\frac{1}{2}}$$

where  $\delta_{bc}$  refers to the chemical shift difference in c.p.s. between  $H_b$  and  $H_c$ . The parameter  $\langle \Delta \nu \rangle_{\frac{1}{2}}$  is the band width at half height of the component lines and has a value of approximately 0.3 c.p.s. for the Varian A-60 Spectrometer. Assuming that  $J_{bc} = 5.5$  c.p.s.,  $J_{ab} = J_{cd}$ , and  $J_{ac} = J_{db}$ , it is found that  $\delta_{bc} \leq 1.9$  c.p.s. Continuing with the ABXY treatment according to Abraham and Bernstein<sup>(7)</sup>, the line separation of the observed triplet will be equal to:

$$(2) \quad \frac{1}{2} \left[ \frac{J_{ab} + J_{ac}}{2} + \frac{J_{cd} + J_{db}}{2} \right].$$

Using the same values found for the exo isomer IVc and assuming that  $J_{ac} = J_{db} \cong 0$ , a line separation of 1.5 c.p.s. is obtained which is quite close to the experimentally observed value of  $1.8 \pm 0.1$  c.p.s.

The treatment given above demonstrates that the chemical shift difference between the vinyl protons is small. Therefore, these protons could be considered as an  $A_2$  system rather than as an AB system. Because the bridgehead protons also have identical chemical shifts, the system of the olefinic and bridgehead hydrogens can appropriately be considered as  $A_2X_2$ . Here again, it is possible to obtain a "deceptively simple spectrum"<sup>(49)</sup>. The treatment of Abraham and Bern-

stein<sup>(49)</sup> will be used to demonstrate that the spectrum for Vc is consistent with the structural assignment. The conditions under which an  $A_2X_2$  system would give a "deceptively simple spectrum" are covered by the limit:

$$(3) \quad (J' - J'')^2 / 2 (J_{bc} - J_{ad}) \ll \mathcal{J} / 2$$

where  $J' = J_{ab} = J_{dc}$  and  $J'' = J_{ac} = J_{db}$ .

Two obvious interpretations are possible for the spectrum observed for the vinyl protons of Vc: (1) the coupling between a vinyl hydrogen and the nearest bridgehead hydrogen is of the same magnitude as the coupling between a vinyl proton and the furthest bridgehead hydrogen; or (2) the coupling constants involved in the vinyl proton region are approximately the same as those found in the exo isomer IVc. In the former case, which is not a "deceptively simple spectrum", the line separation in the triplet would be equal to  $(J' + J'')/2$ . This would lead to a value for  $J'$  of 1.8 c.p.s., which is much smaller than any value previously observed for norbornene derivatives<sup>(48,50,51)</sup>. The likelihood of a drastic distortion or electronic effect which could lead to a change of this magnitude in the vinyl coupling constant is highly improbable<sup>(52)</sup>. In the latter case we are dealing with a "deceptively simple spectrum" and eq. (3) is applicable. Thus, if  $J_{bc} = 5.5$  c.p.s. and  $J_{ad} = 0$  c.p.s., then  $J' - J''$  is equal to or less than 1.8 c.p.s. Experimentally, the line separation in the triplet is  $1.8 \pm 0.1$  c.p.s.

In theory, the line separation for an " $A_2X_2$  deceptively simple spectrum" is equal to  $(J' + J'')/2$ . Assuming the maximum value for  $J' + J''$ , the following values are obtained:  $J' - J'' = 1.8$  c.p.s.;  $J' + J'' = 3.6$  c.p.s. Solving for  $J'$  and  $J''$ , and continuing with the assumptions made, yields the following coupling constants:  $J' = 2.7$  c.p.s.,  $J'' = 0.9$  c.p.s.,  $J_{bc} = 5.5$  c.p.s. and  $J_{ad} = 0$  c.p.s. All of these values are within the ranges reported for comparable spin-spin interactions in the norbornene derivatives studied by Laszlo and von R. Schleyer<sup>(48,50)</sup>. Finally, calculations using the treatment of Pople, Schneider and Bernstein<sup>(53)</sup> for the  $A_2X_2$  system demonstrate that these coupling constants are consistent with the line positions observed and closely approximate the experimental relative intensities. However, the  $A_2X_2$  mathematical treatment is not adequate to explain the unsymmetrical nature of the triplet which is nearly identical to the triplet due to the vinyl hydrogen resonance of bicyclo-(2.2.1)hept-2-ene (XIX) centered at 5.94 p.p.m.<sup>(54)</sup>.

The evidence indicates that the chemical shifts of the vinyl protons of isomer IVc are separated by 15 c.p.s.; whereas the corresponding separation in the 5-endo-trimethylsilyl-2-norbornene (Vc) is equal to or less than 1.9 c.p.s. This phenomenon could be the result of a strong contribution by the magnetic anisotropy of the carbon-silicon bond. Such an effect can be evaluated using the equation developed by McConnell<sup>(55)</sup>:

$$(4) \quad \sigma = \frac{\Delta\chi}{3\rho^3N} \langle 1 - 3 \cos^2\gamma \rangle$$

$\sigma$  represents the contribution of the axially symmetric magnetically anisotropic bond to the chemical shift of a proton;  $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ , the difference of magnetic susceptibility along the symmetry axis from the magnetic susceptibility perpendicular to the symmetry axis;  $\gamma$  is the angle between the symmetry axis of the bond and the vector connecting the substituent with the proton effected;  $\rho$  is the distance from the center of the bond to the proton in question;  $N$  is Avogadro's number. An examination of Dreiding models of IVc and Vc reveals that the angle  $\gamma$  and the distance  $\rho$  have approximately the same values for  $H_b$  and  $H_c$  if measured relative to the endo trimethylsilyl substituent. Because of this, the magnetic anisotropy of the carbon-silicon bond would have approximately the same effect on both of the vinyl protons. Also, the inductive effect<sup>(56)</sup> of the trimethylsilyl substituent would be greatly attenuated after transmission through four bonds to the closest vinyl hydrogen. Thus, the fact that  $H_b$  and  $H_c$  have nearly identical chemical shifts in Vc is to be expected. In the exo isomer IVc a number of factors come into play which could contribute to the chemical shifts observed. For example, any magnetic anisotropic effect on  $H_b$ , due to the silicon substituent must be transmitted in large part through the bicyclo-(2.2.1)heptene carbon skeleton. In contrast, the comparable influence on  $H_c$  can be transmitted through the solvent. In



view of this, little could be learned by comparing the values of  $\gamma$  and  $\rho$  for this isomer. Eq. (4) will be used to explain the influence of the stereochemistry of the carbon-silicon bond on the chemical shift of the adjacent bridgehead proton.

b. Interpretation of bridgehead region. The chemical shifts of the bridgehead protons exhibit interesting behavior which is a function of the stereochemistry at C5 and electronegativity of the silicon functional group. It appears that the carbon-silicon bond shields neighboring protons if the values of  $\gamma$  and  $\rho$  are favorable; a conclusion which will be supported by the following arguments. Firstly, the inductive influence of the trimethylsilyl group on the chemical shift of a proton three single bonds away would be slight. Thus, we find that  $H_a$  and  $H_d$  of Vc have the same chemical shift, 2.92 p.p.m., only 4 c.p.s. below that of the corresponding protons in norbornene itself. While in the exo isomer IVc one bridgehead proton resonance peak appears at 2.92 p.p.m., the other bridgehead proton (presumably  $H_d$ ) is shifted upfield to 2.72 p.p.m. This additional shielding of approximately 10 c.p.s. is probably the result of the magnetic anisotropy of the carbon-silicon bond. In compounds IVb and IVa the diamagnetic anisotropic shielding by the carbon-silicon bond is counteracted by the inductive deshielding of the electronegative methyldichlorosilyl and trichlorosilyl functional groups. As a result the bridgehead

protons of IVb appear as one peak at 3.00 p.p.m. The same protons in IVa appear as one peak at 3.10 p.p.m. The endo compounds Va and Vb each give two peaks separated by approximately 10 c.p.s. for bridgehead protons. The bridgehead proton which appears at highest field has the same chemical shift as the singlet peak present in the corresponding exo isomer (Table III). Consider, for example, the spectrum of

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TABLE III  
Chemical Shifts of Bridgehead Hydrogens  
of 5-Substituted Norbornene Derivatives (IVa-c, Va-c), P.p.m.<sup>a, b</sup>

<u>Compound</u>	<u>H<sub>a</sub></u>	<u>H<sub>d</sub></u>
IVc	2.92	2.72
IVb	3.03	3.03
IVa	3.10	3.10
Vc	2.92	2.92
Vb	3.00	3.18
Va	3.10	3.27

<sup>a</sup> Probable errors are  $\pm 1.0$  to  $\pm 2.0$  c.p.s..

<sup>b</sup> The n.m.r. spectra were obtained on a Varian A-60 spectrometer. The samples were run as 20% solutions in CCl<sub>4</sub> with tetramethylsilane as internal reference.

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5-endo-trichlorosilyl-2-norbornene (Va): the bridgehead protons at C1 and C4 are respectively four and three bonds removed from the trichlorosilyl functional group. The bridgehead resonance peak which occurs at lowest field could then be assigned to H<sub>d</sub> because the inductive deshielding by the silicon substituent would be greatest for that proton. The bridgehead protons H<sub>a</sub> and H<sub>d</sub> of 5-exo-trichlorosilyl-2-nor-

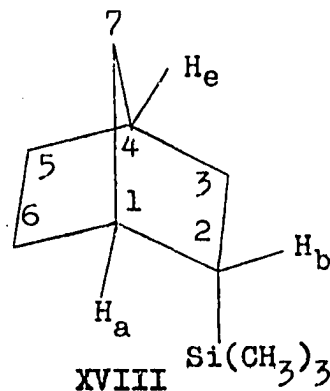
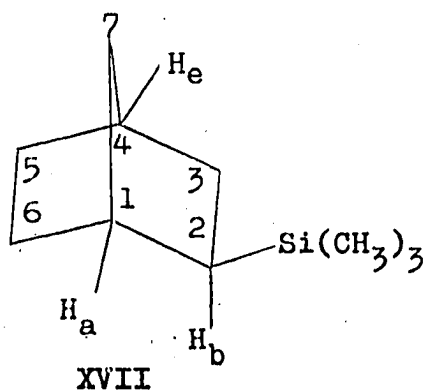
bornene (IVa) have identical chemical shifts. The reduction of the diamagnetic shielding of  $H_d$  caused by the inductive effect of the trichlorosilyl group would be about the same in both IVa and Va. However, since this proton in the exo isomer IVa has the same chemical shift as  $H_a$ , it must be shielded by the magnetic anisotropy of the exo carbon-silicon bond. This line of reasoning leads to the interesting result that the shielding of the bridgehead proton at C4 by the magnetic anisotropy of the exo carbon-silicon bond amounts to about 0.17 p.p.m. in spite of the wide range of electronegativity covered in the series IVa-c. This, of course, could be the result of a fortuitous combination of effects.

These conclusions are consistent with the fact that  $\Delta\chi$  for the carbon-silicon bond would probably be positive. This is generally the case for most C-R bonds<sup>(57)</sup>. Wilcox<sup>(58)</sup> has described a method for calculating internuclear distances of bicyclo(2.2.1)heptane derivatives. Calculations were carried out assuming that the angular and spatial relationships of  $H_d$  to the exo or endo silicon atom at C5 are approximately the same in the bicyclo(2.2.1)heptane derivative as in the bicyclo(2.2.1)hept-2-ene molecule. The angle  $\gamma$  would have a value of approximately  $73^\circ$  in the exo position relative to the bridgehead proton at C4. Thus, the contribution of this bond to the chemical shift of that proton would be a shielding one, whereas in the endo position the value of  $\gamma$  would be approximately  $47^\circ$  and would result in less shielding. The fact that the direction of the shift is correct is the only

agreement sought in these arguments.

Finally, it is apparent that the chemical shift behavior of the bridgehead hydrogen  $H_d$  cannot be rationalized in terms of transannular, inductive deshielding. Calculations using the bicyclo(2.2.1)heptane approximation<sup>(58)</sup> indicate that in the exo position the silicon functional group is slightly closer to the bridgehead  $H_d$  than it would be in the endo position. If the transmission of the inductive effect through space is a dominant factor, the bridgehead proton resonance appearing at lowest field would be present in the n.m.r. spectra of IVa and IVb, contrary to the facts.

The n,m,r, results for the bridgehead protons of XVII and XVIII bear out the observations regarding the magne-



tic anisotropy of the carbon-silicon bond. The bridgehead protons of the 2-endo-trimethylsilyl norbornane (XVIII) appear to have identical chemical shifts. The proton resonances due to  $H_a$  and  $H_e$  would also have nearly identical multiplicities. The trimethylsilyl group has replaced the endo proton which couples only slightly with the adjacent bridge-

head hydrogen because of a dihedral angle of approximately  $79^\circ$ <sup>(59)</sup>. The bridgehead protons of 2-exo-trimethylsilyl norbornane (XVII) give rise to a broad signal at 2.17 - 2.23 p.p.m. with an area corresponding to two protons. This signal seems to be composed of a broad peak with approximately the same width at half height as the signal from the corresponding protons in the endo isomer XVIII. However, imposed upon the upfield side of this peak is another signal of substantially lower multiplicity. This sharper peak has been assigned to  $H_a$ . The broader peak, which is centered at slightly lower field, is from  $H_e$ . These assignments are consistent with both the multiplicities and chemical shifts of the signal. The bridgehead proton at C1 would appear at highest field due to the shielding by the magnetic anisotropy of the carbon-silicon bond. Also, its multiplicity would be less because the trimethylsilyl group has replaced the exo proton at C2. This proton greatly increases the multiplicity of the bridgehead proton both through direct coupling due to a dihedral angle of  $44^\circ$ <sup>(59)</sup> and by making possible "virtual coupling"<sup>(60)</sup>. The proton resonance spectrum of XVII contains an unsymmetrical triplet centered at approximately 0.55 p.p.m. These peaks have a total intensity of one proton and have the appearance of the C part of an ABC type of spectrum<sup>(61)</sup>. These peaks have been assigned to  $H_b$  and appear at least 0.4 p.p.m. upfield from the  $H_b$  proton of the endo isomer VI. This is exactly what one would predict on the basis of previous literature on the subject of exo and

endo hydrogens. The endo-protons are located essentially perpendicular to the plane of the six-membered ring and are therefore "pseudo-axial." The exo-hydrogens are in a plane close to the plane of the six-membered ring ("pseudo-equatorial")<sup>(57)</sup>. According to Jackman<sup>(62)</sup> axial hydrogens appear at 0.13 - 0.51 p.p.m. at higher field than do equatorial protons. This chemical shift difference is believed to arise from the magnetic anisotropy of the carbon-carbon single bonds<sup>(63,64)</sup>. The fact that H<sub>b</sub> appears at higher field in the exo isomer XVII then constitutes independent evidence in favor of the assigned structures.

c. Chemical shifts of silicon substituents. The protons of the trimethylsilyl groups under consideration here always appear as sharp singlets. These peaks have been used to verify the structure assignments established by synthetic means. Because the double bond is magnetically anisotropic, it makes a contribution to the total shielding of neighboring protons. In the bicyclo(2.2.1)hept-2-enes the exo protons on C5 and C6 which are approximately in the plane of the double bond will be shifted downfield. In contrast, the endo protons at C5 and C6 lie above the plane of the double bond, and hence would be shielded. Upon hydrogenation of the double bond the endo and exo protons would be expected to move downfield and upfield respectively. Examples are cited<sup>(62)</sup> which illustrate that this principle can be extended to the protons of a methyl group at C5 and to the

phenyl hydrogens of the benzyne-bicycloheptadiene adducts. The characterization of the two series IVb-d and Vb-d has made it possible to extend Fraser's<sup>(65)</sup> observations to the proton bearing silane substituents. In all cases the chemical shifts of the protons on the endo silane substituents appear at higher fields than do the corresponding protons in the exo isomer. The magnetic influence of the double bond is quite pronounced in the cases of IVd and Vd even though the methyl protons of the ethoxy groups are five bonds removed from C5. These results are given in Table IV.

---

TABLE IV

Variation of Chemical Shifts  
as a Function of the Stereochemistry at C5.

<u>Compound</u>	<u>Assignment</u>	<u>P.p.m.</u>
IVc	Si(CH <sub>3</sub> ) <sub>3</sub>	0.00 <sup>a</sup>
Vc		-0.10 <sup>a</sup>
IVb	SiCl <sub>2</sub> CH <sub>3</sub>	0.78 <sup>a</sup>
Vb		0.60 <sup>a</sup>
IVd	CH <sub>3</sub>	1.19 <sup>b</sup>
	CH <sub>2</sub>	3.81 <sup>b</sup>
Vd	CH <sub>3</sub>	1.14 <sup>b</sup>
	CH <sub>2</sub>	3.75 <sup>b</sup>

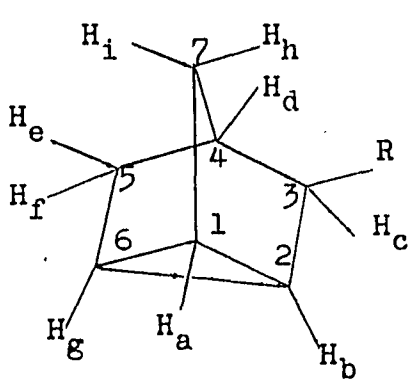
<sup>a</sup> The samples were run as 20% solutions in CCl<sub>4</sub> with added tetramethylsilane as an internal standard.

<sup>b</sup> Samples were run neat with added tetramethylsilane.

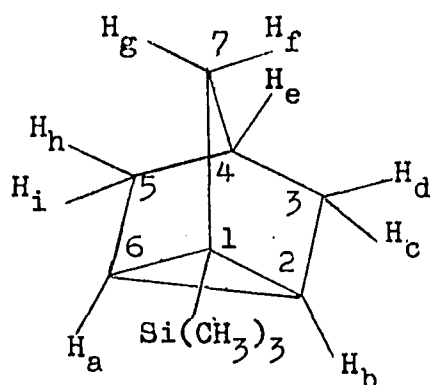
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Upon hydrogenation of compounds IVc and Vc, the trimethylsilyl proton magnetic resonance shifts from 0.00 p.p.m. to -0.04 p.p.m. and from -0.10 p.p.m. to 0.00 p.p.m. respectively. This is exactly what one would predict in view of the generalizations put forth by Fraser<sup>(65)</sup>.

d. Discussion of the silyl nortricyclenes. The n.m.r. spectra of the nortricyclyl silanes VIa-c and XXI



VI

a, R = SiCl<sub>3</sub>

XXI

b, R = SiCH<sub>3</sub>Cl<sub>2</sub>c, R = Si(CH<sub>3</sub>)<sub>3</sub>

proved to be amenable to analysis by first order theory. One reason for this is the lack of complex coupling interactions<sup>(26)</sup>. This is the result of unfavorable dihedral angles which exist between the cyclopropyl methyne protons and the methylene protons which, in turn, are unfavorably disposed for coupling with the bridgehead proton. Trecker and Henry<sup>(26)</sup> have carried out calculations for 3- and 3,5-disubstituted nortricyclenes based upon the model of Lippincott<sup>(66)</sup>. Their results indicate that the dihedral angle between the protons on C3 and C4 is about 80°, while that be-



tween C2 and C3 is about  $64^\circ$ . Coupling between these protons will be very small and can be neglected for practical purposes. The only large coupling constants which must be dealt with in these molecules are those involving geminal hydrogens. The n.m.r. spectrum of 1-trimethylsilyl-nortricyclene (XXI) consists of four peaks; the wide band with little resolved structure at 1.9 p.p.m. is assigned to the bridgehead proton at C4 on the basis of its relative area, characteristic appearance and chemical shift. A doublet assigned to the protons on C7 appears at 1.03 p.p.m. with a relative area of 2. The singlet at 0.92 p.p.m. has been assigned to the cyclopropyl methynyl hydrogens at C2 and C6 because it has a relative area of two and has the same chemical shift as the cyclopropyl hydrogens of VIc. The four methylene hydrogens at C3 and C5 appear as a singlet at 1.17 p.p.m. with a relative area of four.

The assignment of the peaks centered at 1.03 p.p.m. and 0.92 p.p.m. to the C7 methylene and cyclopropyl hydrogens respectively, was based primarily on chemical shift and multiplicity. The C7 methylene group appears at slightly higher field than the methylenes at C3 and C5. Finally, the methylene at C7 would give a simple doublet because it is coupled strongly only to the bridgehead proton at C4. The splitting pattern of the cyclopropyl hydrogens would not be expected to be a doublet. The methylenes at C3 and C5 appear as a broad singlet with no resolved fine structure.

Reference to Table V reveals that the cyclopropyl

TABLE V

Variation of Chemical Shifts<sup>a</sup>  
with Electronegativity of Silicon Substituents

Compound	Cyclopropyl Protons	b	H <sub>c</sub>	b	H <sub>d</sub>	b	SiCH <sub>3</sub>
VIc	1.02	0	0.62	0	1.94	0	-.02
VIb	1.21	.19			2.21	.28	0.72
VIa					2.35	0.41	

<sup>a</sup> P.p.m. downfield from tetramethylsilane

b

hydrogens, as well as the bridgehead proton H<sub>d</sub>, undergo comparable changes in chemical shifts as the substituents on the silicon are varied. One might expect all three cyclopropyl hydrogens of VIa-c to have the same chemical shift because the pseudo-olefinic character of the three membered ring would distribute the electronic effects equally to each of the cyclopropyl protons.

The proton H<sub>h</sub> of VIa appears as an unsymmetrical doublet centered at 1.63 p.p.m. It is shifted downfield due to the close proximity of the highly electronegative trichlorosilyl functional group. The peak immediately upfield from this doublet appears to be the inside peak of the other

half of the AB type of spectrum. A complete analysis of this AB spectrum is not possible due to overlapping peaks. However, it is possible to determine that  $J_{hi} = 11.5$  c.p.s.

It is much more difficult to obtain meaningful information regarding the methylene protons of VIb and VIc. In both of these cases, the resonance peak of the cyclopropyl hydrogens is present as a singlet and is sufficiently separated from the methylene resonance peaks to permit identification. The methynyl proton  $H_c$  is shifted well upfield in the case of VIc and appears as a singlet at 0.62 p.p.m. This peak is lost among the peaks due to the cyclopropyl and methylene protons in the cases of VIa and VIb. The assignments for the compounds are listed in Table V. Also listed are the chemical shift changes which result from varying the substituents on the silicon atom.

e. Discussion of 2-trimethylsilyl norbornene. The vinyl proton region of the spectrum of 2-trimethylsilyl norbornene VII appears as a simple doublet with  $J_{bc} = 2.9 \pm 0.1$  c.p.s. This is, again, consistent with values observed for the vinyl-bridgehead proton coupling in other bicycloheptene compounds. The other spectral assignments can be seen in Table VI.

f. Discussion of 7-trimethylsilyl norbornene. The spectrum of the 7-anti-trimethylsilyl bicyclo(2.2.1)hept-2-ene (XVIb) is consistent with the proposed structure. In

TABLE VI

## N.m.r. Spectral Data

<u>Chem.<sup>a</sup> Shift p.p.m.</u>	<u>Area (Calcd.)</u>	<u>Multiplicity</u>	<u>Coupling<sup>b</sup> Constant</u>	<u>Assign.<sup>c</sup></u>
IVc; 156 <sup>d</sup>				
6.13	1	unsym. quartet	$J_{bc} = 5.5$	b or c
5.87	1	" "	$J_{ab} = J_{cd} = 3.0$	"
2.92	1	broad singlet		a
2.72	1	" "		d
0.19-1.82	5	complex		
0.00	9	singlet		SiCH <sub>3</sub>
Vc; 154 <sup>d</sup>				
5.95	2	triplet	$J_{ab} = J_{cd} = 3.0$	b and c
2.92	2	broad singlet		a and d
0.78-2.10	5	complex		
-0.10	9	singlet		SiCH <sub>3</sub>
VIc; 173 <sup>d</sup>				
1.94	1	broad singlet		d
1.10-1.22	4	complex		
1.02	3	singlet		a, b, g
0.62	1	broad singlet		c
-0.02	9	singlet		SiCH <sub>3</sub>

<sup>a</sup> Probable errors are  $\pm 0.05$  p.p.m.

<sup>b</sup> Given in c.p.s. Probable error is  $\pm 0.2$  c.p.s. Samples were run as CCl<sub>4</sub> solutions.

<sup>c</sup> See text for numbering system.

<sup>d</sup> Spectrum number taken from log book for the Varian A-60 Spectrometer; University of New Hampshire

TABLE VI (Cont.)

<u>Chem.<sup>a</sup> Shift p.p.m.</u>	<u>Area (Calcd.)</u>	<u>Multiplicity</u>	<u>Coupling<sub>b</sub> Constant</u>	<u>Assign.<sup>c</sup></u>
VIb; 133 <sup>d</sup>				
2.21	1	broad singlet		d
1.10-1.13	5	complex		
1.26-1.56				
1.21	3	singlet		a,b,g
0.72	3	singlet		SiCH <sub>3</sub>
VIa; 304 <sup>d</sup>				
2.35	1	broad singlet	J <sub>hi</sub> = 11.5	d
1.63	1	unsym. doublet		h
1.16-1.48	7	complex		
XXI; 87 <sup>di</sup>				
1.91	1	broad singlet		e
1.17	4	" "		c,d,h,i
1.03	2	doublet	J <sub>ef</sub> =J <sub>eg</sub> =11.6	f,g
0.92	2	singlet		a,b
-0.07	9	singlet		SiCH <sub>3</sub>

<sup>a</sup> Probable errors are  $\pm 0.05$  p.p.m.

<sup>b</sup> Given in c.p.s. Probable error is  $\pm 0.2$  c.p.s. Samples were run as CCl<sub>4</sub> solutions.

<sup>c</sup> See text for numbering system.

<sup>d</sup> Spectrum number taken from log book for the Varian A-60 Spectrometer; University of New Hampshire

TABLE VI (Cont.)

<u>Chem. Shift</u> <sup>a</sup> <u>p.p.m.</u>	<u>Area</u> <u>(Calcd.)</u>	<u>Multiplicity</u>	<u>Coupling</u> <u>Constant</u> <sup>b</sup>	<u>Assign.</u> <sup>c</sup>
XVII; 169 <sup>d</sup>				
2.20	2	broad multiplet		a, e
1.13-1.61	8	complex		
0.55	1	unsym. triplet		b
-0.04	9	singlet		SiCH <sub>3</sub>
XVIII; 166 <sup>d</sup>				
2.31	2	broad singlet		a, e
0.78-1.78	9	complex		
0.00	9	singlet		SiCH <sub>3</sub>
XX; 136 <sup>d</sup>				
6.29	1	doublet	J <sub>bc</sub> = 3.0	b
2.85-2.93	2	broad singlet with shoulder		a, c
0.83-1.68	6	couplex		
0.06	9	singlet		SiCH <sub>3</sub>

<sup>a</sup> Probable errors are  $\pm 0.05$  p.p.m.

<sup>b</sup> Given in c.p.s. Probable error is  $\pm 0.2$  c.p.s. Samples were run as CCl<sub>4</sub> solutions.

<sup>c</sup> See text for numbering system.

<sup>d</sup> Spectrum number taken from log book for the Varian A-60 Spectrometer; University of New Hampshire

TABLE VI (Concl.)

<u>Chem.<sup>a</sup> Shift p.p.m.</u>	<u>Area (Calcd.)</u>	<u>Multiplicity</u>	<u>Coupling<sub>b</sub> Constant</u>	<u>Assign.<sup>c</sup></u>
XVIb; 202 <sup>d</sup>				
5.88	2	triplet		b, c
2.92	2	singlet		a, d
0.93-1.69	4	complex		
0.69	1	singlet		i
-0.10	9	singlet		SiCH <sub>3</sub>

<sup>a</sup> Probable errors are  $\pm 0.05$  p.p.m.

<sup>b</sup> Given in c.p.s. Probable error is  $\pm 0.2$  c.p.s. Samples were run as CCl<sub>4</sub> solutions.

<sup>c</sup> See text for numbering system.

<sup>d</sup> Spectrum number taken from log book for the Varian A-60 Spectrometer; University of New Hampshire

many ways the spectrum is similar to that of norbornene itself.

The vinyl hydrogens appear as a slightly unsymmetrical triplet found at 5.88 p.p.m. The bridgehead hydrogens at C1 and C4 appear as a multiplet superficially resembling a singlet. The proton at C7 appears at quite high field, 0.69 p.p.m. This is probably a result of the electropositive character of the trimethylsilyl group. The sharp singlet due to the trimethylsilyl group is located at -0.10 p.p.m.

The general n.m.r. spectral information for the pure compounds prepared in this study is summarized in Table VI.

#### 4. Discussion of Preparative Methods

a. Reactivity of bicycloheptadiene. The number and diversity of reagents which have been added to bicycloheptadiene (XV) challenge the imagination. Powerful dienophiles such as maleic anhydride<sup>(67)</sup>, bis-(trifluoromethyl)-acetylene<sup>(68)</sup>, dicyanoacetylene<sup>(69)</sup>, tetracyanoethylene<sup>(70)</sup> and acrylonitrile<sup>(71,72)</sup> react with XV via 2,6 addition to produce 6,7 substituted products of tetracyclo(3.2.1.1<sup>3,8</sup>.0<sup>2,4</sup>)-nonane. Dimethyl diazodicarboxylate<sup>(73)</sup> also reacts by 2,6 addition; however, contrary to the other dienophiles, an olefinic substance of unknown structure is also produced. Under ionic conditions water, methanol, performic acid, hydrogen bromide<sup>(74)</sup>, bromine<sup>(75)</sup>, iodine<sup>(76)</sup> and t-butylhydroperoxide<sup>(77)</sup> yield, predominantly or exclusively, nortricyclene derivatives. Recently, boron trichloride, phenylboron di-



chloride<sup>(78)</sup>, stannic chloride and stannic bromide<sup>(79)</sup>, methylphosphonous dichloride<sup>(80)</sup>, and 1-iodoperfluoropropane<sup>(81)</sup> have been reported to react with bicycloheptadiene XV by 2,6 addition to yield nortricyclic products. Benzynes<sup>(38)</sup>, tetrafluoroethylene<sup>(82)</sup>, diborane<sup>(83)</sup>, nickel carbonyl<sup>(84)</sup>, methylene iodide-zinc-copper couple<sup>(85)</sup> and triphenylchromium<sup>(86)</sup> undergo reaction with XV to give the product resulting, primarily, from exo addition to one double bond. The free radical additions of thiophenol<sup>(87)</sup> and p-thiocresol<sup>(26)</sup> produce mixtures of 3-nortricyclic aryl thioether and exo-5-norbornenyl aryl thioether. Diethyldithiophosphoric acid<sup>(27)</sup> is the only other reagent described in the literature which yields norbornenyl products upon free radical-promoted additions to XV. Nitrosyl chloride<sup>(88)</sup> undergoes exo-cis addition to bicycloheptadiene.

b. Hydrosilation of bicycloheptadiene. The chloroplatinic acid-catalyzed hydrosilation of bicycloheptadiene is the first reported case of endo addition which produces a norbornenyl product. This is a surprising result in view of the fact that the exo side of XV is the least hindered<sup>(88)</sup>. This is amply illustrated by the literature survey summarized above. In all cases in which the stereochemistry of the norbornenyl products have been determined, the course of reaction has involved exo addition of the initial fragment. This is true whether the reaction took place via a free radical or via ionic mechanism. The novel stereochemical course

of the hydrosilation illustrates an interesting property of the bicycloheptadiene molecule. It is ideally suited for a test of the relative importance of steric and coordinative effects. Previous studies<sup>(89)</sup> have shown that the endo side of XV displays powerful coordination ability. Apparently, the hydrosilation using chloroplatinic acid catalysis yields the product of "coordination control". The data presented in Table I demonstrates that platinum catalysis with a variety of silanes gives predominantly the product of "coordination control" although the reactions are substantially less selective at higher temperatures. Interestingly, the mode of hydrosilation of XV can be changed from "coordination control" to "steric control" by using a different kind of catalysis. Thus, the use of chloroplatinic acid with methyl-dichlorosilane yields a norbornenyl fraction which consists of 90% endo isomer V; whereas free radical catalysis produces a norbornenyl fraction consisting of 80% exo isomer IV.

c. Mechanism of hydrosilation. The results presented in Table I have an important bearing on the mechanism of silicon hydride additions. The hydrosilation of carbon-carbon multiple bonds has been extensively studied. Recently, Pike<sup>(90)</sup> has reviewed and expanded the use of base catalyses. The stereochemical consequences of platinum on charcoal, chloroplatinic acid and peroxide catalyzed hydrosilations have been determined for carbon-carbon double and triple bonds<sup>(91,33)</sup>.

The mechanism of the chloroplatinic acid catalysis has been the subject of much speculation<sup>(33,92,93)</sup>. However, the nature of the active species is still unknown. This catalysis has the interesting property of giving terminal silanes upon reaction of methyldichlorosilane with pentene-1, pentene-2,<sup>(94)</sup> 2-methylbutene-1, 3-methylbutene-1 and 2-methylbutene-2<sup>(93)</sup>. Saam and Speier<sup>(93)</sup> suggest that the interaction of the olefin, silane and platinum catalyst brings about the attack of a hydride upon the olefin. The resulting carbanion isomerizes to form the most stable carbanion which can then interact with additional silane or can donate a hydride to another olefin yielding a new olefin and carbanion. These workers suggest that all this may be taking place through a platinum-silane-olefin complex. Benkeser et al<sup>(33)</sup> have suggested that the active species in chloroplatinic acid catalysis is metallic platinum which could be formed by reduction of the platinum salts by silicon hydride. These workers noted that small droplets of silicone which formed in the reaction mixture appeared to be coated with black after the reaction had undergone an induction period. This observation, coupled with the fact that chloroplatinic acid, as well as platinum on charcoal, gave stereo-specific cis addition of silicon hydride to acetylenes, supports their postulate. However, in the addition of methyldichlorosilane to bicycloheptadiene XV at 50-60°, platinum on charcoal and chloroplatinic acid give profoundly different results. Thus, the former produces a product mixture which con-

sists of 94% VIb; whereas the same reaction utilizing the latter catalyst yields a mixture which contains only 30% VIb. In view of this evidence, it can be said that there are some fundamental differences between the two catalytic systems.

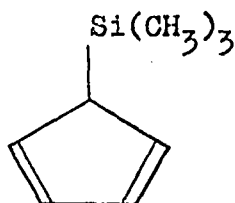
d. The Diels-Alder reaction. The predominant formation of the endo product, V, by the low temperature Diels-Alder reaction of the vinyl silanes with cyclopentadiene is consistent with the rule of Alder and Stein<sup>(95)</sup>. It was necessary, however, to establish the stereochemistry of the products, as exceptions to this rule have been noted before<sup>(96)</sup>. At higher temperatures, the relative percentage of exo product, IV, increases. This type of behavior has been noted before<sup>(97)</sup>.

At temperatures above 230°, the Diels-Alder reactions produced an unexpected result. For example, at temperatures close to 300°, much polymer was produced along with a trace amount of 1-trimethylsilyl nortricyclene (XXI) by the reaction of vinyltrimethylsilane with cyclopentadiene. The same isomer was found in significant amounts along with the normal adducts upon methylation of the reaction mixtures which resulted from the reactions of trichlorovinylsilane and methylvinylchlorosilane with cyclopentadiene at temperatures in excess of 230°. The identity of this product was established by infrared and n.m.r. comparison with a sample isolated from certain electrophilic cleavage studies. This material had a band of medium intensity at 790 cm.<sup>-1</sup> which is within

experimental error of the invariant peak characteristic of 1-substituted nortricyclene derivatives<sup>(37)</sup>. The band of medium intensity at  $3060\text{ cm}^{-1}$  and the absence of significant peaks in the double bond stretching region establish the substance as a nortricyclenic compound. The material is contaminated with a small amount of 2-trimethylsilyl norbornene (XX) as indicated by a weak absorbance at  $1555\text{ cm}^{-1}$ .

e. Attempted preparation of 7-trimethylsilyl norbornene.

Attempts to prepare the 7-trimethylsilyl bicyclo(2.2.1)hept-2-ene isomers (syn and anti) by an unequivocal route proved to be unsuccessful. One of the routes that was explored extensively utilized the Diels-Alder reaction between 5-trimethylsilyl cyclopentadiene (XXII) and vinyl chloride. Sub-



XXII

sequent reduction of this adduct with lithium metal in a mixture of t-butyl alcohol and tetrahydrofuran would lead, it was hoped, to a mixture of XVIB and its isomer. Also, from exploratory experiments carried out on the same reduction of 5-chloro bicyclo(2.2.1)hept-2-ene, the production of a substantial amount of the nortricyclene VIc was expected. The preparation of XXII was carried out as described before<sup>(98)</sup>.

Gas liquid chromatography (g.l.c.) examination of this material indicated that it was homogeneous. This conclusion was confirmed by the n.m.r. spectrum which had a narrow singlet due to trimethylsilyl protons. The exact nature of this compound could not be established from the spectrum.

The proposed Diels-Alder reaction and reduction were carried out in an overall yield of about 40%. G.l.c., using 20% Apiezon L on chromosorb P, gave three major peaks. The substance with the longest retention time, which constituted approximately 13% of the reaction mixture, was identified as 3-trimethylsilyl nortricyclene VIc. The vinyl region, which is shown in Figure 4, of the n.m.r. spectrum of the mixture proved to be quite complex. However, the doublet due to the vinyl proton of 2-trimethylsilyl bicyclo(2.2.1)hept-2-ene (XX) was clearly discernible at lowest field. This compound, which could only arise from the Diels-Alder reaction of 2-trimethylsilyl cyclopentadiene accounts for 48% of the olefinic product present in the mixture. Also discernible in the vinyl region is an AB-type spectrum with one of the protons undergoing an additional coupling of 2.9 c.p.s. The AB analysis gives  $J_{AB} = 5.5$  c.p.s. This spectrum is consistent with a coupling between vinyl protons of a norbornene derivative. The fact that only one vinyl proton is split by a bridgehead hydrogen would suggest that the other bridgehead proton has been replaced by a substituent (presumably the trimethylsilyl group). Thus, this portion of the vinyl proton resonance spectrum is consistent with 1-trimethylsilyl



The Vinyl Region in the N.M.R. Spectrum of the Product Mixture  
Resulting from Diels-Alder Reaction of Trimethylsilylcyclopentadiene.

Figure 4

bicyclo(2.2.1)hept-2-ene which constitutes 33% of the olefinic compounds in the mixture. This product would result from the reduced Diels-Alder adduct between 1-trimethylsilyl cyclopentadiene and vinyl chloride. Finally, the remainder of the vinyl region suggested a triplet with a line separation of 2.0 c.p.s. which would be expected for the vinyl proton signal from either XVIb or the syn isomer. Hydrogenation studies of the reaction mixture using Adams catalyst at room temperature indicated nortricyclenyl products other than VIc were present in the mixture. However, it was more difficult to obtain information regarding their structures.

While this work was in progress, a publication<sup>(99)</sup> appeared describing the propensity of substituted cyclopentadienes toward rearrangement. For example, methylation of cyclopentadienylmagnesium bromide under the usual conditions produces a mixture of 1- and 2-substituted cyclopentadienes instead of the expected 5-methylcyclopentadiene. It is only when the alkylation of cyclopentadienylmagnesium bromide with dimethylsulfate is carried out in di-n-butyl ether at  $-10^{\circ}$  to  $-15^{\circ}$  that the expected product is found. If this material is warmed to  $25 - 30^{\circ}$  for 3 hours, it undergoes a rapid change to 1-methylcyclopentadiene. Mironov et al<sup>(99)</sup> have studied numerous examples of these rearrangements and have concluded the following: (1) the isomer or isomers having an unsubstituted methylene appear to be the most stable; (2) isomers substituted in positions 1- and 2- are generally present in approximately equal concentrations; (3) in the ab-



sence of thermodynamic preference, the mixture will contain equal concentrations of all of the isomers. For example, 5-deuteriocyclopentadiene, when heated at 60° for 1 hour, leads to the production of all three possible isomers in equal amounts. During this process no polydeuterated material was formed. This is good evidence for the intramolecular character of the rearrangement.

In view of this evidence, it is not surprising that Diels-Alder reaction of the trimethylsilyl cyclopentadiene with vinyl chloride at 180° leads to the formation of products derived from all three isomers.

The Grignard reaction of 7-syn-bromobicyclo(2.2.1)hept-2-ene with trimethylchlorosilane resulted in the formation of tar. This further illustrates that the reaction of hindered Grignard reagents with chlorosilanes proceeds poorly if at all. For example, Selin and West<sup>(91)</sup> have observed anomalous reactions when 1-methylcyclohexyl and 2-methylcyclohexyl Grignard reagents were allowed to react with silicon tetrachloride.

## 5. Reactions with Electrophilic Reagents

### a. Properties of silicon-substituted norbornenes.

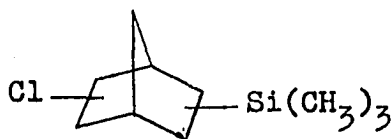
An indication of the electronic effect of the trimethylsilyl group on the rate of addition of electrophilic reactants to the double bonds of IVc and Vc was gained from relative rate studies. A 4:1 mixture of IVc and Vc was allowed to react

with hydrogen chloride in glacial acetic for a short time. The isolated starting material proved to consist of 80% of Vc and 20% of IVc. In other studies, the addition of hydrogen chloride to the exo isomer, IVc, was complete in less than 50 minutes, while a substantial amount of the endo isomer, Vc, remained after 2.5 hours. One of the most significant aspects of this work is the fact that the exo isomer reacts much faster than the endo even though no electrophilic cleavage of the carbon-metal bond takes place.

Numerous studies were carried out in the quest for a convenient electrophilic medium in which to study the cleavage of the carbon-silicon bond in compounds of the types IV and V. The major result of this work was to reveal difficulties in the study of this type of reaction. Most of these attempts were frustrated by the difficulty with which the carbon-silicon bond is cleaved; the only result being the addition of the reagent to the double bond. Thus, the reaction of Va with bromine in carbon tetrachloride results, primarily, in addition of bromine to the double bond. The same reaction with Vc produces a very small yield of a material having the same retention time as 3-bromo nortricyclene. The use of bromine in acetic acid or in dioxane under a wide variety of conditions leads to complex mixtures of products, including high boiling substances in which the carbon-silicon bond had remained intact.

Electrophilic attack by acid proved to be more fruitful. Heating Vc with 2 M aqueous methanolic solution of per-

chloric acid produced a high yield of 2-methoxynorbornane. The identity of this product was established by infrared comparison with a sample of the authentic material. This product presumably arises from the acid-promoted addition of methanol to the norbornene or nortricyclene formed by cleavage of the carbon-silicon bond. This reaction showed little promise for more detailed study as the reaction mixture is heterogeneous until the reaction is nearly complete; therefore, kinetic data could not be obtained easily. The course of the reaction of Vc with hydrogen chloride in glacial acetic acid could be followed by g.l.c. However, the initial product resulted from the addition of the elements of hydrogen chloride to the double bond. The adduct was isolated and characterized by infrared spectrum. Upon reaction with potassium t-butoxide, a complex mixture of trimethylsilyl substituted norbornenes and nortricyclenes was isolated. The adduct seems to be of type XXIII. Soon after the adduct



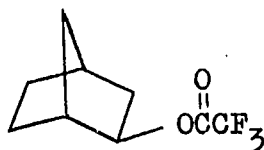
XXIII

was formed, it apparently underwent solvolysis to form nortricyclene as well as 1-trimethylsilyl nortricyclene (XXI). This product appears to readily isomerize to 2-trimethylsilyl norbornene (XX).

In view of the difficulty with which the carbon-trichlorosilyl bond is cleaved, it was interesting to find that Va reacted with aqueous, ethanolic hydrogen fluoride to produce a 21% yield of 2-ethoxynorbornane. The product could arise from the cleavage of the carbon-silicon bond followed by the acid-promoted addition of ethanol to the norbornene and/or nortricyclene. The electrophilic medium described here is exactly that used to prepare alkylfluorosilanes from alkylchlorosilanes<sup>(100)</sup>. If the fluoro compound Va is formed in the reaction with hydrogen fluoride, the resulting cleavage is surprising in view of the difficulty with which the trifluorosilyl group is removed under electrophilic conditions<sup>(18)</sup>. Conceivably, the cleavage is encouraged by nucleophilic complexing of fluoride ions with the vacant d-orbitals of the silicon atom.

Trifluoroacetic acid has proven to be an interesting medium in which to study carbonium ion reactions. It appears that the low nucleophilicity of this acid permits an intermediate cation to undergo further reactions<sup>(101)</sup>. For example, the solvolysis of cyclooctene oxide in trifluoroacetic acid gives, exclusively, products resulting from a transannular hydride shift; while the same reaction in acetic acid with sodium acetate gave 76% normal and 24% rearranged products. The strongly acidic nature of trifluoroacetic acid is shown by the fact that it has an  $H_0$  of  $-4.4 \pm 0.3$ <sup>(102)</sup>. The endo isomer underwent a vigorous reaction with this acid.

to yield eventually a trifluoroacetate, XXIV. The proposed

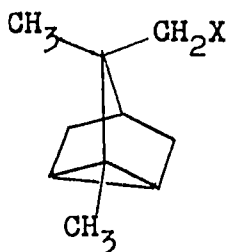


XXIV

structure is consistent with the infrared spectrum as well as the combustion analysis. Also, norbornene forms the same trifluoroacetate under the same reaction conditions. Closer examination of this reaction reveals that it is quite complex in nature. Initially, the bicyclic olefin undergoes rearrangement to a mixture of 2-trimethylsilyl norbornene (XX) and 1-trimethylsilyl nortricyclene (XXI) as indicated by infrared spectrum and g.l.c. retention times. It was not possible to isolate the hydrocarbon intermediates, norbornene and nortricyclene, as they add the elements of trifluoroacetic acid faster than the organosilane reacts with this reagent.

b. Properties of silicon-substituted nortricyclene.

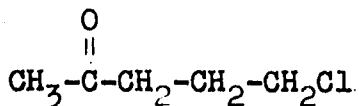
Recently, the electrophilic cleavage of cyclopropyl derivatives has received a great deal of attention. Corey *et al*<sup>(103)</sup> studied the electrophilic cleavage of pi-substituted tricyclene XXV. It was hoped that the substituent X (Br, I, CN)



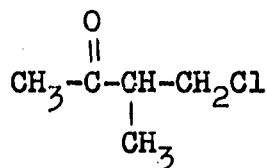
XXV

would exert control over the direction of cleavage. However, the results indicated that the substituent X had no influence over the direction of cleavage when formic or trifluoroacetic acid was used.

Hart<sup>(104)</sup> has published a series of papers concerned with the chemistry of cyclopropyl derivatives. The acylation of cyclopropane by a 1:1 acetyl chloride-aluminum chloride complex produces the anticipated gamma-chloroketone (XXVI) along with a beta-chloroketone (XXVII).

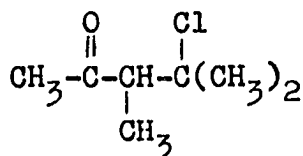


XXVI

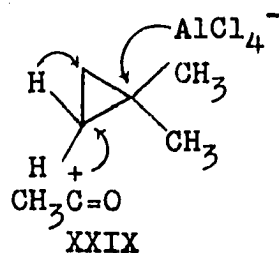


XXVII

The same reaction with 1,1-dimethylcyclopropane yielded a single chloroketone, which proved to be 4-chloro-3,4-dimethyl-2-pentanone (XXVIII); the product resulting from rearrangement. Presumably, this product results from a hydrogen shift of the type depicted in XXIX. The acetylation of nortricy-



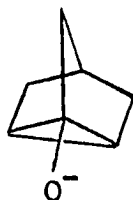
XXVIII



XXIX

clene seemed to be a logical extension of this work. Also, such a study promised to give information regarding the stereochemistry of the cleavage of the three-membered ring, a question which had not been previously investigated. The chloroketone isolated proved to be the product of 2,6-addition<sup>(37)</sup>. Due to the unstable character of this ketone, little could be learned about the stereochemistry of addition.

The emerging outlines of a better understanding of the stereochemistry of the cleavage of the cyclopropyl ring are gradually becoming apparent.. The homoketonization, which is a type of electrophilic cleavage, of the ion XXX can be



XXX

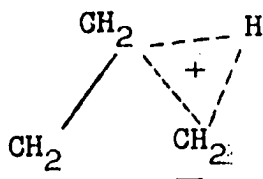
made to proceed with retention or inversion of configuration<sup>(105)</sup>. Ketonization in deuterated alkaline media pro-

duces 6-exo-deuterionorbornan-2-one, the product of electrophilic cleavage with inversion. The same process carried out in deuterated acidic media yields the product of electrophilic cleavage with retention. It might be suggested at this point that the cleavage in acidic media represents a true case of electrophilic cleavage because attack by the proton on the anion XXX probably occurs. While the homoketonization in alkaline media formally involves electrophilic attack, perhaps it more precisely involves homoketonization followed by proton abstraction by the carbanion. In this case, exo attack would be clearly favored by steric requirements.

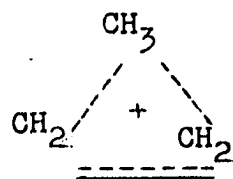
Cleavage of nortricyclene by deuterio-acetic acid media resulted in the incorporation of one atom of deuterium in the exo-norbornyl acetate produced<sup>(106)</sup>. The location and stereochemistry of this deuterium is consistent with the formation of a non-classical carbonium ion upon attack by the deuterium. This same mechanism accounts for the stereochemistry of the products formed in other studies<sup>(107,108,109)</sup> involving electrophilic cleavage of cyclopropyl groups incorporated in bicyclic compounds. Hanack and Eggenesperger<sup>(107)</sup> also studied the effect of the electronegativity of substituents on the three-membered ring on the rates of cleavage. The results indicate that electron withdrawal decreases the rate of reaction; similar observations were reported by Hart and Levitt<sup>(104)</sup>.



Recently, work which investigates the more subtle aspects of electrophilic cleavage of cyclopropyl compounds has been published. Baird and Aboderin<sup>(110)</sup> studied the solvolysis of cyclopropane in deuteriosulfuric acid. The results are consistent with an equilibration between ions XXXI and XXXII, either one of which can be formed, initially, by at-

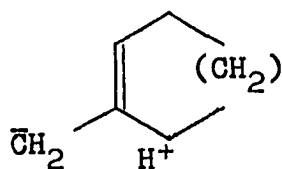


XXXI

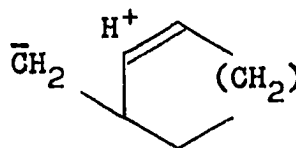


XXXII

tack by a proton. It was assumed that ions such as XXXI reacted with the lyate anion. LaLonde and Forney<sup>(111)</sup> found that the acid-promoted opening of the three-membered ring in bicyclo(4.1.0)heptane and bicyclo(3.1.0)hexane is controlled by the polarization of the ring by a perturbing electrophile. Apparently, this polarized state is best represented by structures XXXIII and XXXIV. The ring opening of bicyclo-



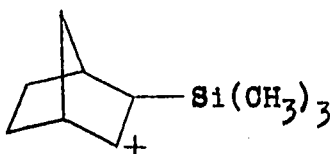
XXXIII



XXXIV

(2.1.0)pentane is best understood in terms of relief of strain. The attack by the solvent on a protonated (or protonating) cyclopropyl ring proceeds with inversion of configuration; a mode of cleavage somewhat analogous to the same reaction involving epoxides. This is proven by the observation that the reaction of bicyclo(4.1.0)heptane in acetic acid produces a large percent of the acetate of trans-2-methyl cyclohexanol. These conclusions were confirmed by further work<sup>(112)</sup>.

A study of electrophilic cleavage of the 3-trimethylsilyl nortricyclene (VIc) proved interesting. The protonation of the three-membered ring could give rise to a number of different carbonium ions due to the unsymmetrical nature of VIc. Should protonation of the three-membered ring lead to the carbonium ion XXXV, then loss of a siliconium ion in



XXXV

an E1 type of reaction can easily occur. This, indeed, turned out to be the case as VIc reacted with trifluoroacetic acid as well as 2 M sulfuric acid in acetic acid to produce a high yield of norbornene.

Preliminary results indicate that in trifluoroacetic acid VIc reacts substantially faster than nortricyclene. Perhaps this is a consequence of the electropositive character of the trimethylsilyl group which makes the three-membered ring more electron rich and, therefore, more susceptible to electrophilic attack. Another factor which might play a significant role would be the relative ease with which the protonated species can undergo further reactions. Thus, the carbonium ion XXXV can relieve the charge concentration by loss of a siliconium ion in an E1 type of reaction; whereas, the carbonium ion generated by protonation of the three-membered ring in nortricyclene must await nucleophilic attack by trifluoroacetic acid, which is an extremely poor nucleophile.

## C EXPERIMENTAL

### 1. Preparative Methods

a. General considerations. Reagents were used without purification unless otherwise specified. The silanes were purchased from the Union Carbide Company; the norbornene was obtained from the Aldrich Company. The author is grateful to the Shell Chemical Company for providing a generous quantity of bicycloheptadiene.

The infrared spectra were all taken using a Perkin Elmer Model 21 spectrometer. The n.m.r. data were recorded using a Varian A-60 instrument. The gas liquid chromatographic (g.l.c.) analyses were carried out using a F & M Model 300 Programmed Temperature Gas Chromograph with helium as the carrier gas at a flow rate of 30 ml. per min.

All yields are based on reacted starting material.

Analyses were made by Galbraith Laboratories, Knoxville, Tennessee.

b. Analysis of product mixtures. The reaction mixtures resulting from the use of halosilanes were methylated and the product analysis was carried out on the alkylated silanes. The exo and endo bicyclo(2.2.1)hept-2-en-5-yl trimethylsilanes always appeared as one peak on gas chromatograms; separation of the isomers remains to be achieved.

However, the tricyclo(2.2.1.0<sup>2,6</sup>)hept-3-yl trimethylsilane VIc is easily separated from the norbornenes IVc and Vc using a 4 ft. column of 20% Apiezon L on Chromosorb 60 to 80 mesh with the temperature programmed at 13° per minute from an injection temperature of 100°. Mixtures consisting of IVc and Vc only were assayed by measuring the areas under the respective peaks in the n.m.r. spectra due to the protons of the methylsilyl functional group. In mixtures containing all three compounds IVc - VIc the exo to endo ratios were determined by inspection of the vinyl region. The downfield half of the symmetrical exo multiplet is free of interference by the endo triplet; thus measurement of the areas of the vinyl region as diagrammed in Figure 5 could be used to determine the relative amounts of each. The percentage of exo trimethylsilyl norbornene IVc is given by the equation  $100 \cdot 2X / (X+Y)$ .

Positive identification of the products of the Diels-Alder reaction was made by hydrogenating the mixture of IVc and Vc under conditions identical to those used to hydrogenate bicyclo(2.2.1)hept-2-en-2-yl trimethylsilane. The resulting two saturated isomers were then isolated in quantities sufficient for positive infrared spectral identification by using a copper column ¼ in. by 17 ft. packed with 20% Silicone Oil 200 on Chromosorb P. The infrared spectra of the saturated Diels-Alder products were identical to authentic samples of XVII and XVIII.

The methylated products from the chloroplatinic acid

## Illustrative Analysis of a Mixture of IVc and Vc.

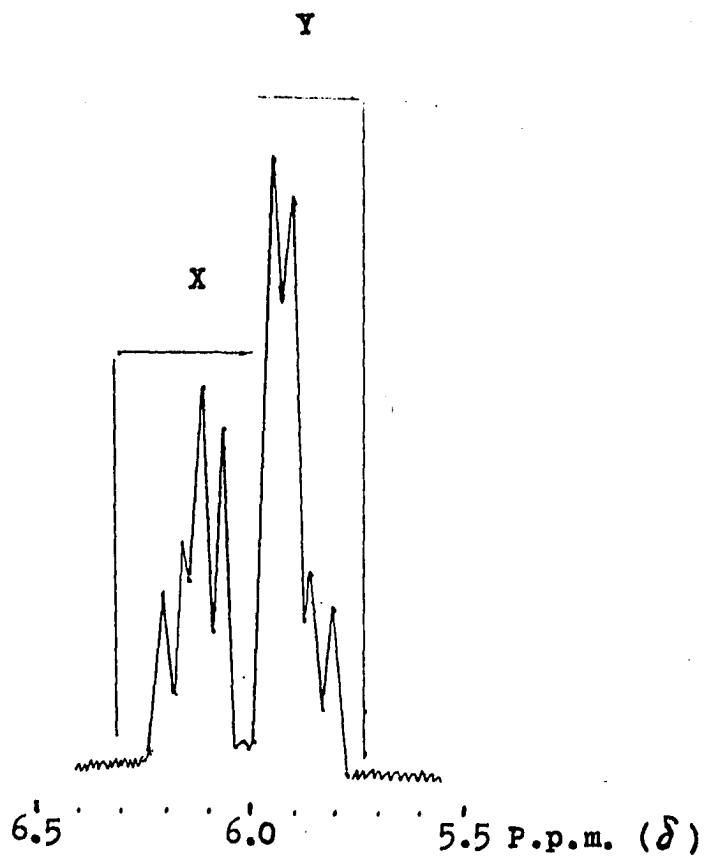


Figure 5

catalyzed addition of methylchlorosilane to bicycloheptadiene were separated by careful fractional distillation. Identification of the components was made by infrared spectra and hydrogenation of the unsaturated components. The methylated products from the free radical reaction were identified by a combination of fractional distillation, g.l.c., n.m.r., and infrared spectra.

c. Preparation of platinum on charcoal catalyst.

The procedure used is identical to that described by Baltzly<sup>(113)</sup>. Because of the capricious nature of catalysis, the materials used are listed here: (1) chloroplatinic acid prepared by dissolving 3 g. of platinum chloride in 100 ml. of water with 0.02 g. of lead acetate; (2) Norit A produced by Matheson, Coleman and Bell; and (3) palladium chloride.

d. Methylation procedure for chlorosilanes. The

chlorosilane was added slowly to a 10% excess of 0.5 M methylmagnesium bromide in diethyl ether. After the addition was complete the reaction mixture was stirred under reflux for six hours, poured into a mixture of saturated aqueous ammonium chloride, ice and 100 ml. of ether. The ether layer was separated, washed successively with water and saturated aqueous sodium chloride and dried over magnesium sulfate. The ether was removed at atmospheric pressure and the product distilled at reduced pressure.

e. Bicyclo(2.2.1)hept-2-en-2-yl-trimethylsilane (XX).

The bicyclo(2.2.1)hept-2-en-2-yl bromide was prepared as described by LeBel<sup>(96)</sup>.

A suspension of 1.5 g. of lithium sand containing 2% sodium in 25 ml. of anhydrous tetrahydrofuran was placed in a 50 ml. round-bottom flask, equipped with a condenser, drying tube, stirrer and pressure equalizing dropping funnel. The system was frequently flushed with nitrogen during the course of the reaction. The reaction flask was chilled to 0° and 8.64 g. (0.053 mole) of bicyclo(2.2.1)hept-2-en-2-yl bromide was added dropwise with rapid stirring. Fifteen minutes after the addition was complete 5.94 g. (0.055 mole) of freshly distilled trimethylchlorosilane was added dropwise. This reaction mixture was stirred for two hours at 0°. It was then poured onto a mixture of saturated aqueous ammonium chloride, ice and 200 ml. of diethyl ether. The ether layer was separated and extracted successively with 50-ml. portions of water, and saturated aqueous sodium chloride and dried over magnesium sulfate. The ether was removed by distillation at atmospheric pressure. Vacuum distillation of the residue yielded 3.0 g. (36%) of XX having b.p. 30° (0.55 mm.),  $n_D^{24}$  1.4630. A gas chromatogram obtained with a 4 ft. column of 20% Apiezon L on Chromosorb 60-80 mesh, indicated greater than 99% purity. Infrared spectrum: max. (film) 3105 (wk), 2920, 2850, 1555, 1298, 1248, 1120, 1038, 855, 810, 792, 750  $\text{cm.}^{-1}$ .

Anal. Calcd. for  $\text{C}_{10}\text{H}_{18}\text{Si}$ : C, 72.22; H, 10.91; Si,



16.87. Found: C, 72.15; H, 11.04; Si, 16.61.

f. Bicyclo(2.2.1)hept-2-yl endo trimethylsilane (XVIII). A sample of 1.75 g. (0.01 mole) of the bicyclo(2.2.1)hept-2-en-2-yl trimethylsilane was added to 10 ml. of ethyl acetate containing a 50 mg. of Adams catalyst and pre-reduced Adams catalyst. The mixture was hydrogenated at 25 p.s.i. in a Parr hydrogenator for 12 hours. The ethyl acetate was removed and the product distilled, yielding in excess of one gram of the anticipated product, b.p.  $31^{\circ}$  (0.75 mm.),  $n^{24}$  1.4637, infrared spectrum:  $\nu_{\text{max}}$  (film) 2965, 2875, 1248, 910, 868, 832, 749, 743  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{10}\text{H}_{20}\text{Si}$ : C, 71.34; H, 11.97; Si, 16.68. Found: c, 71.11; H, 12.07; Si, 16.58.

g. Bicyclo(2.2.1)hept-2-yl exo trimethylsilane (XVII). A mixture of 20 g. (0.21 mole) of norbornylene, 26.4 g. (0.23 mole) of methylchlorosilane and 0.25 g. of the platinum on charcoal was heated at reflux for two hours until the temperature increased to  $100^{\circ}$ . Distillation of the reaction mixture yielded 24.4 g. (55%) of adduct, b.p.  $85.2 - 87.5^{\circ}$  (0.20 mm.).

Methylation in the usual way yielded 11.5 g. (32%) of XVII, b.p.  $34^{\circ}$  (1.25 mm.),  $n^{24}$  1.4624. G.l.c. analysis of this product using a 17 ft. x  $\frac{1}{8}$  in. column of 20% Paraffin Oil on Chromosorb P indicated that it consisted of 97% exo isomer XVII plus 3% endo isomer XVIII. A pure sample col-

lected by g.l.c. provided the following spectral data;

$\nu_{\text{max}}$ . (film) 2970, 2865, 1248, 906, 873, 851, 828, 745, and 682  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{10}\text{H}_{20}\text{Si}$ : C, 71.34; H, 11.97; Si, 16.68. Found: C, 71.31; H, 12.04; Si, 16.89.

h. Bicyclo(2.2.1)hept-2-en-5-yl endo trimethylsilane (Vc). A 90% pure sample of Vc with 9% of IVc and a trace of VIc was obtained by fractional distillation of the methylated product from the chloroplatinic acid catalyzed reaction of methyldichlorosilane and bicycloheptadiene. The fraction having a b.p.  $70^{\circ}$  (15 mm.) provided the following spectral data;  $\nu_{\text{max}}$ . (film) 3140 (v wk), 3060, 2958, 2865, 1623 (wk), 1572 (wk), 1448, 1334, 1248, 1124, 1033, 962, 952, 911, 888, 828, 803, 774, 755, 743, 710, and 685  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{10}\text{H}_{18}\text{Si}$ : C, 72.22; H, 10.91; Si, 16.87. Found: C, 72.15; H, 11.10; Si, 16.64.

i. Bicyclo(2.2.1)hept-2-en-5-yl exo trimethylsilane (IVc). The Diels-Alder reaction between vinyl chloride and cyclopentadiene was carried out as described previously<sup>(36)</sup>. To 23.5 g. (0.19 mole) of the bicyclo(2.2.1)hept-5-en-2-yl chloride, thus prepared, was added 0.4 ml. of 0.1 M ethanolic chloroplatinic acid. This mixture was placed in a 250 ml. flat-bottom flask equipped with a magnetic stirrer, condenser with a drying tube and a pressure equalizing dropping funnel; and 21.2 g. (0.18 mole) of methyldichlorosilane was added

dropwise over a 30-minute period as the mixture was refluxed in a nitrogen atmosphere. At this time the solution suddenly turned black and the reaction proceeded vigorously. It was then stirred and heated at 60-70° for fifteen minutes. Distillation yielded 2.8 g. of starting material and 36 g. (92%) of 1:1 adduct, b.p. 104-110° (1.3 mm.).

The usual workup yielded two fractions: (1) b.p. 63-64° and (2) b.p. 76-79° (1.5 mm.). The first fraction is as yet unidentified. The second fraction, 7.0 g. (23%) was used in the next step to prepare the exo isomer IVc.

Anal. Calcd. for C<sub>10</sub>H<sub>19</sub>ClSi: C, 59.22; H, 9.44.  
Found: C, 59.51; H, 9.63.

The potassium t-butoxide solution was prepared by adding 7 g. of potassium metal to 100 ml. of anhydrous t-butyl alcohol. As the solution was boiling, 5.5 g. (0.027 mole) of the trimethylsilylchloronorborene was added quickly. The mixture was stirred and heated under reflux overnight. It was poured into 150 ml. of ice water and 200 ml. of diethyl ether. The ether layer was separated and washed once with water and once with saturated aqueous sodium chloride. The washings were added to the aqueous layer which was then extracted with 200 ml. of ether. The ether layer was separated and washed as before. Finally the aqueous layers were extracted with 100 ml. of pentane. The combined pentane and ether layers were dried over magnesium sulfate, and concentrated at atmospheric pressure. Distillation of the residue yielded two fractions. The first fraction 0.25 g. (10%),

b.p. 34-36.2° (0.75 mm.), proved to be the desired bicyclic olefin IVc with 10% of the endo isomer Vc and 20% of the starting material. The second fraction 2.5 g., b.p. 63-64° (0.50 mm.), appeared to be starting material in which the number of isomers had been reduced. The identity of this product was established by the hydrogenation to the saturated analog which was then purified by preparative g.l.c. for infrared spectral comparison with authentic bicyclo(2.2.1)-hept-2-yl exo trimethylsilane. The infrared data for IVc was obtained using a sample purified by preparative scale g.l.c. with a 4 ft. column of 20% Apiezon L on Chromosorb 60-80 mesh:  $\nu_{\text{max}}$ . (film) 3140 (v wk), 3065 (wk), 1569 (wk), 1333, 1248, 950, 888, 847, 827, 751, 715, and 684  $\text{cm}^{-1}$ .

This same reaction was carried out using the norbornenyl chloride prepared from the reaction of hydrochloric acid with bicycloheptadiene in petroleum ether at  $-70^{\circ}$ <sup>(114)</sup>. Presumably the chlorine would be in the exo position. This reaction sequence resulted in a mixture of 73% IVc and 27% Vc as indicated by n.m.r. and g.l.c. analysis.

Anal. Calcd. for  $\text{C}_{10}\text{H}_{18}\text{Si}$ : C, 72.22; H, 10.91; Si, 16.87. Found: C, 72.03; H, 10.88; Si, 16.75.

j. Chloroplatinic acid catalyzed reactions.

(1) Methyldichlorosilane with bicycloheptadiene.

Because the results obtained in these laboratories are different from those previously reported<sup>(25)</sup>, the experimental

procedure will be described in detail. To a flat-bottom flask equipped with a magnetic stirrer, pressure equalizing dropping funnel and a condenser with a drying tube was added a mixture of 0.5 ml. of 0.1 M ethanolic chloroplatinic acid and 18 g. (0.20 mole) of bicycloheptadiene. To this was added dropwise 22.8 g. (0.20 mole) of methyldichlorosilane. The reaction was initiated by heating to 50°, and it then proceeded exothermically. The temperature was maintained at 40-50° by controlling the rate of addition of the silane. After the addition was complete the reaction mixture was stirred for one hour. Distillation yielded one fraction 32.3 g. (80%), b.p. 56-56.2° (0.35 mm.). The n.m.r. analysis carried out by measuring the areas under the appropriate peak due to the methyl protons of the Si-CH<sub>3</sub> group indicated that the mixture contained 64% of the endo norbornenyl compound Vb and the remaining 36% consisted of a mixture of the nor-tricyclene VIb and the exo norbornenyl methyldichlorosilane IVb. These results were confirmed by methylation of the reaction mixture and separation of the norbornenyl and nortricyclenic products by fractional distillation. Hydrogenation of the norbornenyl fraction and g.l.c. analysis of the resulting saturated products indicated that the endo isomer XVIII was contaminated by 9% of XVII.

(2) Trimethylsilane with bicycloheptadiene. This reaction was carried out in a sealed ampoule at 175° for five hours. A mixture of 2.06 g. (0.022 mole) of bicyclo-

heptadiene and 1.64 g. (0.021 mole) of trimethylsilane with 0.1 ml. of ethanolic chloroplatinic acid yielded 1.3 g. (45%), b.p. 46-47° (1.5 mm.), of the product mixture and 0.8 g. of starting material.

k. Platinum on charcoal catalyzed reactions.

(1) Trichlorosilane with bicycloheptadiene. A mixture of 45.5 g. (0.49 mole) of bicycloheptadiene, 40.2 g. (0.29 mole) of trichlorosilane and 0.25 g. of the platinum on charcoal was placed in a round-bottom flask equipped with a condenser with a drying tube. The mixture was heated at reflux for four hours. Distillation yielded 16.6 g. (25%) of VIa, b.p. 48° (0.17 mm.),  $\nu_{\max}$  (film) 3060 (wk), 2937, 2860, 1302, 1156, 822, 803, 742, and 672. N.m.r. and g.l.c. analysis indicated that only a trace of olefin was present in the product.

Anal. Calcd. for  $C_7H_9Cl_3Si$ : C, 36.94; H, 3.99; Cl, 46.74; Si, 12.33. Found: C, 37.04; H, 4.15; Cl, 46.51; Si, 12.15. This material was methylated in the usual way to yield compound VIc, b.p. 81° (18 mm.),  $n^{24}_D$  1.4690,  $\nu_{\max}$  (film) 3061 (wk), 2950, 2862, 1299, 1248, 1152, 965, 930, 888, 855, 832, 795, 746 and 685  $cm^{-1}$ .

Anal. Calcd. for  $C_{10}H_{18}Si$ : C, 72.22; H, 10.91; Si, 16.87. Found: C, 71.88; H, 10.80; Si, 17.13.

(2) Methyldichlorosilane with bicycloheptadiene.

A mixture of 18 g. (0.19 mole) of bicycloheptadiene, 0.1 g.

of the catalyst<sup>(113)</sup>, and 22.0 g. (0.19 mole) of methyldichlorosilane was placed in a flask equipped with a magnetic stirrer, and condenser with a drying tube. The reaction mixture was heated at reflux and stirred for one hour until the temperature increased to about 100°. Distillation yielded some starting material and 22.5 g. (77%) of the adduct, b.p. 57.2 - 57.6° (0.25 mm.). The n.m.r. analysis indicated that this mixture consisted of 92% methyldichlorosilyl nortricyclene VIb and 8% of the endo compound Vb. These results were substantiated by methylation of the mixture. The infrared spectrum gave the following results:  $\nu_{\text{max}}$  (film) 3062 (wk), 2942, 2865, 1299, 1261, 1250, 1152, 964, 928, 824, 805, 785 (v.s.), 761 and 738  $\text{cm.}^{-1}$ .

(3) Trimethylsilane with bicycloheptadiene. A mixture of 3.5 g. (0.04 mole) of bicycloheptadiene, 2.8 g. (0.04 mole) of trimethylsilane and a catalytic amount of the platinum on charcoal was sealed under nitrogen in a glass ampoule. The ampoule was heated at 175-200° for five hours under autogenous pressure. Distillation of the reaction mixture yielded 0.80 g. of starting material and 3.00 g. (55%), b.p. 46-47° (1.5 mm.), of product.

1. Free radical reaction of trichlorosilane with bicycloheptadiene (XV). A solution of 19.70 g. (0.214 mole) of freshly redistilled bicycloheptadiene and 28.82 g. (0.213 mole) of trichlorosilane was separated into three equal por-

tions. Each portion was sealed under nitrogen in a glass ampoule with 0.2 g. of azobisisobutyronitrile. The ampoules were then heated at 80-100° for 13 hours under autogenous pressure. Distillation of the product mixture yielded starting material plus 11.00 g. (75%) of the product, b.p. 70-71° (0.5 mm.).

The methylation of the product was carried out in the usual way in 80% yield.

m. Diels-Alder reactions.

(1) Vinylmethyldichlorosilane and cyclopentadiene at low temperature. To a flat-bottom flask equipped with a magnetic stirrer, pressure equalizing dropping funnel and a condenser with a drying tube was added 84.8 g. (0.6 mole) of methyldichlorovinylsilane. Freshly prepared cyclopentadiene at -70° was added to the silane in 10-ml. portions. After each addition the solution was heated to 50-60° to initiate the reaction. A total of 36 g. (0.54 mole) of cyclopentadiene was used. The reaction mixture was then heated at 50-60° for one hour and distilled yielding 64.1 g. of the methyldichlorovinylsilane and 12 g. (40%) of product.

(2) Vinyltrichlorosilane and cyclopentadiene at low temperature. This reaction was carried out as described above for the methyldichlorovinylsilane. A mixture of 121.2 g. (0.75 mole) of vinyltrichlorosilane and 47 g. (0.74 mole) of cyclopentadiene yielded 115 g. (68%) of the adduct, b.p.



62° (0.75 mm.).

(3) High temperature Diels-Alder reactions. The dicyclopentadiene was purified prior to use by passing it through alumina. The mixture containing one molar equivalent of the vinylsilane and one half molar equivalent of dicyclopentadiene was sealed in a glass ampoule and the ampoule was then heated to 175-200° for six hours, and the contents were distilled. The following results were obtained: (a) a solution of 14.3 g. (0.089 mole) of freshly distilled trichlorovinylsilane and 5.9 g. (0.045 mole) of dicyclopentadiene yielded 13.0 g. (65%) of product on distillation, b.p. 44-45° (0.15 mm.), as well as 2.4 g. of starting material; (b) a solution of 13.2 g. (0.094 mole) of freshly distilled methyldichlorovinylsilane and 6.1 g. (0.046 mole) of dicyclopentadiene yielded 2.0 g. of starting material and 10 g. (58%) of product; (c) a mixture of 6.6 g. (0.050 mole) of dicyclopentadiene and 19 g. (0.10 mole) of triethoxyvinylsilane yielded 1.8 g. of starting material and 3.70 g. (15.5%) of 1:1 adduct, (the rest of the material was high boiling; (d) if the temperature of the Diels-Alder reaction was allowed to exceed 230°, then a substantial amount of the 1-substituted nortricyclene product was produced. This material was isolated, after methylation, by g.l.c. using an Apiezon L column and identified by infrared and n.m.r.

n. Methylation of triethoxysilylnorbornenes. A sample of 3.70 g. (0.014 mole) of the triethoxysilylnorbor-

nene was added to 50 ml. of 4.6% methyllithium in diethyl ether. The solution was stirred for two days at room temperature. The workup was carried out in a fashion identical to that used in the methylations with methylmagnesium bromide. Vacuum distillation yielded 1.5 g. (63%) of the product.

o. Diels-Alder reaction of trimethylsilylcyclopentadiene. A mixture of 5.5 g. (0.04 mole) of trimethylsilylcyclopentadiene (III) and 2.5 g. (0.04 mole) of vinyl chloride was sealed in a glass ampoule and heated at 150-180° for eight hours. Vacuum distillation of the reaction mixture afforded 5.0 g. (63%) of the 1:1 adduct, b.p. 41-43° (0.1 mm.). This material consisted of at least eight different isomers as indicated by the n.m.r. spectrum.

p. Reduction of the adduct of trimethylsilylcyclopentadiene. To a solution of 7.93 g. (0.04 mole) of the trimethylsilylcyclopentadiene-vinyl chloride adduct and 10 g. of t-butyl alcohol in 150 ml. of anhydrous tetrahydrofuran was added 1.1 g. of lithium wire in small pieces. The flask was heated to initiate the reaction which proceeded vigorously for 30 min. It was then heated at reflux for an additional 30 min. The reaction mixture was then poured onto crushed ice. After the excess lithium had decomposed, the aqueous layer was extracted with 250 ml. of diethyl ether. Extracting the organic layer with 750 ml. of water, drying over anhydrous potassium carbonate, evaporation of the ether,

and vacuum distillation of the residue afforded 3.2 g. (49%) of the  $C_{10}H_{18}Si$  mixture, b.p.  $33^{\circ}$  (1.0 mm.).

## 2. Electrophilic Studies

### a. Bromine as the electrophile.

(1) Reaction of bromine with bicyclo(2.2.1)hept-2-en-5-yl endo trichlorosilane (Va). A solution of 15.0 g. (0.066 mole) of Va in 40 ml. of anhydrous carbon tetrachloride was rapidly stirred as a sample of 10 g. (0.062 mole) of bromine was added dropwise. The reaction mixture was stirred for one hour at room temperature and then divided into two equal portions. One portion was treated with zinc dust and filtered; the carbon tetrachloride was removed under reduced pressure. The residue solidified on standing. No 3-bromo nortricyclene could be detected among the products.

The second portion of the reaction mixture was left over copper wire for one month. The workup yielded essentially the same results.

The solid isolated was methylated in the usual way with methylmagnesium bromide. Again, no distillable products could be isolated.

(2) Reaction of N-bromosuccinimide with bicyclo(2.2.1)hept-2-en-5-yl endo trimethylsilane (Vc). A mixture of 20 g. (0.12 mole) of Vc, 60 ml. of carbon tetrachloride, 24 g. (0.13 mole) of N-bromosuccinimide and 0.7 g. of benzoyl

peroxide was placed in a 150 ml. two-necked flask equipped with a condenser and stirrer.

The reaction mixture was heated at reflux, stirred and irradiated with a drying lamp for four and one half hours. The succinimide was removed by filtration; and the carbon tetrachloride was removed by distillation at atmospheric pressure. Vacuum distillation of the residue gave a complex mixture of products; and the presence of a small amount of 3-bromonortricyclene was indicated by g.l.c.

(3) Reaction of bromine with bicyclo(2.2.1)hept-2-en-5-yl endo trimethylsilane (Vc) in carbon tetrachloride. This reaction was carried by adding 5% bromine in carbon tetrachloride to a stoichiometric amount of (Vc). G.l.c. examination of the product indicated that the results were essentially identical to those obtained when N-bromo-succinimide was used.

(4) Reaction of bromine with bicyclo(2.2.1)hept-2-en-5-yl endo trimethylsilane (Vc) in a glacial acetic solution of sodium acetate. Of the many modifications of this reaction which were attempted, the procedure described here seemed to be the most satisfactory.

A solution containing 6.5 g. (0.08 mole) of sodium acetate, 9.6 g. (0.06 mole) of bromine and 100 ml. of glacial acetic acid was cooled until crystals started to form. A sample of 10.00 g. (0.06 mole) of Vc was then added dropwise while the solution was stirred vigorously. After the addi-

tion was complete, the reaction mixture was poured onto 100 ml. of aqueous sodium bisulfite. The aqueous layer was extracted three times with a total of 250 ml. of petroleum ether (40-60° C). Extracting the ether layer with water, drying it over anhydrous sodium sulfate and removing the solvent left a residue which, upon vacuum distillation, yielded two fractions. The first fraction, which was obtained in trace amounts; b.p. 24° (0.15 mm.), consisted of at least two products. The second fraction, b.p. 56-58° (0.15 mm.), 4.0 g., appears to be a nortricyclic product with a trimethylsilyl functional group.

b. Perchloric acid as the electrophile.

(1) Reaction of perchloric acid with bicyclo-(2.2.1)hept-2-en-5-yl trimethylsilane (Vc). To a warm solution of 40 ml. of 70% aqueous perchloric acid and 140 ml. of methanol was added 6.5 g. (0.04 mole) of Vc. This two-phase system was heated on a steam cone for two hours. After cooling, the reaction mixture consisted of one layer. Water was added to this solution to form an emulsion. The aqueous layer was extracted with 4-50 ml. portions of petroleum ether (30-60°). After extracting the organic layer with water and aqueous sodium bicarbonate, it was dried over anhydrous sodium sulfate. The petroleum ether was removed by distillation at atmospheric pressure. Vacuum distillation yielded one fraction, 1.8 g., b.p. 23° (0.25 mm.). This material proved to have identical retention time and infrared

spectrum with those of a sample of authentic 2-methoxy norbornane which was prepared as described by Traylor and Baker<sup>(115)</sup>. The dry ice-acetone trap contained approximately 3.0 g. of this material. The net yield was greater than 70%.

c. Trifluoroacetic acid as the electrophile.

(1) Reaction with a deficit of bicyclo(2.2.1)-hept-2-en-5-yl trimethylsilane (Vc). A solution of 8.2 g. (0.05 mole) of Vc in two ml. of diethyl ether was added dropwise to 190 g. of trifluoroacetic acid which had been cooled to 0°. The reaction mixture was left at room temperature for five days before workup.

The reaction mixture was then poured into water and the emulsion was extracted with pentane. The organic layer was dried over anhydrous magnesium sulfate.

Distillation yielded 5.4 g. (52%), b.p. 32° (1.75 mm.), of the norbornyl trifluoroacetate.

(2) Reaction with an excess of bicyclo(2.2.1)-hept-2-en-5-yl endo trimethylsilane (Vc). When less than a stoichiometric amount of trifluoroacetic acid was added to Vc, the product mixture consisted of starting material, norbornyl trifluoroacetate and a mixture of 2-trimethylsilylnorbornene and 1-trimethylsilylnortricyclene. The identity of these rearrangement products was established by infrared spectrum of samples isolated using a 4 ft. x ¼ in., 20% Apiezon L on Chromosorb P column.

(3) Reaction with a deficit of tricyclo-(2.2.1.0<sup>2,6</sup>)heptan-3-yl trimethylsilane (VIc). Under reaction conditions identical to those used with Vc, exactly the same product mixture was obtained.

(4) Reaction with equimolar amounts of tricyclo-(2.2.1.0<sup>2,6</sup>)-heptan-3-yl trimethylsilane (VIc). The reactants were mixed neat and an exothermic reaction ensued. The only products formed were norbornene and presumably trimethylsilyl trifluoroacetate.

(5) Reaction with a less than equimolar amount of norbornene. This reaction was carried out in a fashion identical to that used for Vc. The yield of the trifluoroacetate and product mixture were identical to that obtained with Vc and VIc. A sample of this material was sent out for C, H, F analysis.

Anal. Calcd. for  $C_9H_{11}F_3O_2$ : C, 51.94; H, 5.29; F, 27.39. Found: C, 51.73; H, 5.39; F, 25.56.

d. Hydrochloric acid as the electrophile.

(1) Relative rate studies concerned with the addition of hydrochloric acid to IVc and Vc in glacial acetic acid. The hydrochloric acid in glacial acetic acid solution was prepared by adding 15.1 g. of acetic anhydride and 3.3 ml. of concentrated hydrochloric acid to 100 ml. of glacial acetic acid. A sample of 0.70 g. (0.004 mole) of each isomer IVc and Vc was added to separate 25 ml. aliquots of

this solution.

The course of the reaction was followed by removing aliquots which were poured into a mixture of petroleum ether (30-60°) and water. The organic layer was separated and analyzed by g.l.c. The only products formed were those which resulted from addition to the double bond. The exo isomer, IVc, reacted much faster.

(2) The addition of hydrochloric acid to a mixture of IVc and V. A sample of 5.14 g. (0.03 mole) of 80% IVc and 20% Vc was added to 200 ml. of solution prepared by mixing 200 ml. of glacial acetic acid, 10 ml. of concentrated hydrochloric acid and 66 g. of acetic anhydride. After five hours at room temperature, this reaction mixture was poured into 200 ml. of water and extracted with a total of 300 ml. of pentane. The pentane layer was extracted with water and saturated aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate. After removal of the pentane, vacuum distillation produced two major fractions. The first one, b.p. 23-24° (0.75 mm.), consisted primarily of the endo isomer Vc as indicated by infrared and n.m.r. spectra.

The second fraction, b.p. 65-66° (0.5 mm.), 2.34 g. (37%) apparently is the product of hydrogen chloride addition to the double bond of IVc. This compound was treated with 4.5 g. (0.04 mole) of potassium t-butoxide in 30 ml. of boiling anhydrous t-butyl alcohol. Immediately, potassium chloride was seen to precipitate. The mixture was stirred and refluxed. After four hours it was poured into a mixture



of water and pentane. The pentane layer was separated, washed with water and dried over anhydrous magnesium sulfate. Removal of the pentane and distillation of the residue yielded a complex mixture of norbornenyl and nortricyclenyl trimethylsilanes.

(3) The appearance of  $C_{10}H_{18}Si$  compound in the hydrochloric acid-acetic acid reaction medium. If a reaction mixture similar to that described in section (2) is left at room temperature for several hours,  $C_{10}H_{18}Si$  compounds will begin to appear in the reaction mixture. A sample of this material was isolated using preparative scale g.l.c. and proved to be 1-trimethylsilyl nortricyclene (XXI).

In another experiment, the reaction mixture was left for several days and distillation at atmospheric pressure yielded a fraction, b.p. 172-173°, which proved to be a mixture of 1-trimethylsilyl nortricyclene (XXI) and 2-trimethylsilyl norbornene (XX) as indicated by infrared spectrum and combustion analysis.

Anal. Calcd. for  $C_{10}H_{18}Si$ : C, 72.22; H, 10.91; Si, 16.87. Found: C, 72.33; H, 10.87; Si, 16.69.

e. Hydrofluoric acid as the electrophile. The procedure used is similar to the one described by Eaborn<sup>(100)</sup> for the conversion of  $R_2SiCl_2$  to  $R_2SiF_2$ . A sample of 32.75 g. (0.14 mole) of bicyclo(2.2.1)hept-2-en-5-yl endo trimethylsilane (Va) was added dropwise to a solution consisting of 150 ml. of 95% ethanol and 70 ml. of 40% aqueous hydrofluoric acid. The reaction mixture was refluxed for a total of three

hours and poured into 200 ml. of water. The aqueous layer was extracted with a total of 500 ml. of diethyl ether. The organic layer was washed with water and saturated aqueous sodium bicarbonate. Removal of the ether and vacuum distillation of the residue yielded one fraction, 4 g. (22%), b.p.  $39^{\circ}$  (0.75 mm.). The infrared spectrum is consistent with that expected for bicyclo(2.2.1)hept-2-yl ethyl ether.

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**NORBORNYL AND NORTRICYCLYL DERIVATIVES**

**PART II**

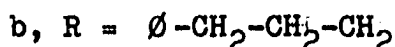
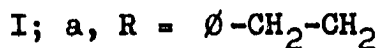
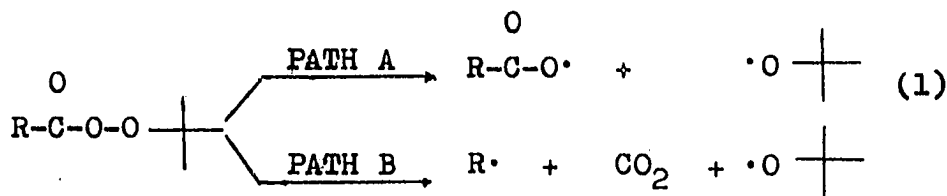
**REDUCTION OF HALIDES BY ORGANOTIN HYDRIDES**

## A INTRODUCTION

The literature contains numerous reports concerning the use of the non-classical carbonium ion concept to explain certain apparently anomalous reactions. This type of intermediate can be used to rationalize the enhanced reactivity of certain compounds, and the dependence of this reactivity on certain well-known stereochemical aspects. The nature of the reaction products is clearly understood in terms of non-classical carbonium ion intermediates.

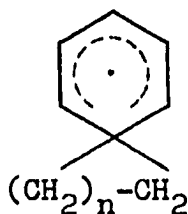
In view of this, it is not surprising that many studies have been carried out in the quest for analogous non-classical radicals. The radical intermediates selected are analogous to the carbonium ions which demonstrate this enhanced reactivity. Of course, the reaction intermediate possesses one more electron. To date, all of these studies have led the investigators to conclude that delocalization of the unpaired electron by sigma- or pi-participation does not lend stability to the free radical intermediate.

Martin<sup>(1)</sup> has studied the free radical decompositions of *t*-butyl 3-phenylperpropionate (Ia) and *t*-butyl 4-phenylperbutyrate (Ib). On the basis of previous detailed and careful



studies of the perester decompositions<sup>(2)</sup>, Martin has been able to determine the path followed in the decompositions of I.

Bartlett and coworkers<sup>(2)</sup> discovered a relationship between the mechanism of decomposition of a t-butyl perester and the activation parameters. In cases involving a relatively unstable radical, bond a cleaves in the rate determining step. As a result, the value of  $\Delta H^*$  is quite large; however, the geometric requirements of the transition state are not rigid. In contrast, the generation of a stable free radical proceeds by simultaneous cleavage of bonds a and b; consequently  $\Delta S^*$  is more negative due to the rigid geometric requirements of the transition state. The value of  $\Delta H^*$  is smaller because of the stability of the free radical. Martin<sup>(1)</sup> reasoned that a bridging transition state of the type represented by II would lead to activation parameters



II

in the same region as those for t-butyl phenylperacetate which involves the formation of a benzyl radical. If there is no participation by the phenyl group, the reaction will proceed in a stepwise manner (Path A). A decomposition of the latter type would be characterized by activation parameters in the same range as those reported for the decomposition of t-butyl peracetate. As the latter situation proved

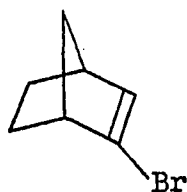
to be true, Martin concluded that the decomposition proceeded in a stepwise fashion with no anchimeric assistance by the phenyl group as depicted by II.

By analogy with the corresponding cationic intermediates, one would expect the decomposition of Ia to demonstrate the properties of a stable radical intermediate, whereas Ib would behave as an ordinary alkyl radical. Within experimental error, the activation parameters for the two peresters are identical. It was concluded that anchimeric assistance by the phenyl group does not play a significant role in the formation of simple 2-phenylethyl or 3-phenylpropyl free radicals. It is apparent that a bridged, "non-classical" radical, analogous to the phenonium ion, either does not exist or does not lend stability to the transition state.

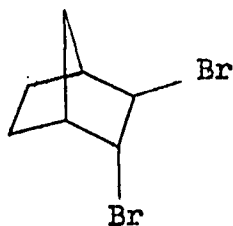
Various cationic derivatives of the bicyclo(2.2.1)-heptane carbon skeleton exhibit surprising behavior which has been attributed to the sigma- and/or pi-bond delocalization of the developing positive charge. Berson, Olsen and Wallia<sup>(3)</sup> have succinctly described the criteria which characterize the non-classical nature of 2-bicyclo(2.2.1)heptyl cations. Five criteria are of most interest here. (1) The cationic intermediates are mesomeric. (2) The solvolytic reaction rate is exceptionally fast because the transition state leading to the intermediate enjoys increased stability due to mesomerism. This is a result of the fact that, as in the case of the exo derivatives, the solvolytic departure of the cleaving group can occur simultaneously with the move-

ment of the bridging carbon atom. As a consequence, the exo derivatives solvolyze at rates many times those of the endo isomers. (3) The same mesomeric cation can be generated by solvolysis of 2-( $\Delta^3$ -cyclopentenyl)-ethyl derivatives. (4) Only exo products are formed because the partial covalences in the intermediate protect the endo side of the bridge from attack by external nucleophiles. (5) An unsymmetrically substituted ion will undergo nucleophilic attack at the cationic site that bears the greater number of alkyl substituents.

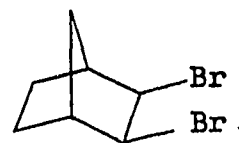
Numerous studies have been carried out to detect such behavior in free radical derivatives of bicyclic compounds. Again, the accumulated evidence gives no indication that a non-classical free radical is capable of existence. Kooyman<sup>(4)</sup> has found that cyclohexane undergoes free radical abstraction of a hydrogen as readily as norbornane. In view of this, the norbornyl free radical obviously does not possess enhanced stability due to mesomerism. Support for the hypothesis that a non-classical radical does not exist has been reported by Le Bel<sup>(5)</sup> in a study involving the free radical addition of hydrogen bromide to 2-bromo norbornene (III). This reaction yields predominantly IV and V.



III



IV

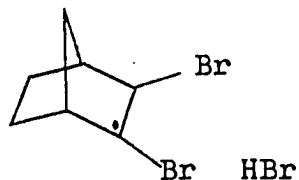


V

Depending on the reaction conditions, the ratio IV/V varies

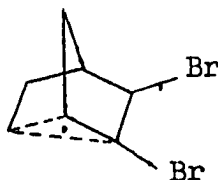
from 2.8 to 1.8. Both IV and V are expected products of non-Markownikoff addition resulting from initial exo attack of a bromine atom at the double bond to produce VI. A non-

III



VI

classical radical such as VII cannot be present as it prob-

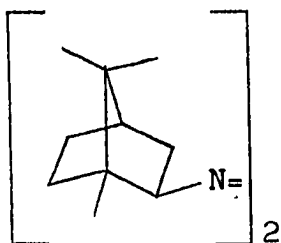


VII

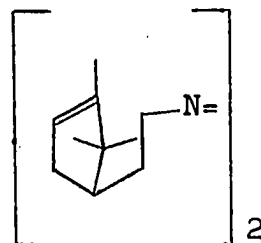
ably would lead to the formation of a large percentage of rearranged products.

Another reason for ruling out VII as an intermediate, although this was not stated by LeBel, is that the 2,3 dibromonorbornane formed from VII would be exclusively IV. If one assumes that VII would exhibit behavior similar to an analogous carbonium ion, then the partial covalences at carbon atom 2 would prevent endo attack by the hydrogen atom.

Berson et al<sup>(3)</sup> have investigated in detail the thermal decomposition of 2-azobornane (VIII) and 1-azo-bis-2-(2,2,3-trimethyl-3-cyclopentenyl)-ethane (IX) in diphenyl ether and n-hexadecane at temperatures above 250°. The thermal decom-

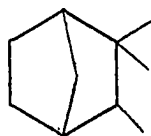


VIII



IX

position of azo compounds VIII and IX in *n*-hexadecane solution yields rate constants and activation parameters remarkably close to those reported for simple azoalkanes. Apparently, the reactivities of VIII and IX are normal. These observations indicate that the transition state does not lead to an intermediate free radical which benefits energetically from mesomerism, i.e., a non-classical radical. The formation of 2,3,3-trimethylnorbornane (isocamphane) -- the product of a formal Wagner-Meerwein rearrangement -- could result from beta-elimination of the initially formed bornyl radical, and recyclization at C2. This hypothesis is supported by the observation that X is found among the decom-

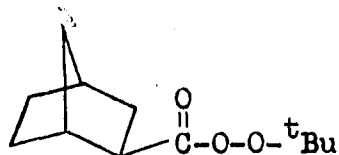


X

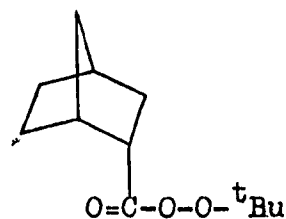
position products of both VIII and IX. Berson and his collaborators illustrate point by point that the criteria for a non-classical radical are not fulfilled.

In a study designed to test the existence of sigma- or pi-participation in the formation of the 2-bicyclo(2.2.1)-

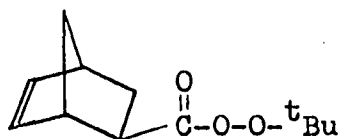
heptyl and 5-bicyclo(2.2.1)hept-2-enyl radicals, Martin and DeJongh<sup>(6)</sup> studied the rates of decomposition of compounds XI - XIV.



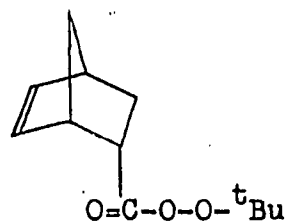
XI



XII



XIII



XIV

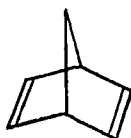
Should the delocalization of the C1-C6 single bond prove to be a significant driving force in the formation of a free radical at C2, then the exo isomer XI would decompose substantially faster than the endo isomer XII. Also, the activation parameters,  $\Delta H^*$  and  $\Delta S^*$  for the exo isomer XI would have values indicative of a concerted homolysis of bonds a and b (reaction 1, Path B). The decomposition of XII, which must take place without sigma-participation, would yield activation parameters indicative of the formation of a relatively unstable radical. The same type of arguments can be applied to test the relative importance of pi-participation in the decomposition of XIII and XIV. In fact, all four compounds XI - XIV are seen to have the same activation



parameters, within experimental error. From this it must be concluded that neither sigma- nor pi-participation is a significant driving force in the formation of the 2-bicyclo(2.2.1)heptyl and 5-bicyclo(2.2.1)hept-2-enyl radicals. Again, it is seen that these radicals fail to fulfill the criteria necessary for a non-classical radical.

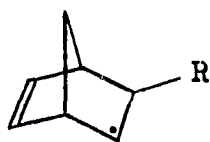
In a similar study, Hart and Chloupek<sup>(7)</sup> found no unusual effects, which would necessitate the evocation of a non-classical radical in the decomposition of the diacyl peroxides from exo- and endo-norbornene-5-carboxylic acids.

Numerous studies have been carried out in which the 5-bicyclo(2.2.1)hept-2-enyl radical was generated by the addition of a free radical fragment to bicycloheptadiene XV.<sup>(8)</sup>

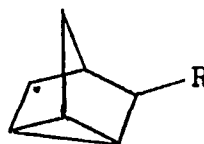


XV

In one of the earliest of these investigations, Cristol and co-workers<sup>(9)</sup> found that *p*-thiocresol reacts exothermally with XV to produce a 1:1 adduct via a free radical mechanism.



XVIa



XVIb

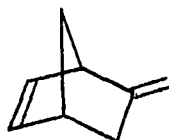
The radical XVIa can capture a hydrogen atom to form exo-5-norbornen-2-yl p-tolyl thioether or can rearrange to the nor-tricyclenyl radical (XVIb, R = -S-p-tolyl) before hydrogen abstraction. Trecker and Henry<sup>(8)</sup> have carried out free-radical additions of carbon tetrachloride, chloroform, butanal, heptanal, diethyl phosphite, and thiophenol to XV under a variety of conditions. The thiophenol proved to be unique as it was the only one of these addends which gave a product derived from XVIa (R = -S-C<sub>6</sub>H<sub>5</sub>).

Studies<sup>(8,10)</sup> designed to test pi-participation by the C2-C3 double bond in the generation of a free radical at C5 have been carried out. Trecker and Henry<sup>(8)</sup> found that the rate of trichloromethyl radical addition to XV is exactly twice that of addition to norbornene (XVII).

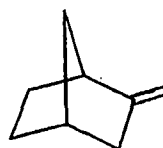


XVII

Competition experiments<sup>(10)</sup> of 5-methylene-2-norbornene (XVIII) and 2-methylenenorbornene (XIX) with the trichloro-



XVIII

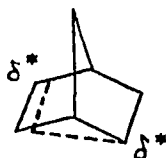


XIX

methyl radical indicate a 28% enhancement of the reactivity of the homoconjugated diene. The rate enhancement caused by the second double bond in XV and XVIII is, apparently, not due to resonance delocalization of the developing free radical, but is simply a result of additive reactivities.

From these results, then, it may be concluded that pi-participation by the C2-C3 double bond does not substantially lower the energy of the free radical development at C5. These results clearly indicate that one of the important criteria for a non-classical radical is not fulfilled. That is, the rate of reaction is not exceptionally fast due to resonance stabilization of the reaction intermediate.

The non-classical intermediate XX has been ruled out by some authors<sup>(8,10)</sup> because the 5-bicyclo(2.2.1)hept-2-enyl radical (XXI) is no more stable than the 2-bicyclo(2.2.1)heptyl radical. To critically evaluate this argument one must consider the basic assumption involved. This assumption states that XX would be a more stable intermediate as a result of resonance than an equilibrium mixture of XXI and XXII.



XX



XXI

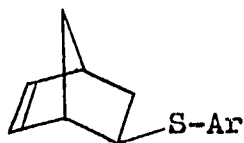


XXII

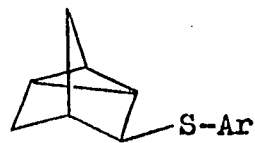
Martin and DeJongh<sup>(6)</sup> suggest that delocalization of the electron in a manner represented by XX might not lead to enhanced stability because the added electron repulsion in the radical could reduce the expected stabilization. To document this argument, these authors cite the fact that the resonance energy of the allyl radical is about 35% that of the allyl cation<sup>(11)</sup>. This phenomenon is the result of increased electron repulsion in the radical. They also note that a beta-vinyl group is roughly 40% as effective as an alpha-vinyl group in the stabilization of a cation. A corresponding decrease for the radical system would leave a relatively small degree of resonance stabilization for a beta-vinyl free radical.

In view of this, it is not surprising that the distinction between XX and an equilibrium mixture of XXI and XXII cannot be made on the basis of transition state energetics. Attempts to make this distinction have been carried out by studying the composition of the reaction mixture as a function of initial hydrogen donor concentration. These studies are not conclusive due to complications. Cristol and co-workers<sup>(9)</sup> observed an increase in the relative percentage of the 2,3 addition product of *p*-thiocresol to XV with increased *p*-thiocresol concentration. Using kinetic arguments, it was established that the initially formed intermediate (presumably XVIa, R = -S-*p*-tolyl) required a finite time before conversion to a second intermediate (presumably XVIb, R = -S-*p*-tolyl). One need only assume that first in-

intermediate reacts with *p*-thiocresol to yield the 5-exo-(*p*-tolyl-sulfide)-bicyclo(2.2.1)hept-2-ene (XXIII), and the second intermediate leads to XXIV to arrive at the conclusion.

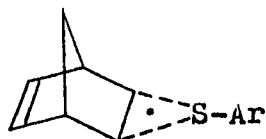


XXIII

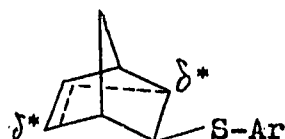


XXIV

that there are two different intermediates. The previous workers suggested that these two intermediates are XVIa (R = -S-*p*-tolyl) and XVIb (R = -S-*p*-tolyl). However, the two intermediates in question could be XXV and a non-classical radical such as XXVI. These two intermediates



XXV

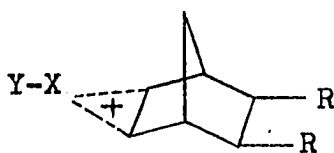


XXVI

would also be consistent with the dependence of the product composition upon the initial concentration of *p*-thiocresol.

Interconversion of two structures such as XXV and XXVI is reminiscent of a similar system discussed by Kaplan, Kwart and von R. Schleyer<sup>(12)</sup> involving the analogous cationic

intermediates. These workers point out that the relative amounts of rearranged(2,7) vs. unrearranged(2,3) products obtained from norbornene (XVII) and its derivatives are dependent upon the nature of the attacking reagent. Thus, the addition of XY to the double bond will give an appreciable amount of 2,3 product if the intermediate XXVII has stability comparable to or exceeding that of XXVIII.

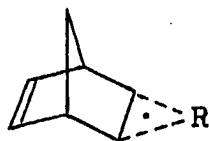


XXVII

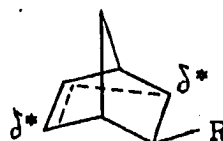


XXVIII

Of course, the relative populations of the two intermediates can be influenced by factors such as solvent, temperature and olefin structure. The same type of reasoning applied to the free radical additions to the bicycloheptadiene XV could be used to explain the relative amounts of products derived from 2,3- and 2,6-additions. An intermediate such as XXIX,



XXIX



XXX

upon reaction with a free radical or radical source would yield the product of 2,3-addition. The reaction of XXX would probably yield predominantly the product of 2,6-addition for two reasons: (1) sterically, attack at the 6-position would be favored; (2) the nortricyclic structure apparently is much more stable than the isomeric olefinic compound<sup>(13)</sup>. The fact that the thiophenol addition to bicycloheptadiene (XV) gives some bicycloheptene product, in contrast to many other addends<sup>(8)</sup>, is probably due in part to the stability of XXIX (R = S-phenyl). Also, the rapidity with which the hydrogen atom is donated by the thiophenol traps the radical in the initial form (XXIX) before conversion to XXX can take place. In view of this, the results of Cristol et al<sup>(9)</sup> can also be understood in terms of the intermediates XXV and XXVI or XXV and an equilibrium mixture of the two classical radicals. Thus, the problem of the nature of the radical is still unresolved.

Wilt and Levin<sup>(14)</sup> made some interesting observations regarding the nature of the unsubstituted 5-bicyclo(2.2.1)-hept-2-enyl radical (XXI). They studied the decarbonylation of 5-norbornene-2-carboxaldehyde. It was found that the ratio of norbornene to nortricyclics isolated was not changed by a five-fold dilution of the reaction mixture. A confident evaluation of the significance of these results is prevented by the low yield of hydrocarbon products isolated. To the extent that the product ratios are independent of concentration it appears that a non-classical radical such as XX does

exist or the two radicals XXI and XXII are undergoing rapid interconversion. In spite of the vast amount of data collected about the 5-bicyclo(2.2.1)hept-2-enyl radical (XXI) nothing has been done to study the 3-nortricyclyl radical (XXII).

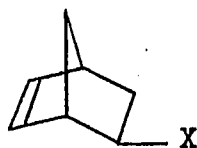


## B. RESULTS AND DISCUSSION

### 1. Purpose of the Study

The tri-n-butyltin hydride reduction of the halide seemed ideally suited for such a study. It has been established that the reduction of alkyl halides by tri-n-butyltin hydride proceeds via a free radical mechanism<sup>(15)</sup>. This reagent provides an extremely convenient method for the generation of alkyl radicals. The reactions can be made to proceed at a convenient rate through the use of solvent and/or free radical catalysis. The site of free radical generation is known, and the reactions give near quantitative yields of the hydrocarbon products. Finally, the relative reactivities of a large number of alkyl bromides are known<sup>(15)</sup>. This would permit comparisons to be drawn with bromides having a wide variety of different structural features.

The preparations of the desired halides XXXIa,b and XXXIIa,b have been described before<sup>(16,17)</sup> and the readily



XXXI



XXXII

a,x = Br

b,x = Cl

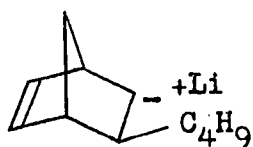
available tri-n-butyltin hydride provided a convenient method for the study of the nature of the radicals XXI and XXII or XX. The nature of this study was unique in two ways: (1) the hydrocarbon products norbornene (XVII) and nortricyclene (XXXIII) would be produced in near quantitative yields. Therefore, the information to be drawn from the relative amounts of each hydrocarbon would not require qualification because of the possibility that one of the isomers is destroyed in a side reaction; (2) for the first time, the 3-nortri-cyclyl radical (XXII) and the 5-norbornenyl radical (XXI) would be generated and studied under identical conditions.

As a secondary objective, it was hoped to further establish the free radical nature of the organotin hydride reductions of alkyl halides. Depending upon the particular experimental conditions, the 5-norbornenyl anion and cation both give products exclusively or predominantly derived from the tricyclic structure. For example, Roberts<sup>(16)</sup> has observed that the Grignard reagents derived from both XXXIa and XXXIIa gave substantially the same results upon reaction with dilute acid, i.e., predominant formation of nortricyclene (XXXIII). Wittig and Hahn<sup>(17)</sup> have reported that the reaction of bicycloheptadiene XV with an equimolar amount

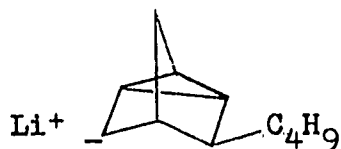


XXXIII

of n-butyllithium gives products expected from ion-pairs XXXIVa and XXXIVb in a ration of 1:9. Thus, it would seem



XXXIVa



XXXIVb

that the 5-bicyclo(2.2.1)hept-2-enyl anion is converted primarily to the closed 3-nortricyclenic form. Also relevant to this question is the reaction of XXXIb and XXXIIb with sodium metal. Freeman, George and Rao<sup>(18)</sup> observed that nortricyclyl chloride XXXIIb reacted with sodium in decane at 85-90° to produce a 19-20% yield of C<sub>7</sub> hydrocarbons. This hydrocarbon fraction consisted 71% of nortricyclene and 10% norbornene. The isomeric chloride XXXIb underwent the same reaction to yield 27% C<sub>7</sub> hydrocarbons of which 64% was nortricyclene and 13% was norbornene. To the extent that this reaction proceeds by an anionic mechanism, it appears that the anion exists primarily in the closed form. However, the formation of nortricyclenic products cannot be considered as definite proof. These products could also arise from an S<sub>N</sub>2'-like attack of the electrophile at C2 of the norbornenyl anion. Finally, it is well known<sup>(19)</sup> that the 5-bicyclo(2.2.1)hept-2-enyl cation gives products derived exclusively from the closed form. However, in cases in which the norbornenyl

free radical has been generated<sup>(6,14)</sup>, the products consist of a mixture of norbornene and nortricyclene with a substantial amount of the former. In view of these observations, it seemed conceivable that the product mixture from the tri-n-butyltin hydride reduction of the bromides (XXXIa) and (XXXIIa) would give evidence concerning the mechanism of the organotin hydride reductions of alkyl bromides.


## 2. Organotin Hydride Reductions

a. Evidence for free radical mechanism. Listed in Table VII are the results of this study along with the results of Martin and DeJongh<sup>(6)</sup> and Wilt and Levin<sup>(14)</sup>. The similarity of the norbornene-nortricyclene product mixtures from the known free radical processes with those of the organotin hydride reductions adds further evidence in favor of the free radical nature of the organotin hydride reductions of the alkyl halides. Strict comparisons between the tri-n-butyltin hydride reductions and the percarboxylate and aldehyde decompositions are not possible because the latter two methods yielded the hydrocarbon mixture in less than quantitative yields. Presumably, the norbornene would be more susceptible than the nortricyclene to destruction in side reactions.

More substantial evidence regarding the free radical nature of the organotin hydride reductions is contained in entries 3, 4, 5 and 6. It has been established that the tri-

TABLE VII

Free Radical Generation of Norbornene and Nortricyclene

Entry	Source	Solvent	Init. concn., M	Method <sup>a</sup>	Temp.	Over- all yield	% XVII	% XXXIII
1	XXXIa	none		A	18-22 <sup>o</sup>	100	57	43
2	XXXIIa	none		A	" "	100	55	45
3	XXXIa	Xylene	1.0-1.5	B	90	>95	59	41
4	XXXIIa	Xylene	" "	B	90	>95	60	40
5	XXXIb	Xylene	" "	C	90	>90	58	42
6	XXXIIb	Xylene	" "	C	90	>90	57	43
7	XIII	Cumene		D	94		40 <sup>b</sup>	60 <sup>b</sup>
8	XIV	Cumene		D	94		40 <sup>b</sup>	60 <sup>b</sup>
9		Chloro- benzene	0.8-4.1	E	132	9	44-47 <sup>c</sup>	56-53 <sup>c</sup>

<sup>a</sup> Method A: The bromide was mixed neat, at room temperature, with an equimolar amount of tri-*n*-butyltin hydride. Method B: a solution of the tri-*n*-butyltin hydride in xylene was added to the appropriate bromide. The solution was sealed in an ampoule and heated at 90<sup>o</sup> for 49 hours. Method C; the same as method B except 3 mole percent of azobisisobutyronitrile is added. Method D: the *t*-butyl percarboxylates were heated at 94<sup>o</sup>, data taken from reference 6. Method E: the aldehyde was decarbonylated in refluxing chlorobenzene using di-*t*-butyl peroxide as the catalyst, data taken from reference 14.

<sup>b</sup> Data taken from reference 6; these authors report norbornene to nortricyclene ratio equals 2:3.

<sup>c</sup> Data taken from reference 14.

n-butyltin hydride reduction of alkyl chlorides proceeds slowly if at all without free radical catalysis<sup>(15)</sup>. The observation that the azobisisobutyronitrile catalyzed reduction of the chlorides XXXIb and XXXIIb yields mixtures of hydrocarbon identical with those obtained from the uncatalyzed reduction of the bromides XXXIa and XXXIIa provides further strong evidence in favor of the free radical mechanism.

b. Relative rate studies. Relative rate studies were carried out to determine if these reductions proceeded at an enhanced rate. As would have been predicted by many previous studies<sup>(6,8,10)</sup> the reductions proceeded at rates comparable to those of alkyl halides. Thus, the endo-isomer of XXXIa and XXXIIa react at the same rate or slightly slower than cyclopentyl bromide. The exo-isomer of XXXIa is reduced at a rate comparable to that of cyclopentyl bromide. On this basis we conclude that the radical<sup>(9)</sup> generated enjoys no enhanced stability.

c. Discussion. One of the most striking features about Table VII, entries 1-6, is the invariance of the norbornene to nortricyclene ratio. For the first time, it has been demonstrated that the 3-nortricyclenyl and 5-bicyclo-(2.2.1)hept-2-enyl radical do indeed yield the same radical system (XX or an equilibrium mixture of XXI and XXII). In view of the invariance of the norbornene to nortricyclene ratio under a wide variety of reaction conditions, one is

tempted to suggest that a representation such as XX is more consistent with the facts. It could be argued that because of the remarkable trapping ability of the organotin hydride<sup>(20)</sup> a significant percentage of the initially formed radical would react before equilibration could take place. Thus, the result would not be independent of the structure of the starting halide, contrary to the facts. Of course, such an argument assumes a relatively slow attainment of equilibrium. Again, as in the past, it becomes impossible to distinguish between XX and an equilibrium mixture of XXI and XXII. If XX has existence it is not energetically more stable than an ordinary secondary radical. This could be the result of the added electron repulsion as suggested by Martin and DeJongh<sup>(6)</sup>;

Let us assume for the purposes of the following discussion that XXI and XXII exist as an equilibrium mixture. The fact that all of the methods presented in Table VII give nearly a 50:50 mixture of norbornene and nortricyclene is interesting in terms of the studies carried out by von R. Schleyer<sup>(13)</sup>. He found that an equilibrium mixture of these two hydrocarbons consists of 23% norbornene and 77% nortricyclene. This behavior poses an interesting question.

We will assume here that the mixture of hydrocarbons isolated has the same composition as the free radical equilibrium system. This assumption is justifiable. The reaction of the radicals with the organotin hydride is a highly energetic reaction and not likely to proceed selectively. This

is verified by the fact that under a wide variety of reaction conditions the ratio of norbornene to nortricyclene changes little. For example, the reduction of XXXIIa was carried out at a concentration of 0.8 M in chlorobenzene at room temperature. The resulting norbornene-to-nortricyclene ratio is identical, within experimental error, to the same ratio found when the reduction is carried out at 90° in xylene. It has been pointed out by von R. Schleyer<sup>(13)</sup> that the greater stability of nortricyclene may be due, in part, to the absence of eclipsed interactions which are present in norbornene. This explanation would account for the greater difference in stability of compounds of the type XXXI and XXXII. Upon equilibration, compounds of this sort exist almost exclusively in the closed form XXXII. The non-bonded interaction between the substituent X and the eclipsed hydrogen in XXXI causes a greater free energy difference between XXXI and XXXII than exists between norbornene and nortricyclene. The major eclipsed ethane interaction which is present in norbornene but not in nortricyclene exists along the C5-C6 bond. The energy of such an interaction is worth about 2.8 kcal./mole. This interaction is greatly reduced by replacement of a hydrogen at C5 by an unpaired electron. Rehybridization of the carbon possessing the unpaired electron would relieve other eclipsed interactions. In view of this, it is not surprising that the norbornenyl and nortricyclenyl radicals appear to be comparable in stability.



## C EXPERIMENTAL

## 1. Preparation of Halides

The tricyclo(2.2.1.0<sup>2,6</sup>)hept-3-yl bromide (XXXIIa), bicyclo(2.2.1)hept-2-en-5-yl bromide (XXXIa) and bicyclo(2.2.1)hept-2-en-5-yl chloride (XXXIb) were prepared exactly as described before<sup>(16)</sup>. The procedure of Hanack<sup>(21)</sup> was used to prepare bicyclo(2.2.1.0<sup>2,6</sup>)hept-3-yl chloride (XXXIIb). The compositions of the halides were checked by infrared spectra and g.l.c. The use of a 20% Silicone Nitrile, XF-1155, on Chromosorb 60-80 mesh permitted the separation of the norbornenyl and nortricycyl halides. The samples used in the reductions were 90% pure. The column described above also caused the separation of the exo and endo bromides of XXXIa. The peaks were assigned on the basis of the relative amounts of each as determined by Cristol et al<sup>(22)</sup>. These workers prepared a solid derivative of the mixture of bromides obtained by the Diels-Alder reaction of vinyl bromide with cyclopentadiene. The two isomers were separated, and the exo and endo derivatives were isolated in 32% and 48% yields, respectively. On the basis of g.l.c. area measurements, it appears that the mixture is composed of 30% of the exo isomer of XXXIa and 65% of the endo isomer of XXXIa. These results were confirmed by the n.m.r. spectrum.

## 2. Determination of Products

The reactants were mixed and sealed in glass ampoules under an atmosphere of pure nitrogen. The products were analyzed using an internal standard. A 20% Apiezon L on Chromosorb 60-80 mesh column was used. The products were identified by separation using preparative g.l.c. and comparing the IR's of these samples with those of the authentic substances.

## 3. Relative Rate Studies

The halides competed for a limited amount of tri-n-butyltin hydride. The amount of halide remaining was determined by the use of an internal standard.

These runs also served as control studies. It was found that the remaining halides XXXIa and XXXIIb did not undergo any interconversion under the reaction conditions. The hydrocarbons, also, do not undergo interconversion under the reaction conditions.

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