ON THE MECHANISM OF IONIC 1,3-ELIMINATION

IN

THE FORMATION OF HALONORTRICYCLENES

Ву

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#### A Thesis

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THE MECHANISM OF IONIC 1,3-ELIMINATION IN NORBORNENE

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#### **ARSTRACT**

The mechanism of 1,3-elimination in the bicyclo(2,2,1)heptyl system was studied using mass spectrometry and gas chromatography. The ionic chlorination, bromination, and iodo monochlorination of 2,3-di-norbornene, em, ent-5,0-di-norbornene, and endo, endo-5,0-dinorbornene were performed to obtain deuterium loss data. In the chlorination of norbornene, most of the tricyclic product arises from the cyclic norbornyl chloronium ion and/or classical em-5-chloronorbornyl cation (classical ion interpretation), or from the cyclic norbornyl chloronium ion (non-classical ion interpretation). bromination of norbornence, most of the tricyclic product arises from the classical syn-7-bromonorbornyl cation and/or ant?-7-bromonorbornyl cation (classical ion interpretation), or from the first formed non-classical 3-bromonorbornyl cation (non-classical ion interpretation). In the iodo monochlorination of norbornene, most of the tricyclic product arises from the classical syn-7-iodonorbornyl cation (classical ion interpretation), or from the first formed non-classical 3-iodonorbornyl cation (non-classical ion interpretation. Three of the products from the reaction of norbornene with iodo monochloride were isolated and identified to be: 3-iodonortricyclene, exc-2-iodo-endo-3-chioronorbornane, and syn-7iodo-exo-2-chloronorbornane.

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CHAPTER 1

INTRODUCTION

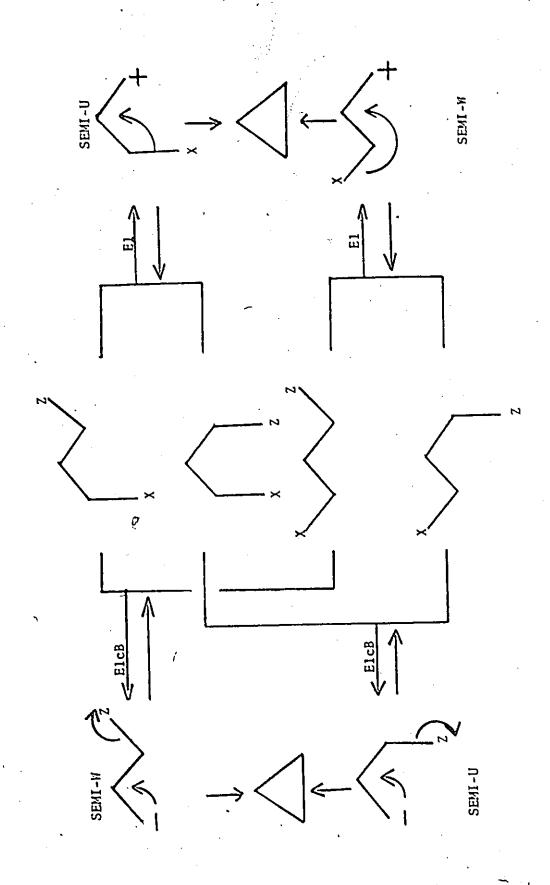
#### A. Nomenclature for 1,3-Eliminations

Terminology for 1,3-elimination has been introduced by Nickon and Werstiuk. The five atom system X-A-B-C-Z (Z is more electronegative than X, unless Z=X) has been considered. Net 1,3-elimination of X and Z under a variety of circumstances results in the formation of a three membered ring. In most systems, due to independent rotation about the A-B and B-C bonds, numerous conformations exist for concerted or non-concerted loss of X and Z.

For concerted 1,3-elimination, as outlined in Chart 1, there are five distinct arrangements (1a-5a) of staggered conformations for the precursor (or for a transition state that resembles reactant) whereas four arrangements (1b-4b) are possible for a transition state that resembles the cyclopropyl ring. A short notation is indicated for each possibility and the stereochemical consequence at the relevant centres is specified. Terminology for concerted 1,3-eliminations is as follows:

1=U; 2=W; 3=exo-Sickle; 4=endo-Sickle; 5=apo-Sickle. The exo and endo refer to Z.

For stepwise 1,3-elimination in which the stereochemistry cannot be defined at the cationic sites and at the anionic sites prior to ring closure, only slight modification of the concerted 1,3-elimination terminology is required. Chart 2 shows the terminology for cationic and anionic intermediates.



(8)

#### B. <u>Investigations</u>

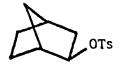
The chemical literature contains numerous studies of 1,3-elimination which were undertaken for synthetic and for mechanistic reasons.

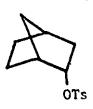
Most of the earlier literature reports synthetic routes to cyclopropanes, to bridged polycyclics, and to oxirane rings; recent literature deals predominantly with obtaining mechanistic information. Because the present investigation is mechanistic in nature and because the chemical literature on 1,3-eliminations is extensive, the following survey will deal with studies that attempt to interpret 1,3-elimination in terms of the terminology introduced by Nickon and Werstiuk or that have information supplementing this research.

#### 1) El-Like 1,3-Eliminations

## i) Bicyclo[2.2.1]heptyl Systems

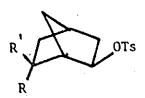
Nith their introduction of stereochemical terminology for 1,3-elimination, Nickon and Werstiuk<sup>2,3</sup> proceeded to investigate whether a preference of geometry existed in 1,3-elimination. The behavior of exo-norbornyl tosylate (6) in alkaline media was studied to determine if a preference for the exo-S or W geometry existed, and the behavior of endo-norbornyl tosylate (7) in alkaline media was studied to determine if a preference for the endo-S or U geometry existed.





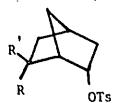
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Since a duality of mechanism existed, the conditions were adjusted to minimize E1-like reaction conditions and to maximize the effect of E2-like reaction conditions. The per cent deuterium loss from 6-exo-d-exo-norbornyl tosylate (6a) and from 6-endo-d-exo-norbornyl tosylate (6b) was 33.4 and 52.9 respectively when 1,3-elimination occurred under E2-like reaction conditions to form nortricyclene (8). It was concluded that the exo-S geometry is favoured over W geometry in the 1,3-elimination from 6 under E2-like reaction conditions. The per cent deuterium loss from 1,3-elimination under E2-like reaction conditions for 6-exo-d-endo-norbornyl tosylate (7a) and 6-endo-d-endo-norbornyl tosylate (7b) was 24.5 and 48.3 respectively indicating that the U geometry is preferred over the endo-S geometry in the 1,3-elimination from 7 under the stated conditions in the formation of 8



6a R =D; R=H

6b R =H; R=D



7a R =D; R=H

7b R =H; R=D



The stereochemistry of 1,3-elimination in the locked norbornyl system,  $endo,endo-5,6-d_2-exo-2$ -bromonorbornane-1-carboxylic acid methyl ester (9), was determined by Werstiuk. Without this study, the interpretation of deuterium loss from the C-5-exo-H, C-5-endo-H, C-6-exo-H, and C-6-endo-H bonds is difficult due to the ability of the norbornyl system to interconvert or to make these bonds equivalent in E1-like reactions. The reaction of 9 in basic media produced 10, 11, 12, and 13 as shown below.

The presence of the carboxylic acid methyl ester on the C-1 of 9 precluded the possibility of 1,2-Nagner-Meerwein rearrangement or the

A locked norbornyl system is one in which the C-6-C-1 bond neither shifts to C-2 nor stabilizes charge at C-2 to any significant degree.

possibility of C-6-C-1 anchimeric assistance resulting in maintenance of of the  $e\infty$  and endo distinction at C-5 and C-6. A 90% loss of one deuterium was observed in the formation of  $\underline{10}$  by 1,3-elimination from  $\underline{9}$  establishing that endo stereoselectivity(semi-U pathway) should be expected for El-like 1,3-elimination in the norbornyl system, provided that the C-6-C-1 bond does not shift or participate to any degree.

The mechanism of hydride shift during the hydrolysis of substituted norbornyl tosylates was studied by Benjamin and Collins. The hydrolysis of 2-exo-hydroxy-2-phenyl-3-exo-tosyloxynorbornane (14) and 7-phenyl-7-syn-hydroxy-2-norbornyl tosylate (15) produced 16, 17, 18, 19, and 20 with identical product ratios in each reaction.

The amount of 20 was not determined when 15 was reacted.

Also, hydrolysis on 2-endo-phenyl-2-exo-hydroxyl-3-exo-norbornane-5,6-exo,exo- $d_2$ -p-toluenesulfonate (21) and 7-phenyl-7-syn-hydroxy-2-exo-norbornane-5,6,-endo,endo- $d_2$ -p-toluenesulfonate (22) was performed. From both 21 and 22, one deuterium atom was eliminated in the formation of 5- $d_1$ -3-phenylnortricyclenol-3 (23). From 21 an original exo-d was lost and with 22 an original endo-d was lost when 1,3-elimination occurred.

From these results it was assumed that both reactions proceeded through common intermediates (or transition states) which could either be described as classical or non-classical ions. However, a more de-

finitive statement about the mechanistic scheme of Collins et al. was suggested by Werstiuk $^{4,5}$  as shown below. Cleavage of the C-OTs bond in

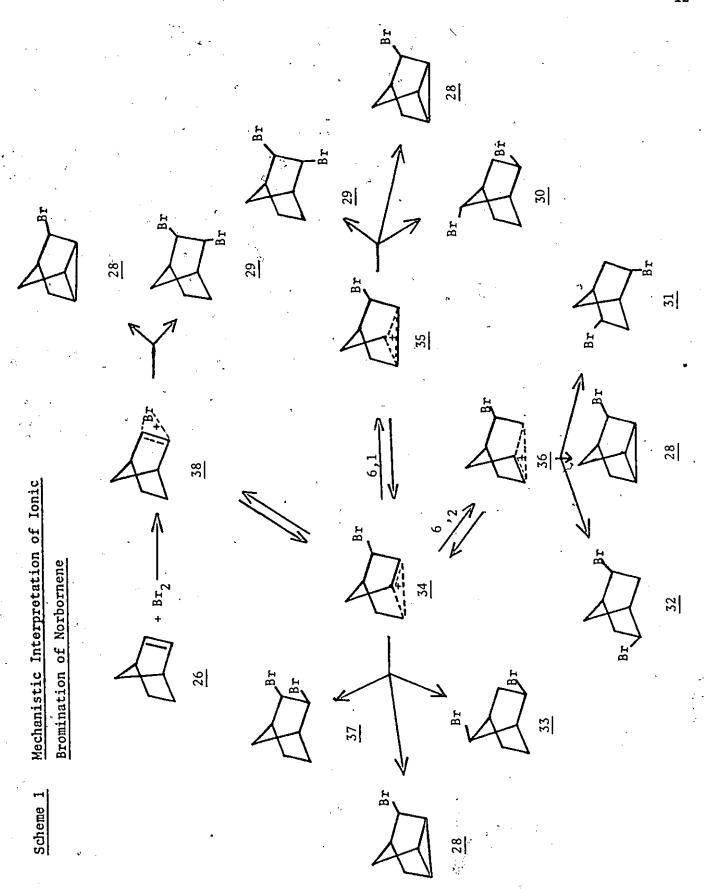
21 yields 24 which undergoes a 1,2-alkyl shift yielding 25. Solvolysis of 22 yields 25 directly. The hydroxyl and phenyl groups provide the necessary lock through an inductive effect and perhaps through OH-4 participation for the former and through an inductive and steric effect for the latter. Cation 25 need be classical and stabilized only through 1,3-hyperconjugation. Reaction of cation 25 with an endo preference in 1,3-elimination as expected would then lead directly to 23 with loss of one deuterium in both cases. The point made here is that the C-D bond originally exo in 21 is cleaved as an endo bond in 25. That 25 resembles a classical ion and that 1,3-elimination occurs from this species is supported by a value of 1.8 for the magnitude of the elimination istope effect which was evaluated from the product data of Collins et al.

1,3-Elimination of a proton is observed in the reactions of norbornene with bromine, chlorine, and bromine monofluoride.

Ionic bromination<sup>7,8</sup> of norbornene has been shown to give the seven major products drawn below, and some minor products which could not be identified. The reaction conditions were chosen to suppress

free radical processes. The kinetically controlled product ratios varied with reaction conditions, i.e., concentration of norbornene, temperature, presence of scavengers, etc.

Scheme 1 shows a mechanistic interpretation of the ionically formed products, 28, 29, 30, 31, 32, and 33. The production of the five dibromonorbornane isomers is consistent with exo-addition of a cationic bromine species to norbornene followed by some 6,1- or 6,2-hydride shifts in the resulting non-classical ion (or Wagner-Meerwein related classical cation) and reaction with bromine or bromine ion. The three non-classical cations, 34, 35, and 36 can give rise to



three pairs of dibromides of which the only one not formed was the exo, exo-2,3-dibromonorbornane (37). Nortricyclyl bromide (28) can be formed by 1,3-elimination from 34, 35, or 36. An alternate route to the formation of 29 is by normal trans-addition of bromine to norbornene via bromonium ion 38. Alternatively, 28 can result from 1,3-elimination from 38.

Chlorination 9,10,11 of norbornene (26) has been reported to give the six products shown below. Both the radical and the ionic mechanism

occurred simultaneously with the reaction conditions determining the relative importance of each type of mechanism. The products resulting from a pure radical reaction were exo-5-chloronorbornene (39), endo-5-chloronorbornene (40), nortricyclyl chloride (41), trans-2,3-dichloronorbornane (43), and exo,exo-2,3-dichloronorbornane (44). The products from a pure ionic reaction were 41, 43, 44, and syn-7-exo-2-dichloronorbornane (42).

The mechanistic interpretation of the ionically formed products is shown in Scheme 2. Ion  $\underline{45}$  is formed initially, and it can either

# Scheme 2 Mechanistic Interpretation of Ionic Chlorination of Norbornene

proceed to form ion 46, or it can form 43 by trans-addition of a chloride ion. Ion 46 can expel hydrogen from C-6 to form 41, or it can react with a chloride ion to form 42 and 44 depending on the carbon atom attacked.

The addition of bromine monofluoride (N-bromoacetamide and hydrogen fluoride) to norbornene ( $\underline{26}$ ) produced the three products shown below.  $^{12}$ 

$$\frac{\text{NBA}}{\text{HF}} \Rightarrow \frac{\text{Br}}{28} + \frac{\text{Br}}{47} + \frac{\text{Br}}{48}$$

Scheme 3 shows a mechanistic interpretation of the ionically formed products that are nortricyclyl bromide (28), anti-7-bromo-exo-2-fluoronorbornane (47), and syn-7-bromo-exo-2-fluoronorbornane (48).

Compounds 28, 47, and 48 can be considered to arise from the common intermediate 34 formed by attack of an electrophilic bromine species on the exo-side of the double bond of 26. Loss of a proton at C-6 from 34 gives 28. Attack of a fluoride ion at C-1 of 34 gives rise to 48. Hydride shift from C-6 to C-1 in 34 leads to cation 35 and then to 47 via attack of a fluoride ion at C-6. 35 can also give 28 by loss of a hydrogen.

Scheme 3 Mechanistic Interpretation of Ionic Bromo monofluorination of Norhornene

#### ii) Acyclic Systems

Only one example of E1-like 1,3-elimination in an acyclic system will be discussed. The aqueous deamination of 1-aminopropane  $^{13}$  (49) gave 1-propanol (50), 2-propanol (51), propene (52) and cyclopropane (53) in over all yield of 60-70%. In order to obtain mechanistic data

the aqueous acid deaminatons of 1-aminopropane-1,1- $d_2$ , -2,2- $d_2$ , -3,3,3- $d_3$ , and -1- $^{13}$ C were performed. The products were separated by gas chromatography, and after conversion to the trimethylsilyl ether, the propanol fractions were analyzed by mass spectrometry. The results can be explained by the formation of a primary n-propyl carbonium ion which can form edge-protonated cyclopropanes as shown below.

### 2) E2-Like 1,3-Eliminations

An example of a fully concerted E2-like 1,3-elimination has not yet been reported; however, studies under selected conditions on 5-oxo exo-2-norbornyl derivatives <sup>14</sup> may set a precedent.

#### 3) Elcb-Like 1,3-Eliminations

#### i) Acyclic Systems

In order to investigate the stereochemistry of 1,3-eliminations, Bordwell  $^{15,16}$  et al. studied the Ramberg-Bachlund and related reactions. The Ramberg-Bachlund reaction involves 1,3-elimination of hydrogen halide from an  $\alpha$ -halo sulfone by the action of a base. The first formed product, a thirane 1,1-dioxide (episulfone), undergoes thermal decomposition to form an alkene. To maximize the informaton obtained, systems were chosen in which the carbanion centre initiating attack in

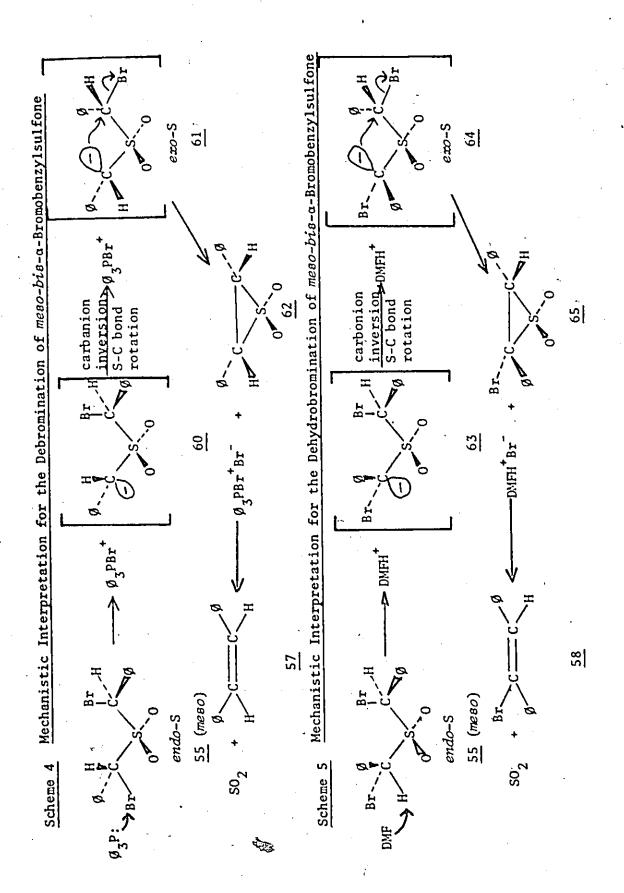
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1,3-elimination reacted prior to epimerization. For example, the dl (54) and meso (55) isomers of  $bis-\alpha$ -bromobenzylsulfone were treated individually with triphenylphosphine in refluxing benzene and in DMF respectively. The results are shown below.

The mechanistic pathway showing the formation of the major product is outlined in Scheme 4 for the debromination of meso-55 with  $\emptyset_3^P$  and in Scheme 5 for the dehydrobromination of meso-55 with DMF. An initial carbanion was established as an intermediate from trapping experiments which indicated that the anion maintains its configuration at the chiral centre. With  $\emptyset_3^P$  in benzene the carbanion was formed by abstraction of  $Br^+$  by  $\emptyset_3^P$  from an endo-S ground state conformation, so that  $Br^+$  was cis to and flanked by the oxygen atoms of the sulfone group. With DMF, the carbanion was formed by abstraction of  $H^+$  by DMF

a) Total yield was 85-90% with no other products detected.

b) Based on 100% α-bromostilbene: Actual yields were 73-75% α-bromostilbene, 2-4% stilbenes, 19-24% diphenylacetylenes. Total yield 85-90%



from a similiar *ando-*S ground state configuration. This is in agreement with Pearson's theory 17,18 of hard and soft acids and bases; the "soft" base triphenylphosphine attacks the "softer" atom bromine, whereas the "hard" base DMF attacks the "harder" atom hydrogen.

Further evidence for carbanions was the formation of appreciable quantities of reduction products benzyl a-bromobenzyl sulfone and dibenzyl sulfone when methanol was included in the  $\emptyset_3$ P-C<sub>6</sub>H<sub>6</sub> reaction mixtures. Furthermore, with D<sub>2</sub>O in DMA, reversible carbanion formation was consistent with the observation that epimerization competes with dehydrobromination. Stereoselectivity was greater with neutral than with negatively charged nucleophiles, and stereoselectivity decreased with increased dissociating ability of the solvent suggesting that ion-pair formation occurred.

The overall geometry of the debrominations or dehydrobrominations can be described as W, hence double inversion; thus the ground state geometry is probably ando-S and the transition state geometry is probably axo-S since inversion occurs at the nucleofugal chiral centre undergoing bromine displacement by intramolecular carbanion attack after both inversion of the carbanion and S-C bond rotation.

Jarvis  $^{19}$  et al. used bis( $\alpha$ -bromobenzyl) sulfoxide in an attempt to determine if a preference for geometry in 1,3-elimination existed. Scheme 6 shows the results predicated from W geometry and from U geometry when moso-bis( $\alpha$ -bromobenzyl) sulfoxide ( $\underline{66}$ ) is reacted, and Scheme 7 shows the results for the dl-bis( $\alpha$ -bromobenzyl) sulfoxides ( $\underline{67}$ ) and ( $\underline{68}$ ).

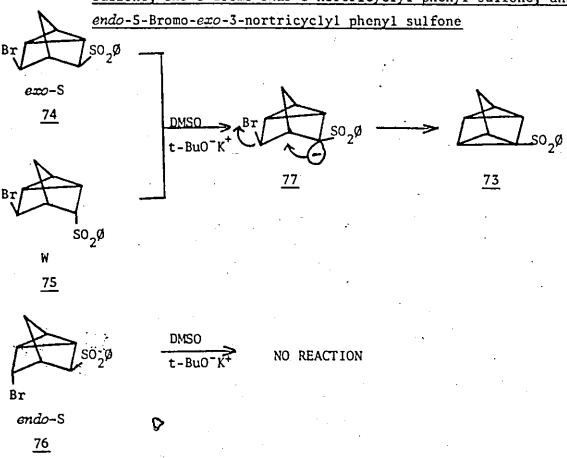
The reaction with 66 produced 69 with no detectable amount of 70; so 1,3-elimination must have gone through W geometry. The reaction with 67 and 68 produced 71 and 72 indicating that W geometry or U geometry could have been the mode of elimination. The results of Scheme 6 suggest that W geometry was the mode of elimination.

#### ii) Cyclic Systems

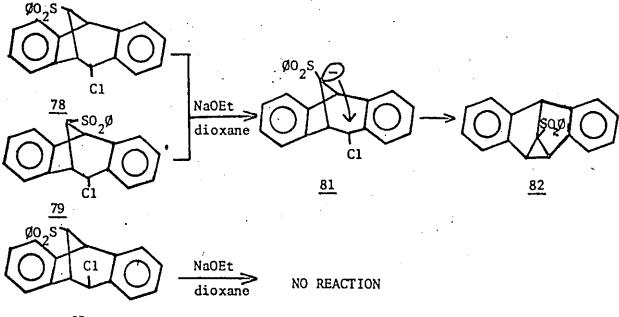
The 1,3-elimination of hydrogen bromide to form the bridged polycyclic 2-quadricycloheptyl phenyl sulfone (73) was reported by Cristol 20 et al. Potassium t-butoxide in t-butanol and dimethyl sulfoxide was the basic medium used to carry out elimination studies on the following compounds; exo-5-bromo-exo-3-nortricyclyl phenyl sulfone (74), exo-5-bromo-endo-3-nortricyclyl phenyl sulfone (75), and endo-5-bromo-exo-3-nortricyclyl phenyl sulfone (76). As illustrated in Scheme 8, compounds 74 and 75 reacted to produce 73; however, 76 was inert to the basic medium. It was postulated that a carbanion intermediate 77 was formed by hydrogen abstraction at C-3, followed by elimination of bromine with inversion of configuration at C-5. The exo-S geometry is present in 74 and W geometry is present in 75, both of which require inversion at C-5 when bromide is eliminated. Compound 76 has endo-S geometry which requires retention at the C-5 position when bromide is eliminated.

The 1,3-elimination of hydrogen chloride from a γ-chloro sulfone in the dibenzobicyclo[3.2.1]octadiene system has been reported by Cristol<sup>21,22</sup> et al. Scheme 9 shows the results of endo-4-chloro-anti-8-phenylsulfonyldibenzobicyclo[3.2.1]octadiene (78), endo-4-chloro-syn-8-phenylsulfonyldibenzobicyclo[3.2.1]octadiene (79), and exo-4-chloro-anti-8-phenylsulfonyldibenzobicyclo[3.2.1]octadiene (80) being reacted respec-

# Scheme 8 Dehydrobromination of exo-5-Bromo-exo-3-nortricyclyl phenyl sulfone, exo-5-Bromo-endo-3-nortricyclyl phenyl sulfone, and endo-5-Bromo-exo-3-nortricyclyl phenyl sulfone



#### 



tively with sodium ethoxide in dioxane.

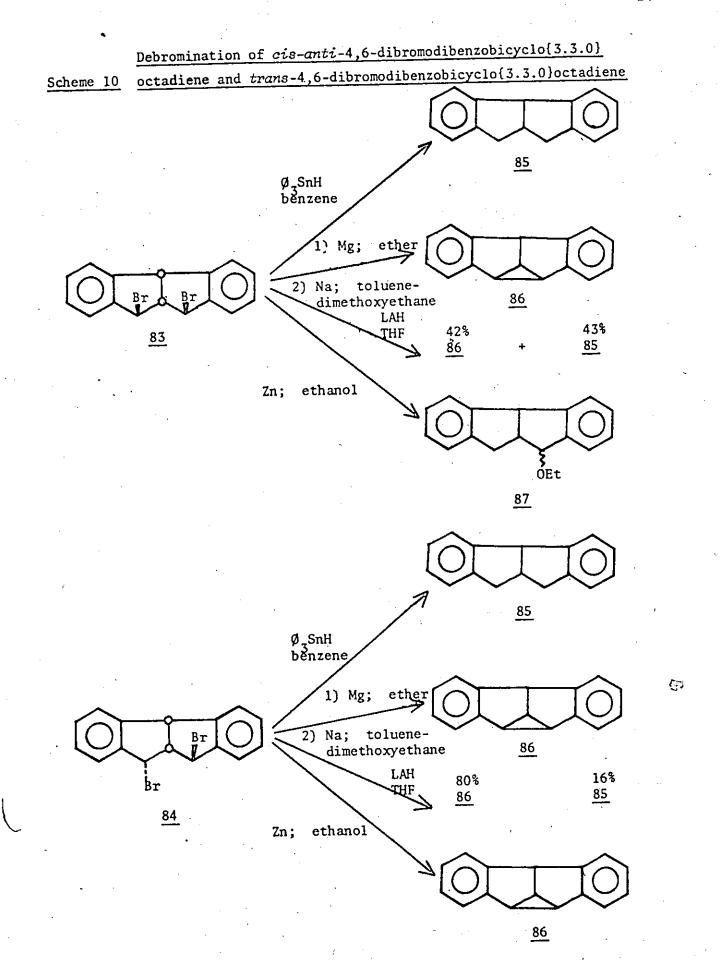
It was postulated that carbanion 81 was formed initially. With 78 and 79 the carbanion could react to displace chloride with inversion of configuration at C-4 to produce 82; on the other hand, 80 did not react since displacement with inversion at C-4 was not possible.

Another investigation by Cristol<sup>23</sup> et al. involved 1,3-elimination of bromine from cis-anti-4,6-dibromodibenzobicyclo[3.3.0]octadiene (83) and trans-4,6-dibromodibenzobicyclo[3.3.0]octadiene (84). Various reducing agents were used producing the products shown in Scheme 10.

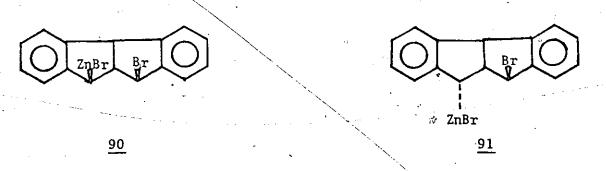
The mode of reaction of triphenyltin hydride with 83 or 84 was assumed to be similiar to its reaction with alkyl halides involving a free radical chain in which  $R_3Sn$ . abstracts a halogen atom from 83 or 84 giving a carbon radical 88 which reacts with  $R_3SnH$  to give a carbon-hydrogen bond forming anti-4-bromodibenzobicyclo[3.3.0]octadiene (89) and a  $R_3Sn$  species.



The reactions of 83 and 84 in aprotic solvent with reducing agents [i) lithium aluminium hydride, ii) magnesium, or iii) sodium probably involved the formation of a long-lived organometallic intermediate which could lead to epimerization and subsequent loss of stereochemical identity.



With zinc in protic solvent, <u>83</u> produced the *syn-* and *anti-*epimers of the monoethyl ether <u>87</u> which resulted from solvolysis of <u>89</u>. In contrast, <u>84</u> produced <u>86</u>. With zinc, <u>83</u> and <u>84</u> led to carbanionoid species with retention resulting in <u>90</u> and <u>91</u> respectively. Carbanion <u>90</u> is captured by protation from ethanol to give <u>89</u> before transformation to <u>86</u> (*via* the epimerization of <u>90</u> to <u>91</u>) can occur. On the other



hand, carbanion 91 has a benzylic carbon to attack, leading to 86. These results support the contention that an exo-S conformation is needed for ready 1,3-elimination since 83 displays a relatively rigid W conformation whereas 84 displays an exo-S conformation.

Paquette and Houser<sup>24</sup> studied the 1,3-elimination from 1-chloro-9-thiabicyclo[3.3.1]nonane 9,9-dioxide (92) with aqueous potassium hydroxide at 100°C as shown. Hydrogen chloride was eliminated from 92

which has W geometry. The intermediate carbanion 93, which also has W geometry, must have undergone inversion of configuration followed by in-

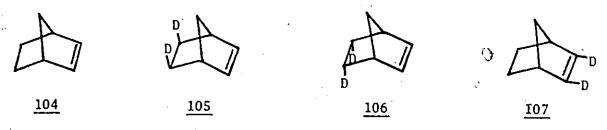
version at the C-1 position when chloride was expelled resulting in the production of episulfone 94 which lost sulfur dioxide to produce  $v^{1,5}$  bicyclo[3.3.0]octene (95).

Corey<sup>25</sup> et al. in a similiar study showed that the W geometry led to 1,3-elimination of hydrogen bromide as indicated below.

The 1,3-elimination of bromine from 1,3-dibromoadamantane (101) was shown to proceed with W geometry. Compound 101 when debrominated resulted in the formation of elimination product tetracyclo[3.3.1.1.3,7 0<sup>1,3</sup>]decane (102) and reduction product adamantane (103).

#### C. Statement of Problem

The purpose of the following investigation was to study the 1,3-elimination in the reaction of norbornene (104) with the reagents chloring, bromine, and iodine monochloride, respectively, in protic and aprotic solvent. To gain mechanistic information on the 1,3-elimination pathway in these reactions, the following deuterated compounds were used:  $exo_1, exo_2, 6-d_2$ -norbornene (105);  $endo_1, endo_2, 6-d_2$ -norbornene (106); 2,3- $d_2$ -norbornene (107).

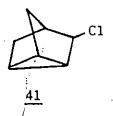


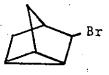
Previous workers had shown that the chlorination 9,10,11 and bro7,8
mination of norbornene (104) in aprotic solvent can proceed by ionic
and by free radical mechanisms simultaneously. In order to determine
the conditions which could maximize the per cent of ionic component and
minimize the per cent of free radical component, these reactions were to
be repeated. By identifying the major products in these reactions, it
would perhaps be possible to determine the per cent of free radical components.

Since the addition of iodine monochloride to 104 in aprotic solvent had not been reported, the isolation and identification of the major products formed were to be performed.

After completion of the preliminary work mentioned above, the plan was to obtain stereochemical information on the three reactions by

carrying out the additions to 105, 106, and 107, respectively, in methylene chloride and in acetic acid. Mass spectral analysis was to be used to determine the per cent of deuterium which was lost in the formation of nortricyclyl chloride (41), nortricyclyl bromide (28), and nortricyclyl iodide (108). The effect of varying the concentration of 105, 106, and 107, the concentration of pyridine, and the temperature was also to be determined.







CHAPTER 2
RESULTS



#### A. Syntheses and Stereochemical Purities of Deuterated Compounds

# 1) Synthesis of $2,3-D_2$ -norbornene

The multistep synthesis, as described in Scheme 11, yielded 2,3- $d_2$ -norbornene ( $\underline{107}$ ) in high purity.

## Scheme 11 Synthesis of 2,3-D<sub>2</sub>-norbornene

In step 1, base catalyzed deuterium exchange of 2-norbornanone ( $\underline{109}$ ) produced a single product, 3,3- $d_2$ -2-norbornanone ( $\underline{110}$ ). After

a reaction period of eight days of exchange, mass spectral analysis of  $\frac{110}{100}$  indicated the following deuterium content:  $d_0 = 1.4\%$ ;  $d_1 = 2.1\%$ ;  $d_2 = 96.5\%$ ; or 1.95 excess deuterium atoms per molecule.

Step 2 involved reduction of  $\underline{110}$  with lithium aluminium deuteride to produce 2,3,3- $d_3$ -endo-2-norbornanol ( $\underline{111}$ ) and 2,3,3- $d_3$ -exo-2-norbornanol ( $\underline{112}$ ).  $\underline{111}$  and  $\underline{112}$  were present in a ratio of 85:15 based on the results from the reaction of undeuterated material. Compounds  $\underline{111}$  and  $\underline{112}$  were converted to their respective acetates in order to determine the deuterium content. Mass spectal analysis indicated that the acetates had the following excess deuterium content:  $d_0 = 0.0\%$ ;  $d_1 = 1.2\%$ ;  $d_2 = 3.5\%$ ;  $d_3 = 96.5\%$ ; or 2.97 excess deuterium atoms per molecule.

To convert the mixture of 111 and 112 predominantly to 2,3,3-d<sub>3</sub>-exo-2-bromonorbornane (113) and partially to 2,3,3-d<sub>3</sub>-endo-2-bromonorbornane (114), the method of Schaefer and Weinberg<sup>27,28</sup> was used as shown in step 3. Compound 111 reacts by bimolecular displacement accompanied by Walden inversion to produce 113; however, 112 reacts partially by bimolecular displacement accompanied by Walden inversion to yield 114, and predominantly by an El mechanism resulting in the formation of a norbornyl cation which captures a bromide ion to yield 113. Nmr analysis of the undeuterated mixture of 113 and 114 indicated that they were formed in a ratio of at least 10:1. The nmr analysis of 113 and 114 indicated that the deuterium content was at least 95% in each of the following positions: endo-C-2; exo-C-3; endo-C-3.

In the final step of the synthesis,  $\underline{113}$  and  $\underline{114}$  were subjected to a strongly basic medium resulting in the formation of 107. Mass spectral

analysis of 107 showed:  $d_0 = 0.3\%$ ;  $d_1 = 1.7\%$ ;  $d_2 = 93.0\%$ ;  $d_3 = 5.0\%$ ; or 2.03 excess deuterium atoms per molecule. Integration of the nmr spectrum of 107 (nmr spectrum 1, 60MHz, CCl<sub>4</sub> and TMS) revealed the following deuterium distribution: 93%  $\pm$ 5% of the deuterium was located at C-2 and C-3, 6%  $\pm$ 5% was located at C-4, and 1%  $\pm$ 5% was located at C-5, C-6, and C-7.

2) Stereochemical Purity of Exo, exo-5,6-d<sub>2</sub>-norbornene and Endo, endo-5,6-d<sub>2</sub>-norbornene

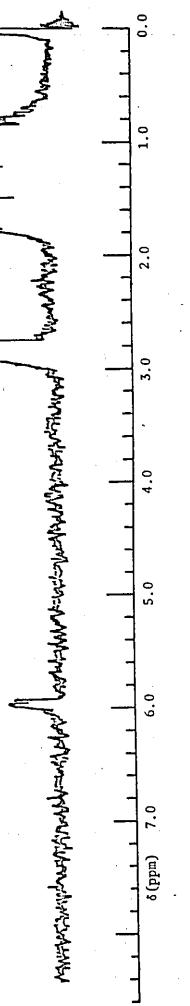
 $Exo, exo-5, 6-d_2$ -norbornene (105) and  $endo, endo-d_2$ -norbornene (106) were prepared by N. H. Werstiuk as described in a recent publication. Phe deuterium content of 105 was determined by mass spectral analysis of one of its precursors,  $exo, exo-5, 6-d_2$ -norcamphor, which showed the following excess deuterium content:  $d_0 = 1.8\%$ ;  $d_1 = 17.4\%$ ;  $d_2 = 80.0\%$ ; or 1.79 excess deuterium atoms per molecule. A similiar deuterium content was assumed for 106 because 105 was a precursor in a synthetic route that precluded deuterium loss or gain. The 100 MHz nmr spectrum of 105 indicated that the deuterium at C-5 and C-6 stereochemically was 85-90% exo, and integration of the spectrum of 106 indicated that the deuterium at C-5 and C-6 was 85-90% endo.

## B. Chlorination of Norbornene

1) Chlorination of Norbornene in Methylene Chloride

In order to preclude the free radical mechanism, the reaction conditions for the ionic chlorination of norbornene in methylene chloride were determined from the information made available by Pouts-





Nmr spectrum 1 2,3- $d_2$ -norbornene

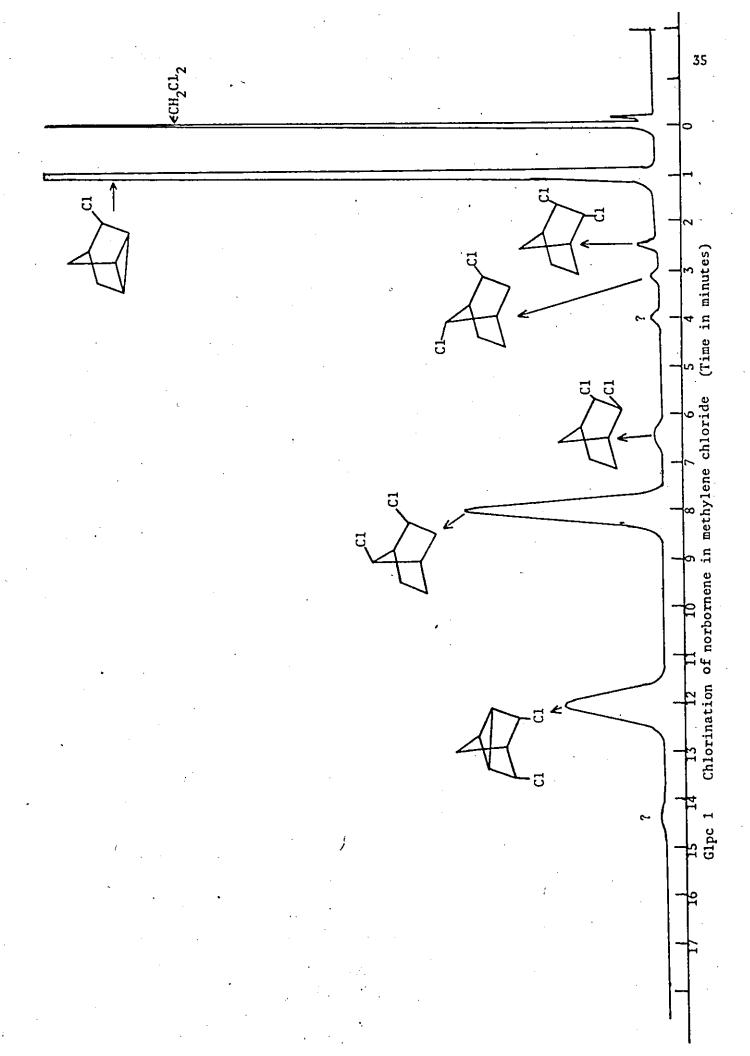
ma. 10 The reaction was carried out in the dark which prevents photodecomposition of chlorine into free radicals. A low temperature of
0°C was used to suppress the thermal cleavage of chlorine into free
radicals. Methylene chloride was used instead of carbon tetrachloride
because of its polarity which makes the ionic pathway more favourable.

The concentration of norbornene was kept low because the free radical
component was found to increase as the norbornene concentration was
increased. In addition to Poutsma's suggestions, dry nitrogen was bubbled
throughout the reaction mixture for five minutes before and during the
reaction in order to flush out any moisture or gases present.

In order to identify the products in the chlorination of nor-bornene in methylene chloride, a large scale reaction was performed, and the crude product was fractionated on a spinning band distillation column which resulted in partial separation of the components. Only six pure components could be obtained by preparative gas-liquid partition chromatography (glpc) even though analytical glpc (I,150°C) of the reaction mixture indicated that there were at least eight products as shown in glpc 1.

Scheme 12 shows the results of the chlorination with the identified products listed in order of increasing retention time. Table 1 lists the retention times and describes the mode of identification of products.

<sup>\*</sup> The Roman numeral indicates the type of column used as described in the experimental section.



Products from the Chlorination of Norbornene in Methylene Chloride Retention Time Compound Means of Identification Nmr spectrum identical to that reported for 1.0 3-chloronortricyclene in reference 30; Mass spectrum (m/e 128,130) Nmr spectrum identical to that reported for 2,4 trans-2,3-dichloronorbornane in reference 10; Mass spectrum (m/e 164,166,168) C1 Nmr spectrum identical to that reported for 3.2 anti-7-exo-2-dichloronorbornane in reference 30; Mass spectrum (m/e 164,166,168) 4.0 unknown Cl Nmr spectrum identical to that reported for C1 exo, exo-2,3-dichloronorbornane in reference 6.5 30; Mass spectrum (m/e 164,166,168) CIC1 Nmr spectrum identical to that reported for 8.0 syn-7-exo-2-dichloronorbornane in reference Mass spectrum (m/e 164,166,168) Nmr spectrum(interpreted; 12.1 Mass spectrum (m/e 162,164,166) C1 14.1 unknown

All retention times are in minutes relative to CH2Cl2.

Scheme 12 Chlorination of Norbornene in Methylene Chloride

The nmr spectra of the products, assumed to be 3-chloronortricyclene (41), trans-2,3-dichloronorbornane (43), exo-2-anti-7-dichloronorbornane (115), exo,exo-2,3-dichloronorbornane (44), and exo-2-syn-7-dichloronorbornane (42), were consistent with their respective spectra reported in the literature. The mass spectrum of 41 was consistent with the empirical formula  $C_7H_9C1$ , and the mass spectra of 43, 115, 44, and 42 were consistent with the formula  $C_7H_{10}C1_2$ . 41, 43, 44, and 42, listed in order of increasing retention times, were identical to the four products Poutsma reported in a similiar experiment with the same order of elution on analytical glpc.

Neither Roberts et al. or Poutsma had reported exo-2-anti-7-dichloronorbornane (115) as a product in similiar experiments. The failure to report 115 could have been due to its low yield. However, compound 115 was reported by Masson as a product in the reaction shown on the following page.

$$\frac{\text{CHC1}_{3}; \ \text{C}_{6}^{\text{H}_{5}}\text{IC1}_{2};}{\text{CF}_{3}^{\text{C0}_{2}}\text{H}; \ \text{reflux}} + \frac{\text{C1}}{41} + \frac{\text{C1}}{42}$$

Compound 116 has yet to be reported in the literature; its two stereoisomers 117 and 118 have been produced by Masson 30 (vide infra). The identification of 116 was accomplished as follows: The mass spec-

$$\frac{\emptyset IC1_2}{CHC1_3} \longrightarrow C1 \longrightarrow C1$$

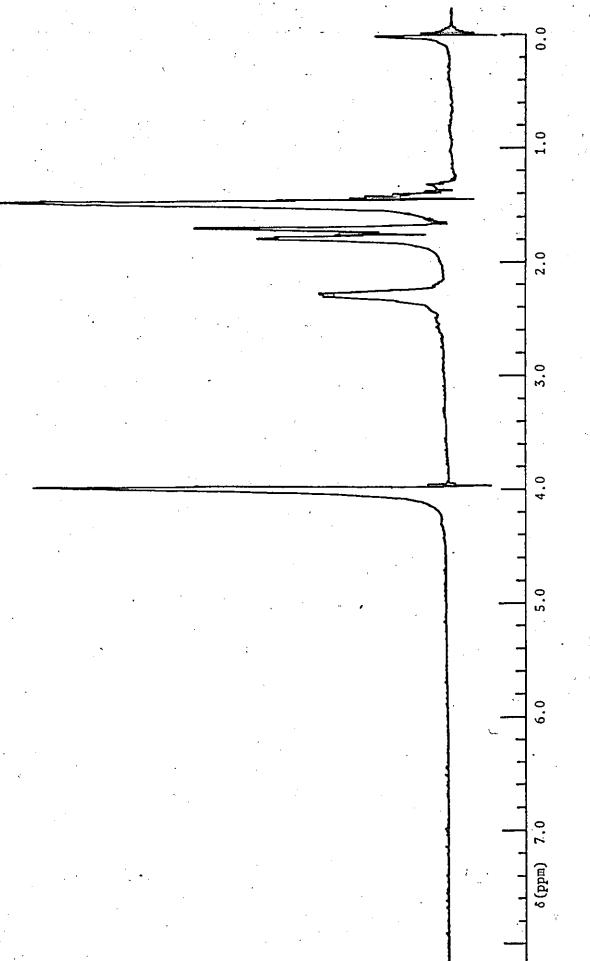
$$\frac{119}{CHC1_3} \longrightarrow \frac{117}{C1} \longrightarrow C1$$

trum of 116 was consistent with the empirical formula  $C_7H_8Cl_2$ . The nmr spectrum of compound 116 (nmr 2) did not correspond to the nmr spectrum of 117 or 118 as reported by Masson. The nmr spectrum of 116 indicated that the nortricyclyl skeleton was present based on the following facts: no absorption due to methyl or vinyl groups was present; absorptions indicative of a cyclopropyl group and of a bridgehead hydrogen were present. The nmr spectrum showed  $\delta$  1.42(broad singlet, cyclopropyl hydrogens, 3H), 1.68(doublet, J = 5Hz, two C-7 hydrogens coupled to a cyclopropyl hydrogen, 2H), 2.30(broad singlet, bridgehead hydrogen, 1H), and 4.00 (singlet, exo-C-3 and exo-C-5, 2H). Thus 116 was tentatively identified as endo, endo-3,5-dichloronortricyclene.

#### 2) Effect of Base

The ionic chlorination of norbornene in methylene chloride was





Nmr spectrum 2 endo, endo-3,5-dichloronortricyclene

performed in the absence and also in the presence of pyridine as shown in Table 2. When no pyridine was present, the results in column 2 were obtained; when the concentration (M/l) of pyridine was equivalent to that of norbornene, the results in column 3 were obtained; also when the concentration (M/l) of pyridine was ten times that of norbornene, the results in column 4 were obtained. All the reactions were performed on a small scale with a norbornene concentration of about 2.0 X  $10^{-2}$  M/l.

#### 3) Chlorination of Norbornene in Acetic Acid

The ionic chlorination of norbornene (104) in acetic acid, which has yet to be reported, was performed. The reaction conditions were similiar to those used in the ionic chlorination of 104 in methylene chloride except for the temperature which was raised to 25°C because the freezing point of acetic acid is 17°C.

In order to identify the products a large scale reaction was performed, and the crude product was fractionated on a spinning band distillation column which resulted in partial separation of the components. Eight pure components were obtained by preparative glpc and identified by mass spectrum analysis and nmr analysis. A ninth component was identified using glpc analysis using a sample of endo,endo-3,5-dichloronortricyclene obtained from the reaction of chlorine with norbornene in methylene chloride. Analytical glpc (I, 150°C) indicated that there were at least ten products. See glpc 2.

Scheme 13 shows the results of the reaction with the nine identified products listed in order of increasing retention time. Table 3 shows the retention times and mode of identification, and Table 4, columns

Table 2 Chlorination of Norbornene in Methylene Chloride

Relative Per Cent Yield by Weight\*

Compound	Norbornene + CH <sub>2</sub> Cl <sub>2</sub> + Cl <sub>2</sub>	Norbornene + $CH_2Cl_2$ + = pyridine + $Cl_2$	Norbornene + CH <sub>2</sub> Cl <sub>2</sub> + 10 X pyridine + Cl <sub>2</sub>
<i>N</i>			
C	51.8	42.6	55.4
A			
C	1.2	1.3	1.1
C1 C1	21		
Ly	0.5	0.8	0.5
unknown	1.0	0.9	0.5
N	•		
CI	0.6	0.9	0.7
LC1			
	28.2	32.6	25.9
A			. •
$c_1$	16.2	20.7	15.6
9	0.5	,	
unknown	0.5	0.2	0.3
	•		<u> </u>

The analytical glpc was calibrated for response differences between non-isomeric compounds and these differences were corrected for in determining the yield based on 100%.

#### Products from the Chlorination of Norbornene in Acetic Acid Means of Identification Retention Time Compound Nmr spectrum identical to the nmr spectrum C1 of an authentic sample of exo-2-chloro-0.8 norbornane; Mass spectrum (m/e 130,132) Nmr spectrum identical to that reported for 3-chloronortricyclene in reference 1.0 30; Mass spectrum (m/e 128,130) Nmr spectrum interpreted; Mass spectrum (m/e 154) -1.8 Nmr spectrum identical to that reported for trans-2,3-dichloronorbornane in reference 2.4 10; Mass spectrum (m/e 164,166,168) C1-C1 Nmr spectrum identical to that reported for anti-7-exo-2-dichloronorbornane in reference 3.2 30; Mass spectrum (m/e 164,166,168) 4.0 unknown C1 -Nmr spectrum identical to that reported for ÓAc anti-7-chloro-exo-2-norbornyl acetate in 6.9 reference 31; Mass spectrum (m/e 188,190) C1 Nmr spectrum identical to that reported for syn-7-exo-2-dichloronorbornane in reference 8.0 30; Mass spectrum (m/e 164,166,168) Nmr spectrum identical to that reported for OAc syn-7-chloro-exo-2-norbornyl acetate in 9.2 reference 31; Mass spectrum (m/e 188,190) Glpc retention time identical to that of

All retention times are in minutes relative to CH2Cl2 as solvent.

12.1

endo, endo-3,5-dichloronortricyclene already

discussed; Mass spectrum (m/e 162,164,166)

Table 4	1
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#### Chlorination of Norbornene in Acetic Acid

•	Relative Per Cent Yield by Weight				
	Norbornene + CH <sub>3</sub> CO <sub>2</sub> H +	+ Cl,	Norbornene + CH <sub>3</sub> CO <sub>2</sub> H + Cl <sub>2</sub>		
Compound	Large Scale	2	Small Scale		
$\Delta$					
	7.5				
<i>N</i> .					
CI	25.4		21.2		
<b>N</b>	,		•		
OAc		• .	•		
	1.3		· .		
<b>K</b>					
C1	•		•		
	1.1		0.9		
Cl—k čl		*			
C1					
	5.1	•	6.6		
~	•	•			
,					
unknown	1.1	•	0.9		
C Took			3		
OAc			•		
$\mathcal{M}$	4.0	_	5.7		
-CI					
,cı					
	40.9		48.0		
	40.5	•	48.0		
C1 OAc	• "		•		
		•			
	9.1		12.9		
N "	-				
	•				
	4.5		3.8		
C1 C1					

See Table 2 for details.

2 and 3, show the relative per cent yield of each product for the large scale and small scale reactions respectively.

## Scheme 13 Chlorination of Norbornene in Acetic Acid

$$\frac{\text{C1}_{2}; \text{ CH}_{3}\text{CO}_{2}\text{H};}{25^{\circ}\text{C}; \text{ dry N}_{2};} + \frac{\text{C1}}{25^{\circ}\text{C}; \text{ dry N}_{2};} + \frac{\text{120}}{25^{\circ}\text{C}; \text{ dry N}_{2};} + \frac{\text{C1}}{25^{\circ}\text{C}; \text{ dry N}_{2};} + \frac{\text{C1}}{25^{\circ}\text{C};} + \frac{$$

Compounds 41, 43, 115, and 42 were identified by comparing their respective nmr spectra with the nmr spectra of the products with similiar retention times from the chlorination of norbornene in methylene chloride. Compound 116 was not obtained in high enough yield for nmr analysis, but it was assigned the structure endo, endo-3,5-dichloronortricyclene (116) because its retention time was similiar to that of 116 obtained from the reaction of norbornene with chlorine in methylene chloride and because its mass spectrum was similiar to that of compound 116.

Compound 120 had an nmr spectrum identical to that of an authentic sample of exo-2-chloronorbornane, and its mass spectrum was consistent with the empirical formula  $C_7H_{11}C1$ .

Compound 121 was assigned the structure exo-2-norbornyl acetate based on the following observations. The mass spectrum of 121 showed a molecular ion consistent with the empirical formula  $C_9H_{14}O_2$ . Its nmr spectrum, by the absence of cyclopropyl and vinyl absorptions and by the presence of characteristic exo, endo, and bridgehead absorptions, indicated that the norbornyl skeleton was retained. The assignment of the absorptions was as follows:  $\delta$  4.2(multiplet, endo-C-2-H, 1H), 2.2(broad singlet, bridgehead hydrogens, 2H), 1.9(sharp singlet, methyl hydrogens, 3H), 1.0-1.8(norbornyl envelope, exo- and endo-C-3-H, exo- and endo-C-5-H, exo- and endo-C-6-H, exo- exo-

Compound 122 was assigned the structure anti-7-chloro-exo-2-norbornyl acetate and compound 123 was assigned the structure syn-7-chloro-exo-2-norbornyl acetate by their similiarity to reported nmr spectra of these two compounds 31 and by their mass spectra which were consistent with the empirical formula  $C_0H_{1,3}ClO_2$ .

Table 4 shows the per cent of each product for the large scale and for the small scale reactions. Compounds 120 and 121 were not detected in the small scale reaction. The only experimental differences in these two reactions were that the large scale reaction was carried out at significantly higher norbornene and chlorine concentrations.

## 4) A Check for Free Radical Products

Evidence that there was either no or an undetectable amount of free radical reaction in the chlorination was obtained. If a free radical mechanism operated to any significant degree, exo-5-chloronorbornene (39) and endo-5-chloronorbornene (40) would have been produced in

at least detectable quantities as reported by Poutsma. 10 Authentic samples of 39 and 40 were prepared, and none of the detectable products in the chlorination reactions had similiar retention times to 39 or 40. Possibly, 39 and 40, if produced, could react further to form trichlorides; however, there were no products detected by analytical glpc that had retention times expected from trichlorides.

#### C. Bromination of Norbornene

#### 1) Bromination of Norbornene in Methylene Chloride

The ionic bromination of norbornene (104) in methylene chloride was carried out using reaction conditions similiar to the ionic chlorination of 104 in methylene chloride. The reaction was performed in the dark at a low temperature (0°C) and with a low norbornene concentration. Dry nitrogen was passed throughout the reaction mixture for five minutes before the reaction and during the reaction.

In order to identify the products in the bromination of 104 in methylene chloride, a small scale reaction was performed. Analytical glpc (glpc 3, I) indicated that there were at least seven products. Scheme 14 shows the results of the reaction with the seven identified products listed in order of increasing retention time. Table 5 shows the retention times and mode of identification.

Authentic samples of exo-2-bromonorbornane (27), 2-bromonortricyclene (28), trans-2,3-dibromonorbornane (29), anti-7-exo-2-dibromonorbornane (30), and syn-7-exo-2-dibromonorbornane (33) were obtained from the ionic bromination of 104 in acetic acid as described later. These five compounds were used to identify by analytical glpc five of the pro-

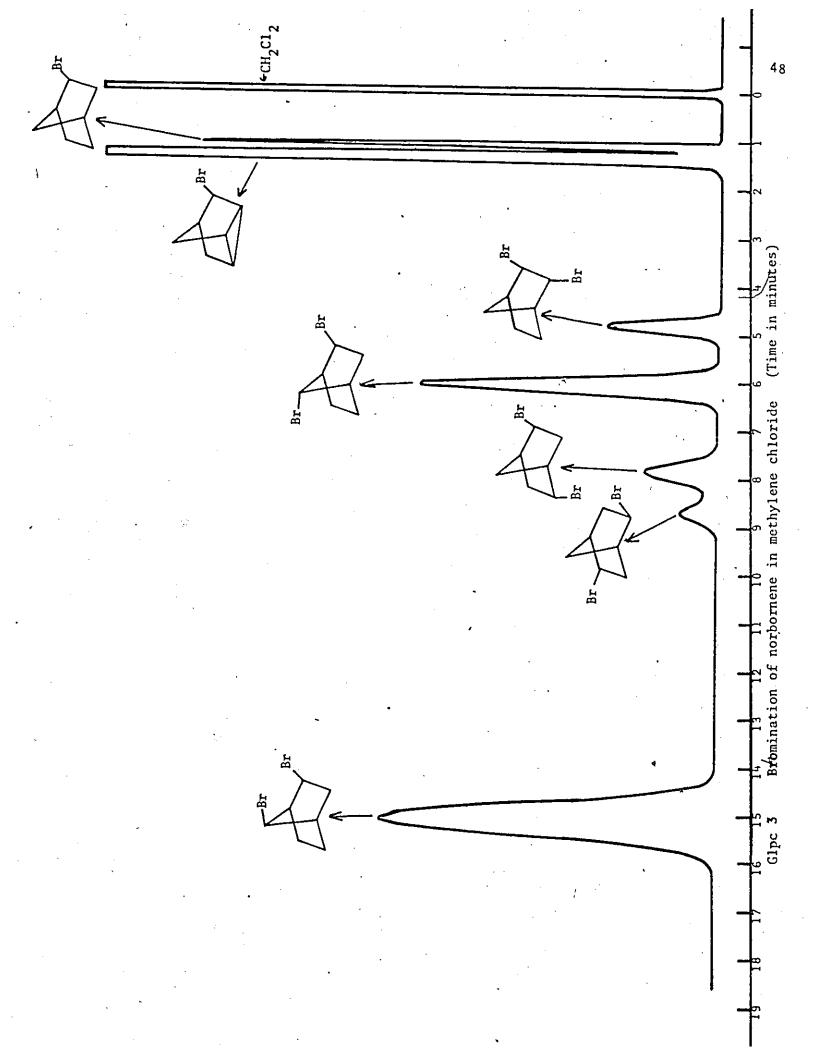


Table 5 Products from the Bromination of Norbornene in Methylene Chloride

Retention Time*	Compound	Means of Identification
- 1.1	Br	Retention time identical to that of an authentic sample of $exo-2$ -bromonorbornane
1.4	Br	Retention time identical to that of an authentic sample of 3-bromonortricyclene
4.8	$B_{r}$	Retention time identical to that of an authentic sample of trans-2,3-dibromonor-bornane
6.1	Br	Retention time identical to that of an authentic sample of anti-7-exo-2-dibromo-norbornane
7.8	Br	Retention time identical to that reported for endo-5-exo-2-dibromonorbornane in reference 7
8.7	Br	Retention time identical to that reported for $exo_1, exo_2, 5$ -dibromonorbornane in reference 7
15.2	· Br	Retention time identical to that of an authentic sample of syn-7-exo-2-dibromonorbornane

All retention times are in minutes relative to the solvent CH2Cl2.

## Scheme 14 Bromination of Norbornene in Methylene Chloride

ducts in the bromination of  $\underline{104}$  in methylene chloride.

The reaction mixture from the ionic bromination of 104 in methylene chloride was divided up and placed in six separate vials labelled 1,2,...,6. In addition, 27 was added to vial 1, 28 to vial 2, 29 to vial 3, 30 to vial 4, and 33 to vial 5. The retention times of each authentic sample of 27, 28, 29, 30, and 33 was determined by analytical glpc (I,150°C) and compared to the retention times of the products from the reaction of bromine with 104 in methylene chloride. The retention times of 27, 28, 29, 30, and 33 were identical to the retention times of the 1st, 2nd, 3rd, 4th, and 7th eluted products respectively. Repetition of the above by analytical glpc (II,150°C) produced similiar results. Also, the content of each vial was analyzed by analytical glpc (II,150°C). Each indicated the presence of seven different products, but the seven different products within each vial always had similiar retention times to the seven different products of each of the other vials. The only difference in the glpc results of each vial was that the ratio of products 27, 28, 29, 30, and 33 increased in vial 1, 2, 3, 4, and 5 respectively. Thus the lst, 2nd, 3rd, 4th, and 7th eluted

products were assumed to be 27, 28, 29, 30, and 33 respectively.

The five major products identified by Warnhoff et al. were identical to the five major products identified above. In addition, Warnhoff identified the following two minor products: endo-5-exo-2-dibromonorbornane (31) and exo, exo-2, 5-dibromonorbornane (32). By comparing the reported retention times of 31 and 32 with the retention times of the 5th and 6th eluted products of glpc 3, the 5th and 6th eluted products were assumed to be 31 and 32, respectively, because of the correspondence in retention times.

#### 2) Effect of Base

The ionic bromination of norbornene in methylene chloride was performed in the absence and also in the presence of pyridine. Table 6 shows the per cent of each product when no pyridine was present, when the concentration of pyridine was equal to that of norbornene (M/1), and when the concentration of pyridine was ten times the concentration of norbornene (M/1). These results show that exo-2-bromonorbornane was only produced when no pyridine was present. The other six products were identical except for changes in the product ratios.

#### 3) Bromination of Norbornene in Acetic Acid

The ionic bromination of norbornene (104) in acetic acid, which has yet to be reported, was carried out. The reaction conditions were similar to those used in the ionic bromination of norbornene in methylene chloride.

Table 6

# Bromination of Norbornene in Methylene Chloride

# Relative Per Cent Yield by Weight

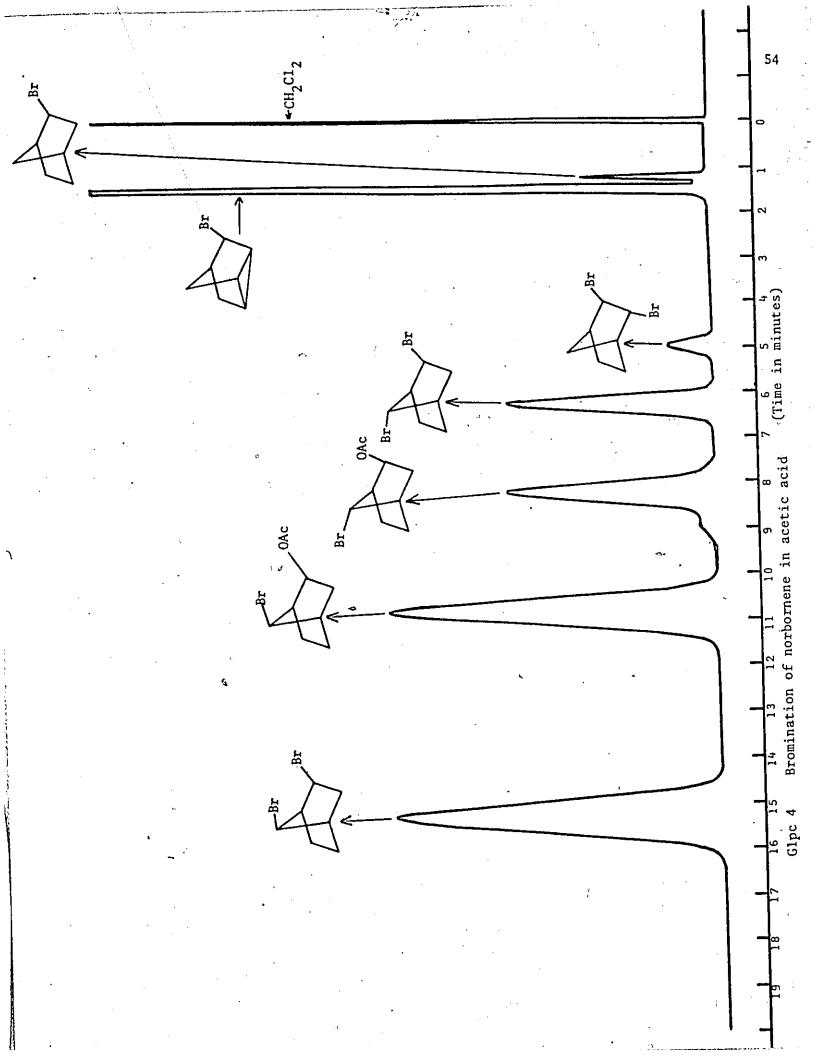
Compound	Norbornene + CH <sub>2</sub> Cl <sub>2</sub> + Br <sub>2</sub>	Norbornene + CH <sub>2</sub> Cl <sub>2</sub> + = pyridine + Br <sub>2</sub>	Norbornene + CH <sub>2</sub> Cl <sub>2</sub> + 10 X pyridine + Br <sub>2</sub>
	3r		
	3.2	0.0	0.0
			*
	31.5	40.0	44.0
•	· ·	•	-a
	Pr r	/	
Br	6.6	7.7	27.7
Br			
	Br 23.4	16.5	7.3
<u>.</u>			
- A	Br	•	
Er	6.5	3.3	1.2
N.	, '		
Br	Br 3.7	1.0	
	<b>4.</b> <i>.</i>	1.0	0.2
Br	Br		
	25.1	31.5	19.6

See Table 2 for details.

In order to identify the products, a large scale reaction was performed. Analytical glpc (glpc 4) showed there were at least eight products. The crude mixture was fractionated on a spinning band distillation column which resulted in partial separation of the components. From selected fractions of the mixture, seven relatively pure components were obtained by preparative glpc. Mass spectral analysis and nmr analysis were used to identify these seven products.

Scheme 15 shows the results of the reaction with the seven identified products listed in order of increasing retention time. Table 7 shows the retention times and mode of identification of seven products. Table 8 shows the per cent yield of each product for the small scale reaction.

The nmr spectra of the 1st, 3rd, 4th, and 8th eluted products were identical to those reported by Warnhoff for exo-2-bromonorbornane (27), trans-2,3-dibromonorbornane (29), anti-7-exo-2-dibromonorbornane (30), and syn-7-exo-2-dibromonorbornane (33) respectively. The mass spectrum of the 1st eluted product was consistent with the empirical formula  $C_7^H_{11}^{Br}$ ; each mass spectrum of the 3rd, 4th, and 8th eluted product was consistent with the empirical formula  $C_7^H_{10}^{Br}$ .



Table\_7 Products from the Bromination of Norbornene in Acetic Acid Retention Time Compound Means of Identification Nmr spectrum identical to that reported 1.1 for: exo-2-bromonorbornane in reference 32; Mass spectrum (m/e 174,176) Br Nmr spectrum interpreted; Glpc retention 1.4 time identical to that of 3-bromonortricyclene in reference 32; MS (m/e 172,174) Nmr spectrum identical to that reported for 4.8 trans-2,3-dibromonorbornane in reference 32; Mass spectrum (m/e 252,254,256) Br  $\mathtt{Br}$ Br Nmr spectrum identical to that reported for 6.1 anti-7-exo-2-dibromonorbornane in reference 32; Mass spectrum (m/e 252,254,256) OAc. Nmr spectrum interpreted; 8.1 Mass spectrum (m/e 232,234) 8.7 unknown OAc Nmr spectrum interpreted; 10.5 Mass spectrum (m/e 232,234) Nmr spectrum identical to that reported for 15.2 syn-7-exo-2-dibromonorbornane in reference 32; Mass spectrum (m/e 252,254,256)

All retention times are in minutes relative to the solvent CH2Cl2.

#### Table 8

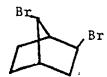
## Bromination of Norbornene in Acetic Acid

## Relative Per Cent Yield by Weight

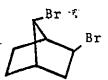
#### Compound

3.3





unknown



See Table 2 for details.

The mass spectrum of the 2nd eluted product was consistent with the empirical formula  $C_7H_9Br$ . The nmr spectrum of this product indicated the presence of the nortricyclyl skeleton by the absence of absorptions due to methyl and vinyl hydrogens and by characteristic absorptions of cyclopropyl hydrogens. The interpretation of the nmr spectrum of this product, which was assumed to be 3-bromonortricyclene, was as follows: 6 3.87(broad singlet, C-3-H, 1H), 2.08(broad singlet overlapping with the low field portion of doublet of C-7-H syn to bromide, bridgehead hydrogen at C-4, 1.36H), 2.00(doublet, C-7-H syn to bromide, J=10Hz, high field portion of doublet, 0.64H), and 1.60-1.06(broad multiplet, cyclopropyl hydrogens, exo- and endo-C-5-H, C-7-H anti to bromide, 6H).

The 5th and 7th eluted products, which were identified by nmr analysis and mass spectral analysis, were anti-7-bromo-exo-2-norbornyl acetate (124) and syn-7-bromo-exo-2-norbornyl acetate (125) respectively. The mass spectra of 124 and 125 were consistent with the empirical formula  $C_9H_{13}O_2Br$ . The nmr spectra of both 124 and 125 indicated the presence of the norbornyl skeleton by the lack of absorptions due to vinyl and cyclopropyl hydrogens and by the presence of characteristic exo, endo, bridgehead, and C-7-H absorptions.

The nmr spectrum of 124 was quite similiar to that of anti-7-chloro-exo-2-norbornyl acetate. The nmr spectrum of 124 had the following absorptions: δ 4.60 (quartet, endo-C-2-H is coupled to both the exo-C-3-H and endo-C-3-H, 1H), 4.12 (broad singlet, C-7-H syn to acetate, 1H), 2.33 (broad singlet, C-1-H and C-4-H, 2H), 1.90 (singlet, methyl group, 3H), and 2.17-0.83 (norbornyl envelope, exo- and endo-C-3-H, exo- and endo-

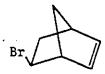
C-5-H, exo- and endo-C-6-H, 6H).

The nmr spectrum of 125 was quite similiar to that of syn-7-chloro-exo-2-norbornyl acetate (123). The nmr spectrum of 125 indicated the presence of the following absorptions: 6 4.60(multiplet, endo-C-2-H, 1H), 3.85(broad peak, anti-C-7-H, 1H), 2.50(broad singlet, C-1-H, 1H), 2.37 (broad singlet, C-4-H, 1H), 1.92(sharp singlet, methyl protons, 3H), and 2.20-1.00(norbornyl envelope, exo- and endo-C-3-H, exo- and endo-C-5-H, exo- and endo-C-6-H, 6H).

In comparing the results of the ionic bromination of norbornene in methylene chloride and acetic acid, it was noted that endo-7-exo-2-dibromonorbornane (31) and exo, exo-2,5-dibromonorbornane (32) were present as minor components in the former but not in the latter. The failure to detect 31 and 32 in the latter could be due to the fact that 124 has a retention time quite close to that of 31 and 32. In fact, the unidentified compound in the acetic acid experiment has a retention time of 8.7 minutes which is identical to that of 32 from the methylene chloride experiment. The isolation of 124 by preparative glpc included minor impurties, as detected by nmr analysis, and these could be due to the presence of minor amounts of 31 and 32.

#### 4) A Check for Free Radical Products

By analogy to the free radical chlorination of norbornene, detectable amounts of exo-5-bromonorbornene (126) and endo-5-bromonorbornene would be produced if free radical bromination occurred to any significant degree. In order to check for this possibility, compounds 126 and 127 were synthesized by heating vinyl bromide and cyclopentadiene in a sealed





126

127

glass tube for 15 hours at 220°C. None of the peaks detected by glpc in the ionic bromination of norbornene in methylene chloride or in acetic acid had retention times similiar to those of 126 and 127. However, 126 and 127 could further react to form tribromides which would be expected to have retention times greater than those of dibromides. When glpc analysis was performed on both reaction mixtures, there was no indication of products which could be tribromides.

#### D. Addition of Iodine Monochloride to Norbornene

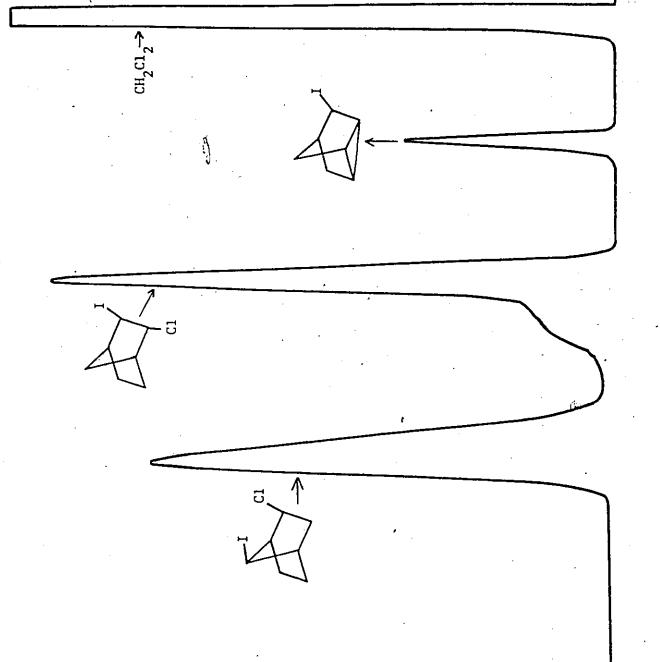
# 1) Addition of Iodine Monochloride to Norbornene in Methylene Chloride

In order to identify the products, a large scale reaction between iodine monochloride and norbornene (104) in methylene chloride and pyridine was performed. The experimental conditions were kept identical to those of the analogous ionic chlorination and ionic bromination in order to minimize the formation of free radical products and to maximize the formation of ionic products.

Analytical glpc (glpc 5) showed: there were three major products which were identified as 3-iodonortricyclene (128), exo-2-iodo-endo-3-chloronorbornane (129), and syn-7-iodo-exo-2-chloronorbornane (130).

Scheme 15 shows the details of the reaction. Table 9 shows the retention times, mode of identification, and product ratios for the products of the reaction.

The partial separation of the three major products was done by



hloride	Relative Per Cent Yield by Weight **	Norbornene + = pyridine $CH_2CI_2 + ICI$	,	40	œ	40
Iodine Monochlorination of Norbornene in Methylene Chloride		Compound Means of Identification	Nmr spectrum identical to that reported for 3-jodonortricyclene in reference 33;  Mass spectrum (m/e 220)	Nmr spectrum interpreted; Chemical techniques; Mass spectrum (m/e 256,258)	unknown	I Nmr spectrum interpreted; C1 Chemical techniques; Mass spectrum (m/e 256,258)
Table 9		Retention Time	3.6	9.9	7.3	11.0

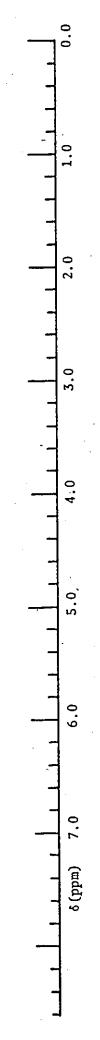
\*\* The analytical glpc was calibrated for response differences between non-isomeric compounds and these differences were corrected for in determining the yield based on 100%. All retention times are in minutes relative to the solvent  $\mathtt{CH}_2\mathtt{Cl}_2$ .

vacuum distillation through a 1.5 foot vacuum jacketed Vigreux column giving six fractions. Fraction 1, b.p. 46-52°C (3.8mm), contained 3-iodonortricyclene (128) plus some unknown minor components; fraction 2, b.p. 56-58°C (3.6mm), contained 128 (90%) pure by glpc analysis); fraction 3 and 4, b.p. 48-50°C (2.5mm), contained exo-2-iodo-endo-3-chloronorbornane (129) and syn-7-iodo-exo-2-chloronorbornane (130); fraction 5, b.p. 50-53°C (4.0mm), contained 130 (95% pure by glpc analysis); fraction 6, b.p. 50-56°C (2.5mm), contained 130 (90% pure by glpc analysis). In order to obtain 128, 129, and 130 in higher purity, they were collected by preparative glpc (III,150°C).

The first eluted component was identified to be 3-iodonortricyclene (128) based on the following information. Its mass spectrum was consistent with the empirical formula C<sub>7</sub>H<sub>9</sub>I, and its nmr spectrum (nmr 3, 60MHz, CCl<sub>4</sub> and TMS) was identical to that reported by Diner<sup>33</sup> et al. for 128. Since the reported nmr spectrum of 128 was not analyzed in very much detail, a more thorough interpretation is given as follows: 6 3.77(singlet, C-3-H, 1H), 2.10(singlet overlapping with doublet which was the low field portion of an AB quartet, C-4-H and C-7-H syn to the iodide, 2H), and 1.67-0.97(nortricyclyl envelope, C-1-, C-2-, C-6-, C-7-, exo-C-5-, and endo-C-5-H, 6H).

The second eluted product and the third eluted product were assumed to be chloroiodonorbornanes based on the following information. Each





Nnr spectrum 3 3-Iodonortricyclene

mass spectrum was consistent with the empirical formula  $C_7H_{10}CII$ . Their nmr spectra (4,5) indicated the presence of the norbornane skeleton by virtue of the complete absence of any absorptions attributable to methyl, cyclopropyl, and vinyl groups and by the presence of characteristic exo, endo, and bridgehead proton resonance patterns.

The stereochemistry of exo-2-iodo-endo-3-chloronorbornane (129) was established by chemical means and by its nmr spectrum. Diagram 1

#### Diagram 1

t-Bu0
$$^-$$
K $^+$ ; t-Bu0H

LAH

LAH

$$\frac{131}{C1}$$

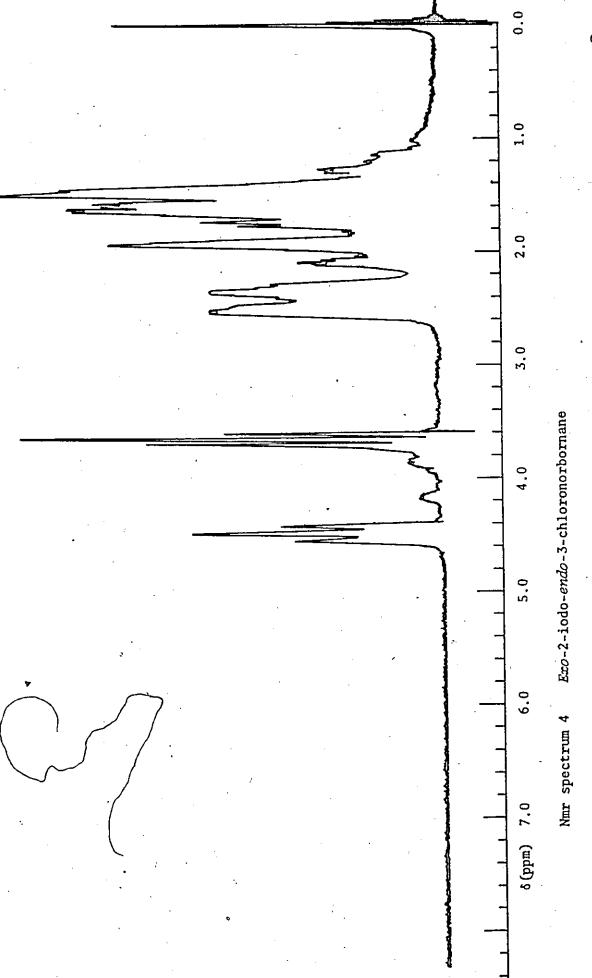
$$\frac{129}{(n-Bu)_3SnH}$$

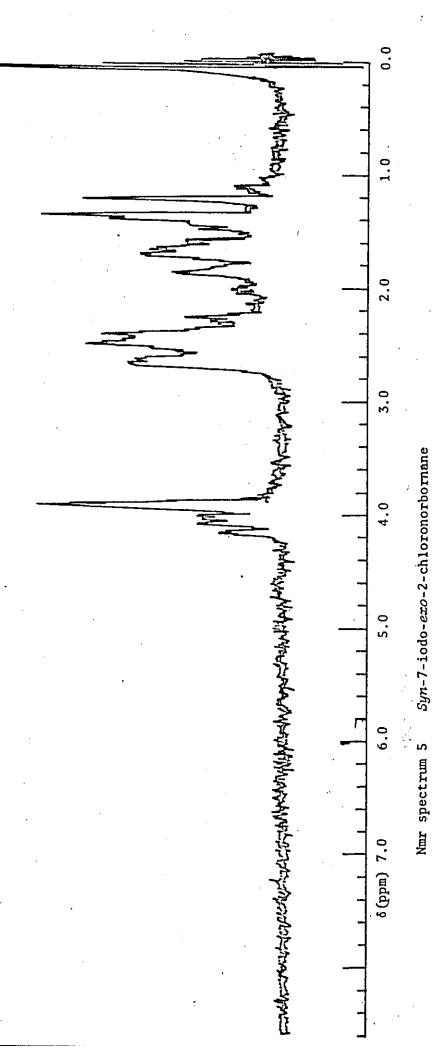
132

shows the chemical reactions performed on 129. The reaction of 129 with approximately 1M potassium t-butoxide in t-butanol produced 2-chloronor-bornene (131) as the major product. When 129 was reduced with lithium aluminium hydride, endo-2-chloronorbornane (132) was the major product. The reaction of 129 with tri-n-butyltin hydride resulted in the formation of 132 as the major product. These results are consistent with the assigned stereochemistry of exo-2-iodo-endo-3-chloronorbornane (129).

The nmr spectrum of 129 (nmr spectrum 4, neat, 60MHz, TMS) showed







the following absorptions: 6 4.48(triplet, J-3.0,3.0Hz, exo-C-3-H, 1H), 3.65(triplet, J=3.0,3.0Hz, endo-C-2-H, 1H), 2.53 and 2.37(broad singlets, bridgehead hydrogens, 2H), 2.13-1.10(norbornyl envelope, exo-and endo-C-5-H, exo- and endo-C-6-H, syn- and anti-C-7-H, 6H).

The stereochemistry of syn-7-iodo-exo-2-chloronorbornane (130) was established by chemical means (diagram 2) and by its nmr spectrum (5, neat, 60MHz, TMS). To establish that the iodine was syn to the chloride, compound 130 was reacted with an approximately 1M solution of potassium t-butoxide in t-butanol. This produced three major products identified

#### Diagram 2

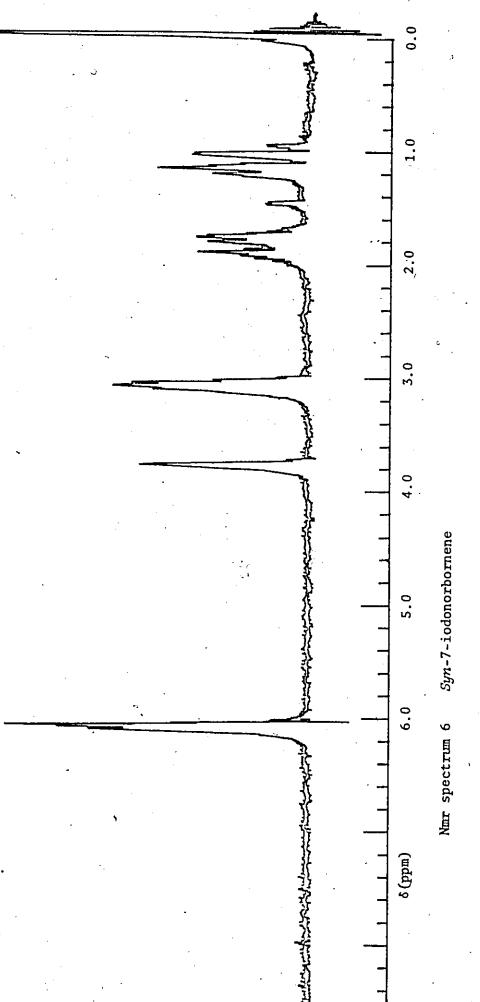
as syn-7-iodonorbornene (133), anti-7-t-butoxynorbornene (134), and endo-2-t-butoxytricyclo[4.1.0.0<sup>3,7</sup>]heptane (135). To establish that the stereo-chemistry of chloride was exo, the following reaction was performed. Compound 130 was reacted with tri-n-butyltin hydride resulting in the production of exo-2-chloronorbornane (120) as the major product.

The nmr spectrum of  $\underline{130}$  (nmr 5) showed the following absorptions:  $\delta$  4.03(multiplet, endo-C-2-H, 1H), 3.90(broad singlet overlapping with endo-C-2-H, anti-C-7-H, 1H), 2.73-1.67(norbornyl envelope, C-1-H, C-4-H, exo- and endo-C-3-H, exo- and endo-C-5-H, exo- and endo-C-6-H, 8H). The broad singlet at  $\delta$  3.90 is that expected from a proton which is  $\alpha$  to a substituent at C-7. The multiplet at  $\delta$  4.03 is in agreement with an endo hydrogen based on its chemical shift and on the characteristic sharpness of its resonance lines. 34

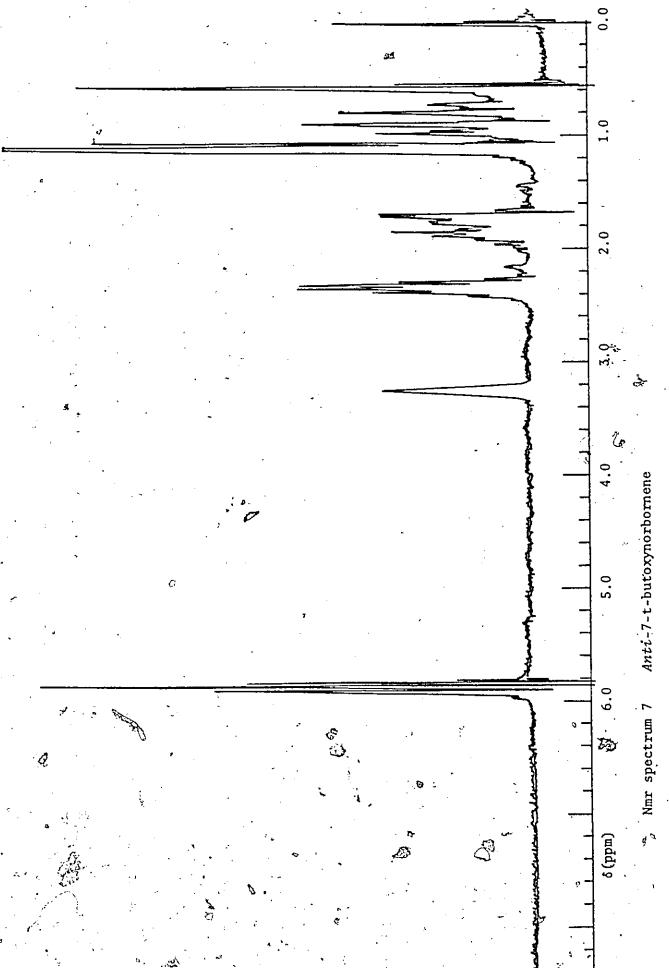
The nmr spectra of syn-7-iodonorbornene (133), anti-7-t-butoxynorbornene (134), and endo-2-t-butoxytricyclo{4.1.0.0 $^3$ ,7}heptane (135) are described below. The nmr spectrum of 133 (nmr 6, 60MHz, CS, and TMS) showed the following signals: & 6.15(multiplet, olefinic hydrogens, 2H), 3.82 (multiplet, anti-C-7-H, 1H), 3.13 (multiplet, bridgehead hydrogens, 2H), 2.00-0.97 (multiplets, lower field multiplet consisting of exo-C-5-H and exo-C-6-H, higher field multiplet consisting of endo-C-5-H and endo-C-6-H, 4H). The nmr spectrum of  $\underline{134}$  (nmr 7, 60MHz, CS<sub>2</sub> and TMS) showed the following signals: 6 5.88(triplet, J=1.5,1.5Hz, olefinic hydrogens, 2H), 3.25(broad singlet, syn-C-7-H, 1H), 2.35(multiplet, bridgehead hydrogens, 2H), 1.95-1.67 (multiplet, exo-C-5-H and exo-C-6-H, 2H), 1.10 (singlet, methyl protons, 9H), and 1.00-0.70(multiplet, endo-C-5-H and endo-C-6-H, 2H). The nmr spectrum of 135 (nmr 8, 60MHz, CS, and TMS) showed the following signals: 6 3.98(quartet, J=4.0,4.0,4.0Hz, exo-C-2-H coupled to C-1-, C-3-, and C-6-H, 1H), 2.50(multiplet, C-3-H, 1H), 2.10-1.20 (multiplet, norbornyl envelope including cyclopropyl hydrogens, 7H), and 1.10(singlet, methyl hydrogens of t-butoxy group, 9H).

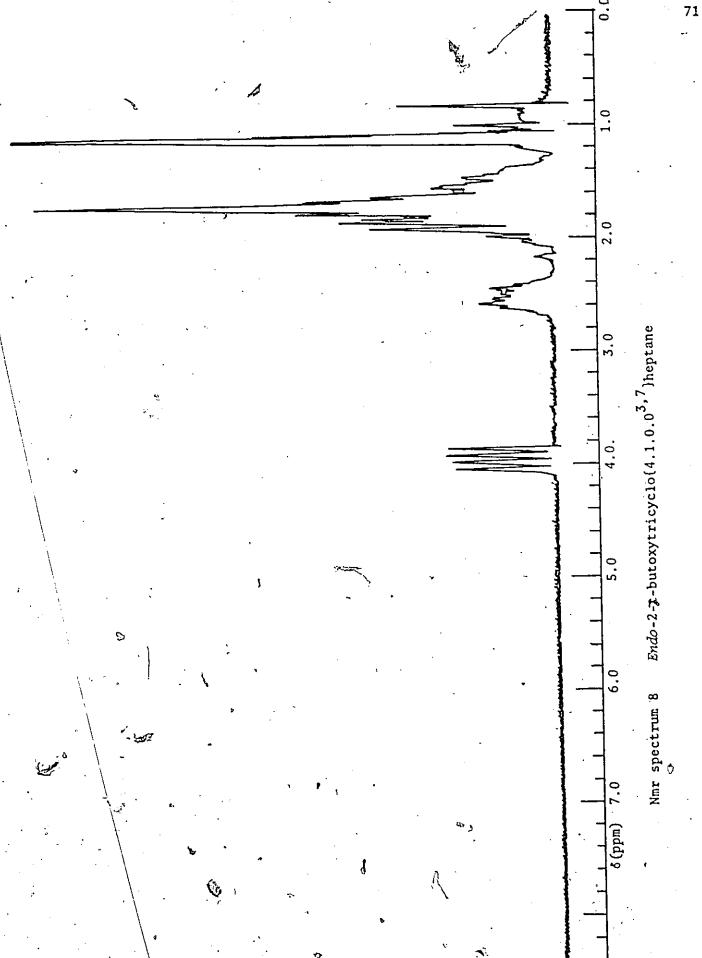
For the purpose of identifying exo-2-chloronorbornane ( $\underline{120}$ ) and











endo-2-chloronorbornane (132) as products, they were synthesized as follows: norbornene in pentane was reacted with hydrogen chloride at -78°C to yield 120 as the major product; 35 diimide and 2-chloronorbornene were reacted to yield 132.

# 2) Reaction of Syn-7-iodonorbornene with Potassium t-Butaxide in t-Butanol

Syn-7-iodonorbornene (133) was reacted with an approximately 1M solution of potassium t-butoxide in t-butanol. Analytical glpc (1,150°C) indicated that two major products were formed. One of these products had a retention time identical to that of anti-7-t-butoxynorbornene (134) and the other had a retention time identical to that of endo-2-t-butoxytricyc-lo{4.1.0.0<sup>3</sup>,7}heptane (135); therefore, they were assumed to be 134 and 135. Shown below are the results of the reaction.

Syn-7-iodonorbornene (133) was used by F. S. Clark<sup>37</sup> to synthesize anti-7-iodonorbornene (136) via photochemical syn-anti isomerization.

Compound 133 and iodine were dissolved in n-hexane which contained a trace of methylene chloride as an internal standard. Irradiation (254nm) of the solution in a quartz nmr tube at 30°C was carried out in a Rayonet reactor.

After 6.8 hours, there was no change in the relative intensities of the peaks in the C-7-H region of the nmr spectrum. The glpc of the recovered oil showed a syn:anti iodide ratio of 1:1.5. These two studies describe the first reported synthesis of these compounds.

# 3) Addition of Iodine Monochloride to Norbornene in Acetic Acid

Iodine monochloride was reacted with norbornene (104) in acetic acid using experimental conditions similiar to those used in the analogous ionic chlorination and ionic bromination. Analytical glpc (glpc 6, 1, 150°C) indicated the presence of a large variety of products. By comparing the retention times of 3-iodonortricyclene (128), exo-2-iodo-endo-3-chloronorbornane (129), and syn-7-iodo-exo-2-chloronorbornane (130) with those of the products of the above reaction, it was shown that three of the products had retention times identical to the retention times of 128, 129, and 130. Further verification was performed only on the compound having a retention time identical to that of 128. The mass spectrum of this compound and its nmr spectrum were identical to the mass spectrum and to the nmr spectrum of 128.

#### E. Reactions with Dideuterated Norbornenes

In order to obtain stereochemical information on the mechanism of ionic 1,3-elimination, the following substrates were halogenated: exo, exo-5,6- $d_2$ -norbornene, endo, endo-5,6- $d_2$ -norbornene, and 2,3- $d_2$ -norbornene. The information obtained from the chlorinations, brominations, and iodo monochlorinations is listed in Tables 10, 11, and 12, respectively.

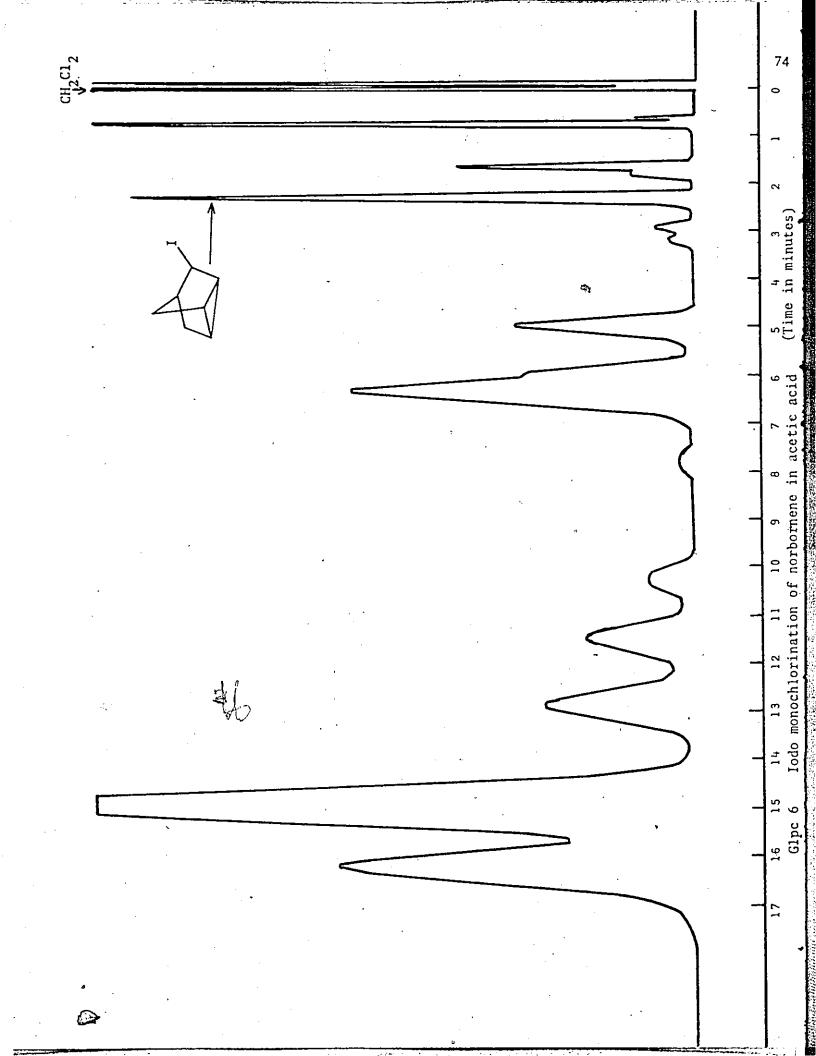


Table 10 Chlorination of Dideuterated Norbornenes (continued on next page)

Entry	Substrate	Concentration of Substrate (M/1)	•	Conditions*	% Loss of One Deuterium
1	eω,eω-5,6-d <sub>2</sub> - norbornene (105)	2.2 X 10 <sup>-2</sup>	o°C;	CH <sub>2</sub> C1 <sub>2</sub>	30
2	105	7.8 X 10 <sup>-2</sup>	0°C;	CCl <sub>4</sub> ; = pyridine	29
3**	<u>105</u>	8.4 X 10 <sup>-2</sup>	O°C;	CC1 <sub>4</sub> ; = pyridine	28
4 <b>*</b>	<u>105</u>	8.4 X 10 <sup>-2</sup>	0°C;	CC1 <sub>4</sub> ; = pyridine	29
5	<u>105</u>	2.2 X 10 <sup>-2</sup>	o°C;	CH <sub>2</sub> Cl <sub>2</sub> ; 10 X pyridine	30

The term " = pyridine " means the pyridine and the norbornene concentration were equal, and the term "  $10 \times 10 \times 10^{-10}$  M means the pyridine concentration was ten times the concentration of norbornene.

A solution of Cl<sub>2</sub>, of equivalent molarity to the norbornene, in the appropriate solvent was added to the norbornene with pyridine as a base unless otherwise stated. All reactions were carried out in the dark with dry nitrogen being bubbled throughout the solution containing the norbornene.

<sup>\*</sup> Cl<sub>2</sub> gas was swept directly into the solution with dry N<sub>2</sub>.

Table	Substrate	Concentration of Substitate	. Conditions *	Loss of
Liicky	Jungtrace	M/2)		One Deuterium
6	exo, exo-5, 6-d <sub>2</sub> - norbornene (105)	2.4 X 10 <sup>-2</sup>	25°C; CH <sub>3</sub> CO <sub>2</sub> H	35
7	endo, endo-5,6-d <sub>2</sub> - norbornene (106)	2.2 X 10 <sup>-2</sup>	o°c; cH <sub>2</sub> C1 <sub>2</sub>	59
8	<u>106</u>	4.1 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub> ; = pyridine	60
9	<u>106</u>	4.0 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub> ; = pyridine	59
10	106	4.0 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub> ; = pyridine	<b>59</b>
11	<u>106</u>	2.0 X 10 <sup>-2</sup>	ObC; CH2Cl2; 10 X pyridine	59
. 12	<u>106</u> .	2.4 X 10 <sup>-2</sup>	25°С; СН <sub>3</sub> СО <sub>2</sub> Н	44
13	2,3- $d_2$ -norbornene (107)	2.6 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub> ; = pyridine	2

Table 11 Bromination of Dideuterated Norbornenes (continued on next two pages)

Entry	Substrate	Concentration of Substrate (M/1)	Conditions*	% Loss of One Deuterium
1	exo, exo-5, 6-d <sub>2</sub> - norbornene (105)	2.1 X 10 <sup>-2</sup>	o°c; $\text{CH}_2\text{Cl}_2$	53
2	105	2.3 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> C1 <sub>2</sub>	53
3	105	6.0 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub> ; = pyridine	46
4	105	55.0 X 10 <sup>-2</sup>	0°C; CCl <sub>4</sub> ; = pyridine	44
5	105	10.0 X 10 <sup>-2</sup>	25°C; CCl <sub>4</sub> ; = pyridine	41
6	105	2.0 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub> ; 10 X pyridine	49

 $\phi$ 

The term " = pyridine " means the pyridine and the norbornene concentration were equal, and the term " 10 X pyridine " means the pyridine concentration was ten times the concentration of norbornene.

A solution of Br<sub>2</sub>, of equivalent molarity to the norbornene, in the appropriate solvent was added to the norbornene with a base when specified. All reactions were carried out in the dark with dry nitrogen being bubbled throughout the solution containing the norbornene.

Table 1	<u>.1</u>	Concentration	·	÷
Entry	Substrate	of Substrate (M/1)		% Loss of One Deuterium
7	105	2.7 X 10 <sup>-2</sup>	25°C; сн <sub>3</sub> ω <sub>2</sub> н	47
8	105	2.7 X 10 <sup>-2</sup>	25°C; СН <sub>3</sub> СО <sub>2</sub> Н	51
en 9 no	<i>do,endo-</i> 5,6- <i>d</i> rbornene ( <u>106</u>	2 <sup>-</sup> 2.3 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub>	12
10	<u>106</u>	0.2 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub> ; = pyridine	23
11 .	<u>106</u>	0.2 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub> ; = pyridine	24
12	106	0.2 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub> ; = pyridine	27
13	106	0.2 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub> ; = pyridine	28
14"	<u>106</u>	7.0 X 10 <sup>-2</sup>	0°C; CCl <sub>4</sub> ; = pyridine	26
15	<u>106</u>	16.0 X 10 <sup>-2</sup>	0°C; CC1 <sub>4</sub> ; = pyridine	25

Table 11		• .		<b>79</b>	-
Entry	Substrate	Concentration of Substrate (N/1)	Conditions *	% Loss of One Deuteriu	
16	106	2.0 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub> ; 10 X pyridine	21	
17	106	2.6 X 10 <sup>-2</sup>	25°C; CH <sub>3</sub> CO <sub>2</sub> H	17	· /
18	106	1.0 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub> ; = 2,6-Lutidine	18	
19	<u>106</u>	0.9 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub> ; = 2,6-Lutidine	17	
20	<u>106</u>	0.9 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub> ; = 2,6-Lutidine	18	
21	<u>106</u>	0.2 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub> ; = pyridine	13	
 . 2, 22	3-d <sub>2</sub> -norbor- nene ( <u>107</u> )	2.5 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub> ; = pyridine	, <b>0</b>	•
23	<u>107</u>	2.6 × 10 <sup>-2</sup>	0°C; CH <sub>2</sub> Cl <sub>2</sub> ; = pyridine	0	
	•				•
ŕ		i			

Table 12 Iodo Monochlorination of Dideuterated Norbornenes

Entry	Substrate	Concentration of Substrate (1/1)	Conditions	% Loss of One Deuterium
1	exo, exo-5, 6-d <sub>2</sub> - norbornene (105)	2.2 X 10 <sup>-2</sup>	O°C: CH <sub>2</sub> Cl <sub>2</sub>	48
. 2	<u>105</u>	3.6 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub> ; = pyridine	48
3	<u>105</u>	2.3 X 10 <sup>-2</sup>	25°C; СН <sub>3</sub> CO <sub>2</sub> H	53
4	endo, endo-5, 6-d <sub>2</sub> - norbornene (106)	4.0 X 10 <sup>-2</sup>	o°C; CH2C12	18
· 5	<u>106</u>	3.5 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub> ; = pyridine	16
6	<u>106</u>	2.1 X 10 <sup>-2</sup>	25°C; CH <sub>3</sub> CO <sub>2</sub> H	21
~ 7	2,3-d <sub>2</sub> -norbor- nene ( <u>107</u> )	3.3 X 10 <sup>-2</sup>	O°C; CH <sub>2</sub> Cl <sub>2</sub> ; = pyridine	2

A solution of ICl, of equivalent molarity to the norbornene, in the appropriate solvent was added to the norbornene with a base when specified.

All reactions were carried out in the dark with dry nitrogen being bubbled throughout the solution containing the norbornene.

The term " = pyridine " means the pyridine and the norbornene concentration were equal, and the term " 10 X pyridine " means the pyridine concentration was ten times the concentration of norbornene.

CHAPTER 3
DISCUSSION

#### A. Cyclic Halonium Ions

# 1) Nature of Initial Attack of a Halogen or an Interhalogen on Norbornene

When the experimental conditions favour an ionic reaction, the electrophilic character of an attacking halogen <sup>38</sup> or an interhalogen in its initial attack on norbornene is beyond contention. The most direct evidence for this assumption comes from the study of the effect of structure on the rate of halogen addition to olefinic systems. C. K. Ingold in discussing bromine addition showed that the reaction was facilitated by electron release to the reaction centre and retarded by electron withdrawal. For chlorine addition, the most extensive documentation comes from studies by Roberston <sup>42-56</sup> et al. of the kinetics and rates of addition of chlorine in acetic acid.

The experimental evidence (vide infra) suggests that the true electrophile in the chlorination of electrons in hydroxylic solvent consists of the electrophilic and of the nucleophilic fragment of the attacking chlorine molecule. To date, there is no evidence for either Cl<sup>+</sup> or Cl<sub>2</sub> cations as stable species in solution. In addition, the second order kinetic form (equation 1) for these reactions, together with the absence of rate-retarda-

$$-\frac{d\{Cl_2\}}{dt} = k_1\{olefin\}\{Cl_2\}$$

tion by added chloride ions, shows that the transition state contains the chlorine molecule. However, the nature of the true electrophile in non-

hydroxylic solvent is made obscure because of the non-reproducibility of kinetic studies and because of the effects of trace amounts of catalysts.

A difficulty in determining the true electrophile in the bromination of olefins in hydroxylic solvent is that the nature of the electrophile is dependant on concentration and solvent. The bromination 42,58-60 in sufficiently dilute bromine in aqueous and alcoholic solvent is of the second order kinetic form (equation 2). Since there is no evidence 57 for the Br<sup>+</sup>

$$-\frac{d\{Br_2\}}{dt} = k_1\{olog(n)\}\{Br_2\}$$

cation, it is quite likely that the electrophile, analogous to the chlorination reaction, consists of the electrophilic and the nucleophilic fragment of the attacking bromine molecule. However, in the concentration-region M/40 in acetic acid, addition of bromine 42,49,51 to unsaturated compounds proceeds by third order kinetics (equation 3). The existence of

$$-\frac{d\{Br_2\}}{dt} = k_1\{olofin\}\{Br_2\}^2$$

 $\mathrm{Br}_3^+$  cations  $^{57}$  has been established in the fluorosulphuric acid solvent system. The true electrophile could be the  $\mathrm{Br}_3^+$  cation formed by the preequilibrium as shown in equation 4. Alternatively, a two stage mechanism

$$Br_2 + Br_2 \Longrightarrow Br_3^+ + Br^-$$

(equation 5) could produce third order kinetics. The first stage is

-6

analogous to the chlorination reaction resulting in the formation of an olefin, bromine intermediate. The role of the second molecule of bromine could be the removal of a bromide ion from this intermediate. Alternatively, it could be thought of as a nucleophile completing the addition. The determination of the true electrochile in non-hydroxylic solvent is hampered because of experimental difficulties. In carbon tetrachloride several mechanisms are available. For the addition of bromine in ethylene chloride as solvent, reproducible results were obtained only when the solvent contained tetramethylammonium tribromide.

The addition of iodine monochloride to olefins has received very little mechanistic investigation. White and Roberston 44 have established that the reaction does obey third order kinetics (equation 6). There is

$$-\frac{d\{IC1\}}{dt} = k_1\{olefin\}\{IC1\}^2$$

no evidence for I cations as stable species in solution, but evidence does exist for  $I_3^+$  cations  $^{63,64}$  in fluorosulphuric acid and in 100% sulphuric acid, for  $I_2^+$  cations  $^{65}$  in fluorosulphuric acid, and for  $IC1_2^+$  cations  $^{66}$ .

# 2) Nature of Halonium Ion Intermediates

The first formed intermediate in each of the following reactions, the chlorination, the bromination, and the iodo monochlorination of norbornene, can be considered as being composed of a molecule of norbornene and of a

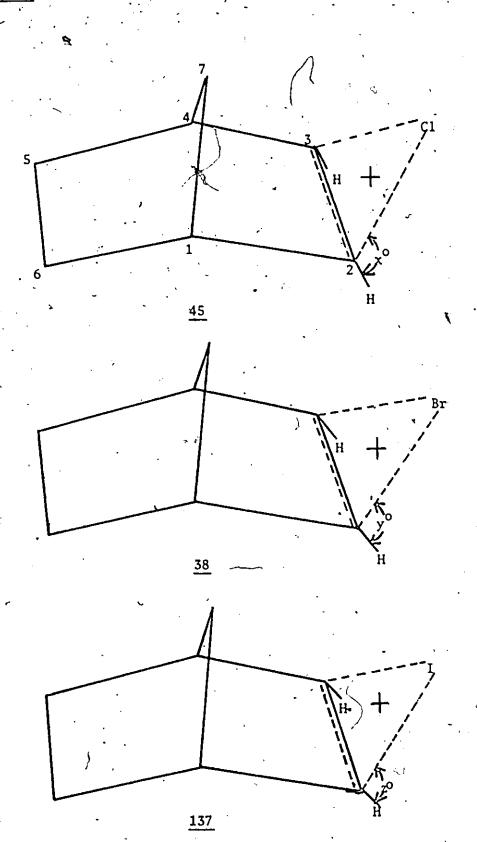
C1<sup>+</sup> cation, of a Br<sup>+</sup> cation, and of a I<sup>+</sup> cation respectively. The first postulation of a similiar type of three-membered ring halonium ion intermediate was by Roberts and Kimball<sup>67</sup>. This was used to explain their observation that in many instances of electrophilical alogen addition a vicinal dihalide is produced by trans addition.

Structures 45, 38, and 137, in diagram 3 indicate the stereochemistry of the cyclic norbornyl halonium ions which result from exo attack of the electrophiles  $C1^+$ ,  $Br^+$ , and  $I^+$  respectively on norbornene. Before perturbation by the incoming electrophile, the following five sigma bonds all lie in the same plane: C-2-H; C-3-H; C-1-C-2; C-4-C-3; C-2-C-3. After the electrophile has perturbed the double bond, resulting in the formation of a cyclic norbornyl halonium ion, the C-2-H and C-3-H bonds are bent out of the original plane (rehybridization). The amount of bending depends on the strength of the interaction between the electrophile and olefin. Extended Huckel  $^{68}$  calculations on symmetrical halonium ions predicate that the strength of this interaction is in the following order:  $C1^+ > Br^+ > I^+$ . Thus in structures 45, 38, and 137,  $x^0 > y^0 > z^0$  in agreement with the following order of electronegativities:  $C1^+ > Br^+ > I^+$ .

In structure 45, the olefin and Cl interact very strongly. The chlorine utilizes mostly its 3p orbitals and partially its 3s orbitals.

The contribution of the p<sub>z</sub> orbitals to the double bond has been significantly reduced and a substantial positive charge has accumulated on C-2 and on C-3. Thus a highly reactive intermediate exists and it is susceptible to the following three reactions. It can undergo nucleophilic attack to form a trans-2,3-disubstituted norbornane. It can undergo ring opening. It can

#### Diagram 3



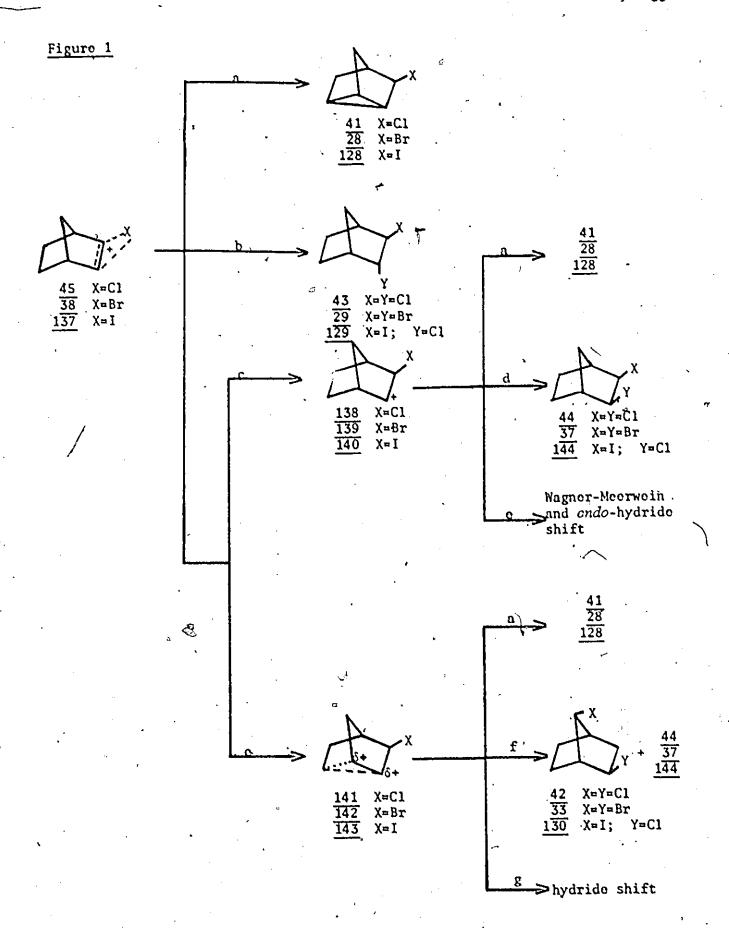
undergo 1,3-elimination to form 3-chloronortricyclene.

In structure 38, the olefin and Br interact strongly, but not as strongly as olefin and Cl. The positive charge is more evenly distributed over the cyclic three-membered ring than in structure 45 as would be expected on the basis of the relative electronegativity of Br which has perturbed the olefin to a lesser extent than Cl. The 4s orbital contribution of Br is less than that of Cl. Thus a highly reactive intermediate, although not as reactive as the corresponding chloronium intermediate, exists that is susceptible to the following three reactions. It can undergo nucleophilic attack to form a trans-2,3-disubstituted norbornane. It can undergo ring opening. It can undergo 1,3-elimination to form 3-bromonortricyclene.

In structure 137, the olefin and  $I^+$  ion interact the least strongly of the three cyclic norbornyl halonium ions as would be expected by the order of electronegativities of the three halogens. The 5s orbital contribution of  $I^+$  is less than that of the corresponding  $Br^+$ . Intermediate 137 can undergo the same three reactions that both 45 and 38 can undergo.

### 3) Reactions of Cyclic Halonium Ions

From the accumulated data of previous investigators and from the products identified in the present investigation, it is evident that each of the three cyclic norbornyl halonium ions 45, 38, and 137, can undergo any of the following three reactions: a) 1,3-elimination of an endo-hy-drogen 4,5 to form its respective nortricyclyl halide; b) trans\_nucleophi-



lic attack to form its respective trans-2,3-dihalonorbornane; c) ring opening to form its respective unsymmetrical exo-3-halonorbornyl cation (as shown in Figure 1). If the unsymmetrical exo-3-halonorbornyl cations are considered as being classical ions, then ring opening of ions 45, 38, and 137 results in the following classical exo-3-halonorbornyl cations: 138, 139, and 140 respectively. On the other hand, if the unsymmetrical exo-3-halonorbornyl cations are considered as being non-classical ions, then ring opening of ions 45, 38, and 137 results in the following nonclassical cations 141, 142, and 143 respectively. Furthermore, each classical ion: 138, 139, and 140 can subsequently undergo any of the following three reactions; , a) 1,3-elimination of an ando-hydrogen4,5 to form its corresponding nortricyclyl halide; d) exo-nucleophilic attack to form its corresponding exo, exo-2,3-dihalonorbornane; e) Wagner-Meerwein and/or endo-hydride shift to yield additional open classical halonorbornyl cations which, in theory, can subsequently undergo reactions "a", "d", and "o" (see Figure 1). If the non-classical ion interpretation is considered, then each 3-halonorbornyl cation 141, 142, and 143 can subsequently undergo any of the following three reactions: a) 1,3-elimination of a hydrogen<sup>4,5</sup> to form its respective nortricyclyl halide; f)  $o\infty$ -nucleophilic attack on either of two carbon atoms to form the corresponding dihalonorbornanes; g) hydride shift to yield additional nonclassical 3-halonorbornyl cations, which might subsequently undergo reactions "a", "f", and "g",

### a) 1,3-Elimination from Cyclic Norbornyl Halonium Ions

Marshall 32 has postulated that whenever norbornene and bromine are

that one of the routes for the formation of nortricyclyl bromide (28) is via 1,3-elimination of a hydrogen from the cyclic norbornyl bromonium ion (38). Thus it would be reasonable to suppose that cyclic norbornyl halonium ions 45 and 137 would lead to formation of at least some of the nortricyclyl chloride (41) and nortricyclyl iodide (128) respectively.

Of paramount relevance is the result of a recent investigation by N. H. Nerstiuk<sup>4,5</sup> which showed that the endo to exp preference is at least 15:1 for 1,3-elimination of hydrogen from a locked norbornyl cation. Since the original exp and endo distinction is maintained in each of the ions 45, 38, and 137 and if the elimination takes place solely from each of those ions, then an endo to exp specificity of about 15:1 should be observed when 1,3-elimination occurs. The present investigation was undertaken to gain mechanistic information on the 1,3-elimination process for the Cl<sup>+</sup>, Br<sup>+</sup>, and I<sup>+</sup> addition to norbornene in various solvents under different reaction conditions.

## c) Ring Opening of Cyclic Norbornyl Halonium Ions

As already described earlier, the ring opening of the cyclic nor-bornyl halonium ions 45, 38, and 137 results in the classical exo-3-halo-norbornyl cations 138, 139, and 140 respectively or in non-classical 3-halonorbornyl cations 141, 142, and 143 respectively. To gain more information about the process of ring opening, Bach and Henneike used "Extended Hückel" calculations to determine the energy required to convert symmetrical halonium ions to their unsymmetrical forms. These calculations were performed on various symmetrical halonium ions of ethylene

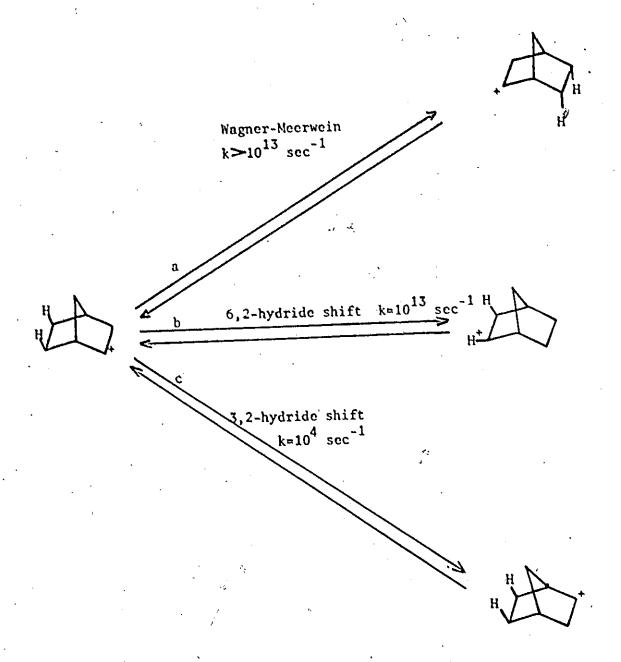
which qualitatively can be extrapolated to those of norbornene. The trend observed was that the more electronegative the electrophile, the more the energy that was required to convert the cyclic halonium ion to its open form. Hence, these results suggest that iodine is a poorer bridging atom than bromine, and bromine is a poorer bridging atom than chlorine. In addition, the unsymmetrical chloronium ion is less stable than the bromonium ion which is less stable than the iodonium ion. In each unsymmetrical ion formed, the stabilization of the adjacent carbonium ion is due to a lone pair of "p" electrons of halogen with the halogen "s" orbitals being antibonding to the distant carbon atom. This is in agreement with the qualitative picture usually envisioned of a lone pair being involved in neighbouring group participation.

### B. Reactions of Classical or of Non-classical Norbornyl Cations

### 1) Classical Ions

Schleyer 69,70 et al. in 1964 reported the nmr spectrum of the 2-norbornyl cation which was prepared by dissolving either exo-2-norbornyl chloride or exo-2-norbornyl fluoride in SbF<sub>5</sub> or in SbF<sub>5</sub>-liquid SO<sub>2</sub>. These authors postulated that the 2-norbornyl cation can undergo the following three reaction processes: a) Wagner-Meerwein rearrangement; b) 6,1- or 6,2-hydride shift; c) 3,2-hydride shift. These processes are illustrated in Figure 2. Their results confirmed that a Wagner-Meerwein rearrangement and a 6,1- or 6,2-hydride shift occur with rate constants of about equal magnitude, whereas the rate of 3,2-hydride shift is considerably slower than the above two processes. Since each of the classical cations formed

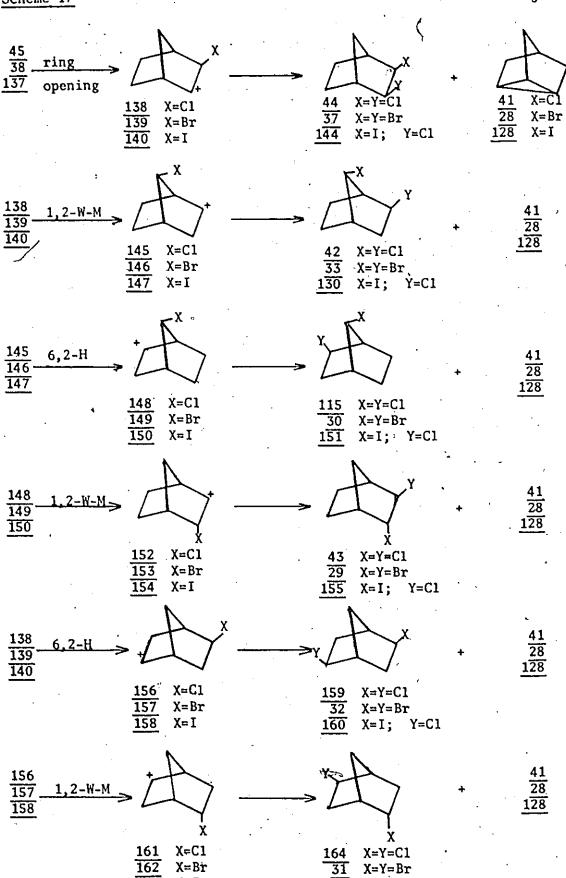
Figure 2



by processes "a", "b", and "c" differ only in the positioning of the positive charge, they are all chemically equivalent. Of particular importance to this investigation is the fact that the hydrogen on C-6 which is originally in an exo-position becomes an endo-hydrogen after a Wagner-Meerwein rearrangement, and the original endo-hydrogen on C-6 becomes an exo-hydrogen after a Wagner-Meerwein rearrangement. All the unsubstituted and 3-substituted norbornyl classical cations maintain this peculiarity.

By analogy, the classical exo-3-halonorbornyl cations 138, 139, and 140 should be capable of undergoing identical processes as those of the classical 2-norbornyl cation with only the rate constants being altered because of substituent effects. Scheme 17 indicates the five different classical halonorbornyl cations that can be formed from each cation 138, 139, and 140, when 6,2-hydride shifts and 1,2-Wagner-Meerwein rearrangements occur. The cations that can result from a 3,2-hydride shift of any of the classical halonorbornyl cations are not included in the scheme because there were no products detected in the chlorination, the bromination, and the iodo monochlorination of norbornene that ould require such a shift. The products that would result from exo-halide attack on each classical halonorbornyl cationare also indicated in Scheme 17. Besides being capable of forming the dihalide product, each cation can produce nortricyclyl halide by elimination of an endo-hydrogen.

The addition of chlorine to norbornene in methylene chloride yielded four different dichloronorbornanes 42, 44, 115, and 43 as shown in Table 2. These products are the result of exp-chloride attack on the cations 145, 138, 148, and 152 respectively. It seems likely that the total amount



31

165

X=Y=Br

X=I; Y=C1

X=Br

X=I

163

of 43 does not only arise from 152, since it can be formed from transchloride addition to the cyclic norbornyl chloronium ion (45). The two
dichloronorbornanes 159 and 164, which according to Scheme 17 are possible
products, were not detected. Since these products were not detected, it
is unlikely that 6,2-hydride shift on ion 138 occurs to any significant
degree. Of the four dichloronorbornanes detected, product 42 was present
in the greatest proportion. This is probably a result of C1-4 participation which can occur with cation 145 but not with cations 138, 148, and
152.

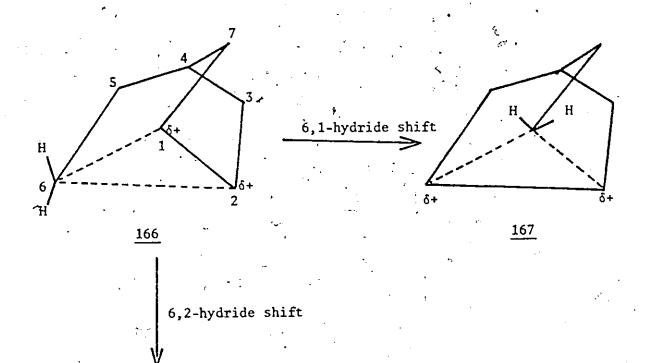
The addition of bromine to norbornene yielded five different dibromonorbornanes 30, 31, 32, 33, and 29, as shown in Table 6. shows that 30, 33, and 29 are present with the uncertainty about 31 and 32 having been previously discussed in the results section. These five dibromonorbornane products 30, 31, 32, 33, and 29 are the result of exobromide attack on the classical bromonorbornyl cations 149, 162, 157, 146, and 153 respectively. According to Scheme 17, cation 139 is formed directly from the cyclic norbornyl bromonium ion (38); however, exobromide attack does not occur on 139, probably because of steric factors. Cation 139 does undergo a 1,2-Wagner-Meerwein rearrangement, a 6,2hydride shift, and possibly 1,3-elimination as is evident by the detected products in the bromination of norbornene. Of the five dibromonorbornanes detected, 33 was produced in the highest proportion. Analogous to the chlorination reaction, this is probably a result of Br-4 participation which can occur with cation 146 but not with cations 149, 153, 157, and 162.

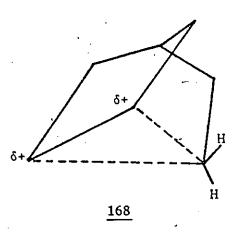
The addition of iodo monochloride to norbornene in methylene chloride yielded two different iodochloronorbornanes 129 and 130 as is shown in Table 9. According to Scheme 17, 130 results from exo-chloride attack on the classical syn-7-iodonorbornyl cation (147). Product 129 (Table 9) can not be formed from exo-chloride attack on any of the classical iodonorbornyl cations 140, 147, 150, 154, 158, and 163; thus it must solely come from trans-chloride attack on cyclic norbornyl iodonium 137. According to Scheme 17, cation 140 is the first formed classical cation from ion 137; however, exo-chloride attack does not occur on 140since no detectalbe amount of  $\underline{144}$  was produced. Cation  $\underline{140}$  can either undergo 1,3-elimination to produce 128 or it can undergo a 1,2-Wagner-Meerwein rearrangement to produce 147. Since the products 151, 155, 160, and  $\underline{165}$  were not detected, cations  $\underline{140}$  and  $\underline{147}$  do not undergo a 6,2hydride shift. However, there was one unidentified minor product which according to its retention time might be an iodochloronorbornane; therefore, a bit of 6,2-hydride shift might have occured.

# 2) Non-classical Ions

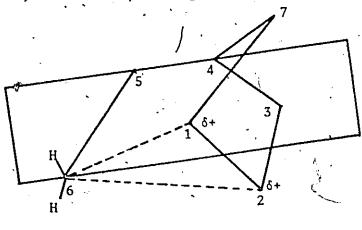
Jenson and Beck<sup>71</sup> studied the 2-norbornyl cation, which they obtained by treating exo-2-norbornyl bromide with gallium tribromide in SO<sub>2</sub>. The nmr spectrum exhibited a fine structure which was not recorded by Schleyer et al.<sup>69,70</sup> It was proposed that these results were not consistent with a classical cation, but were consistent with a non-classical cation. It was suggested that a non-classical cation could undergo a 6,1-hydride shift and a 6,2-hydride shift at a faster rate than a 3,2-hydride shift, because the non-classical cation has to become classical before the 3,2-hydride shift can occur. Figure 3 shows the equivalent non-

Figure 3





classical norbornyl cations produced by a 6,1-hydride shift and a 6,2-hydride shift. Of great significance is the fact that the two hydrogens on C-6 of 166, on C-1 of 167, and on C-2 of 168 have lost their exo and endo distinction. The plane of symmetry that exists in each cation is illustrated below for cation 166. The bond lengths and bond strengths of both  $C_6-C_1$  and  $C_6-C_2$  are equivalent. The partial positive charges on C-1 and on C-2 are also equivalent. Since  $C_s$  symmetry exists, the two  $C_6-H$ 's are equivalent. Thus if a proton is eliminated from C-6 to form nortricyclene via 1,3-elimination, there should be no preference for either hydrogen. Ex-



166

actly 50% of original exo-C<sub>6</sub>-H and exactly 50% of original endo-C<sub>6</sub>-H would be eliminated.

When an original exo-hydrogen on C-3 of 166 is replaced by a halogen, the plane of symmetry disappears. Figure 4 illustrates possible structures for non-classical 3-halonorbornyl cations (halo=Cl, Br, I).

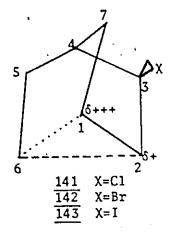
Three possible structures that can be considered for the initially formed non-classical 3-chloronorbornyl cation, are cations  $\underline{141}$ ,  $\underline{46}$ , and and  $\underline{174}$ . Cation  $\underline{46}$  has equal partial positive charges on C-1 and on C-2 with the  $C_6-C_1$  and  $C_6-C_2$  bonds equivalent. This is an unlikely structure

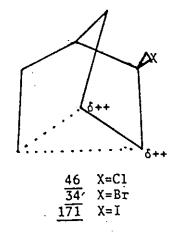
because the electron withdrawing inductive effect of chlorine favours the partial positive charge to be situated more on C-1 than on C-2. In structure 174; the partial positive charge on C-2 is greater than on C-1. The  $C_6$ - $C_1$  bond is stronger than the  $C_6$ - $C_2$  bond. This structure is even more unlikely than that of 46 since the greater positive charge of C-2 is not compatible with the electron withdrawing inductive effect of chlorine. In structure 141 the partial/positive charge on C-1 is greater than on C-2. The  $C_6$ - $C_1$  bond is weaker than the  $C_6$ - $C_2$  bond. This is the preferred structure among the three possibilities. In structure 141, the original exo-hydrogen on C-6 of norbornene has become almost completely endo-like and the original endo-hydrogen on C-6 of norbornene has become almost completely exo-like. By analogy, the preferred non-classical structures are 142 and 143 for the bromo- and iodo-substituted norbornyl cations respectively.

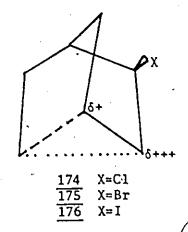
Three possible structures for the non-classical 3-chloronorbornyl cation that results from 6,1-hydride shift of the cation 141, are cations 177, 169, and 180. Cation 169 has partial positive charges on C-2 and on C-6 that are equal whilst the  $C_6$ - $C_1$  and  $C_2$ - $C_1$  bonds are equivalent. Structure 169 in not likely because the electron withdrawing inductive effect of chlorine makes the partial positive charge on C-2 unfavourable. In structure 180, the partial positive charge on C-2 is greater than that on C-1. The  $C_6$ - $C_1$  bond is stronger than the  $C_2$ - $C_1$  bond. This structure,180, is even more unfavourable than 169 because of the electron withdrawing inductive effect of chlorine. In structure 177, the partial positive charge on C-6 is greater than that on C-1. The  $C_6$ - $C_1$  bond is weaker than the  $C_2$ - $C_1$  bond. Cation 177 is the preferred structure among the following three: 177, 169,

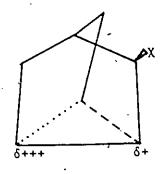
Figure 4

v

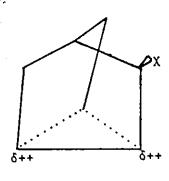




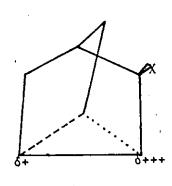




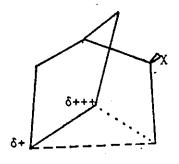
177	X=C1
178	X=Br
179	X=I



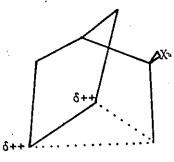
169	X=C1
35	X=Br
172	X=I



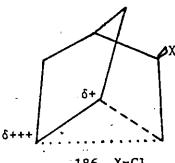
180	X=C1
181	X = Bx
182	X= I



183 X=C1 184 X=Br 185 X=I



170	X=C1
36	X=Br
173	X=Ι



186 X=C1 187 X=Br 188 X=I

and 180. The greater partial positive charge is further removed from the chlorine substitutent. The original exo-hydrogen on C-6 of norbornene which has become endo-like in cation 141, can undergo an endo-like 6,1-hydride shift to produce cation 177. After undergoing this 6,1-hydride shift, the hydrogen still maintains its endo-like character. An endo, endo-hydride shift has been previously shown to occur in the norbornyl system. By analogy, structures 178 and 179 are the preferred 6,1-hydride shift products from cations 142 and 143 respectively.

Besides undergoing a 6,1-hydride shift, cation 141 can also undergo a 6,2-hydride shift to form the following three possible structures: ions 183, 170, and 186 in the non-classical form. In addition, cation 177can undergo a 1,2-hydride shift to form similar possible structures 183, 170, and 186. Cation 170 has equal partial positive charges on C-1 and on C-6; also the  $C_1$ - $C_2$  and  $C_1$ - $C_6$  bonds are equivalent. This structure,  $\underline{170}$ , or a structure very closely ressembling it, is the most likely structure of the three since the chlorine atom is equally distant from both C-1 and C-6. For cations 183 and 186, the chlorine atom is approximately equally distant from C-1 and C-6; therefore, it seems unlikely that there be a much greater positive charge on one carbon than on the other carbon atom. Similarly for the 3-bromo- and 3-iodo-substituted 6,2- or 1,2-hydride shift non-classical cations, the most likely structures are cations 36 and 173 respectively. The 6,2-hydride shift products from cations 141, 142, and 143, and the 1,2-hydride shift products from 177, 178, and 179, all require an exo-like hydride shift. The exo-like hydride shift is of . higher energy than an endo-like hydride shift because of the less effective overlap of the vacant orbital with the migrating hydride ion.

**(**)

Besides considering the electron withdrawing inductive effect of chlorine on cations 141, 177, and 170, of bromine on cations 142, 178, and 36, and of iodine on cations 143, 179, and 173, there also exists the possibility of chloronium, bromonium, and iodonium ion-4 participation. For cations 141, 142, and 143, halonium ion participation with a "p" orbital is feasible at both C-1 and C-2. The halonium ion participation is more likely to be stronger at C-1 than on C-2 because the partial positive charge is greater on C-1 than on C-2. For cations 177, 178, and 179, halonium ion participation is not feasible because of the positioning of the vacant orbitals on C-2 and C-6. Similarly for cations 170, 36, and 173, halonium ion participation is not possible. Thus in considering the effect of halonium ion participation, cation 141 has additional stabilization over cations 177 and 170, cation 142 has additional stabilization over cations 178 and 36, and cation 143 has additional stabilization over cations 179 and 173. The product ratios from Tables 2,4,6,8, and 9 indicate that the dihalonorbornanes which result from exohalide attack on C-1 of 141, 142, and 143 are produced in the greateat proportion, suggesting that halonium ion stabilization does exist.

The various possible non-classical cations which can be produced from the cyclic norbornyl halonium ions 45, 38, and 137, are illustrated in Scheme 18. The non-classical cations which result from 6,2- and 6,1-hydride shifts on cations 141, 142, and 143 are also included. Since there were no products detected in the chlorination, the bromination, and the iodo monochlorination of norbornene that would require a 3,2-hydride

Scheme 18 (Note: Figure 4, page 100 gives a more accurate description of the partial positive charges on non-classical cations which are shown here and later as being equal. solely for convienence.) X=Y=C1 X=Y=Br 44 X=Cl 37 28 X=Br 144 X=I; Y=C1 128 X=I opening 141 X=C1  $\frac{41}{28}$ X=Br 142 143 Χ¤Ι 128 42 33 X=Y=Cl X=Y=Br 130 X=I; Y=C1 115 X=Y=CA 30 X=Y=Br 141 142 151 X=I; Y=C1 143 \$<del>†</del>7 X=C1 178 179 X=Br X=Ι X=Y=Cl X=Y=Br 155 X=I; Y=C1  $\frac{141}{142}$ 6,2-H 143 159 X=Y=C1 32 X=Y=Br 160 X=I; Y=C1 ι, 170 X=C1 36 X=Br 177 178 173 X=Ι 1,2-H 179 164 X=Y=C1 31 X=Y=Br X=I; Y=C1 165

shift, this possibility was not considered in the scheme. The products that would result from exo-halide attack on the non-classical cations are also included in Scheme 18. In addition, the tricyclic product from 1.3-elimination of a proton from each non-classical cation is shown.

As earlier discussed for the classical ion interpretation, the addition of chlorine to norbornene yielded four different dichloronorbornanes 42, 44, 115, and 43 as shown in Table 2. Products 42 and 44 are the result of exo-chloride attack on C-1 and on C-2 respectively on the non-classical cation 141. Product 115 and perhaps some of 43 are produced from exo-chloride attack on C-6 and on C-2 respectively on non-classical cation 177. The two dichloronorbornanes which would be formed from exo-chloride attack on C-1 and on C-6 of cation 170 were not detected, indicating that cation 170 is not present in any significant amount.

For each cation 141 and 177, one can determine which of the two dichloronorbornanes should be produced preferentially. Since C-1 of cation 141 carries greater partial positive charge than C-2, it is expected that exo-chloride attack would preferentially occur on C-1. This indeed is observed in about a ratio of 40:1. Similarly, exo-chloride attack should occur preferentially on C-6 rather than on C-1 for cation 177. However, the ratio of products arising from this route could not be determined since the amount of trans-2,3-dichloronorbornane arising indirectly from the cyclic norbornyl chloronium ion (45) was not known.

The addition of bromine to norbornene yielded five different dibromonorbornanes 29, 30, 31, 32, and 33 as shown in Table 6. Table 8

shows that 29, 30, and 33 are present, but as explained in the results for the bromination of norbornene in acetic acid, 31 and 32 are probably also present. Product 37 would be expected from exo-bromide attack on C-2 of non-classical ion 142, but this product was not detected. However, exo-bromide attack on C-1 of non-classical cation 142 does occur. Product 30 and perhaps some of 29 are produced from exo-bromide attack on C-6 and on C-2 respectively of non-classical cation 178. Products 31 and 32 result from exo-bromide attack on C-1 and on C-6 respectively of non-classical cation 36.

For each of the non-classical cations 142, 178, and 36, the dibromonorbornane which would be formed preferentially, can be predicted from electrostatics. For cation 142, syn-7-exo-2-dibromonorbornane (33) should be formed preferentially over exo,exo-2,3-dibromonorbornane (37). It was observed that about 25% of 33 was formed but there was no detectable amount of 37. The absence of 37 might be due to steric factors. For cation 178, accurate determination of the ratio of anti-7-exo-2-dibromonorbornane (30) to trans-2,3-dibromonorbornane (29) was not possible because the amount of 29 produced from trans-bromide attack on the cyclic norbornyl bromonium ion (38) was not known. From electrostatics, the amount of exo-2-exo-5-dibromonorbornane (32) to endo-2-exo-5-dibromonorbornane (31) should be about the same since the partial positive charges on C-1 and C-6 of cation 36 are equal. The ratio found for 32:31 was about 1:2 which is approximately the expected value.

The two dihalonorbornanes resulting from the iodo monochlorination of norbornene were exo-2-iodo-endo-3-chloronorbornane (129) and syn-7-

iodo-exo-3-chloronorbornane (130). As shown in Scheme 18, 130 results from exo-chloride attack on C-1 of the non-classical cation 143; however, product 144 which would result from exo-chloride attack on C-2 of cation 143, was not detected. This is analogous to the bromination roaction, and it is the electrostatically expected outcome. Compound 129 does not result from exo-chloride attack on any of the non-classical cations 143, 179, and 173, but it arises from trans-attack of chloride on the cyclic norbornyl iodonium ion (137), (see page 88).

# C. 1,3-Elimination: Dideuterated Norbornenes

#### 1) Endo: exo Preference in 1,3-Elimination

The endo:exo preference<sup>4,5</sup> for 1,3-elimination in solvolysis of exo-2-bromonorbornane-1-carboxylic acid methyl ester-endo, endo-5,6-d<sub>2</sub> was determined to be at least 15:1. This preference was calculated from an assumed isotope effect of 1.6. The mechanism was assumed to be E1-like which is that of ionic chlorinations, ionic brominations, and ionic iodo monochlorinations of norbornene. Hence, 1,3-elimination in these latter three reactions should also show a large preference for cleavage of an endo-C-H over an exo-C-H whenever the exo-endo distinction exists.

# 2) 2,3-D<sub>2</sub>-norbornene

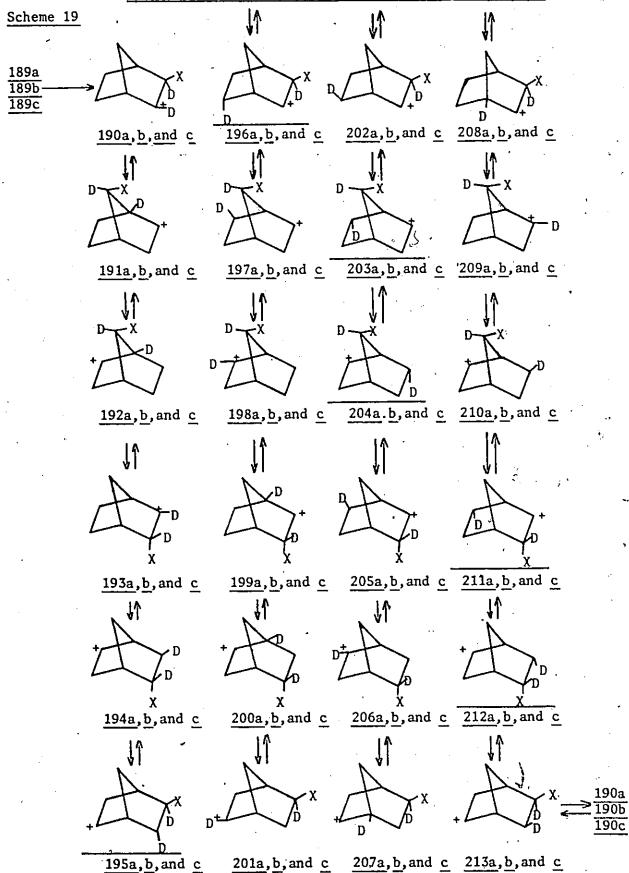
A 0-2% loss of excess one deuterium from  $2,3-d_2$ -norbornene (107) resulted from the formation of nortricyclyl chloride (41), nortricyclyl bromide (28), or nortricyclyl iodide (128) whenever ionic 1,3-elimination occurred.

### i) Classical Ion Interpretation

As already discussed, Scheme 17 shows the six classical halonorbornyl cations that can be produced as a result of ring opening of each
cyclic norbornyl halonium ion. Both Wagner-Meerwein rearrangement and
6,2-hydride shift are assumed to be occuring at appreciable rates relative
to either rate of capture by nucleophile or rate of 1,3-elimination.
However, when a dideuterated norbornene is substituted for norbornene,
there are twenty-four halonorbornyl cations. Scheme 19 shows the twentyfour possibilities for each initially formed cyclic norbornyl halonium
ion which has deuterium substituted in the C-2 and C-3 positions of
norbornene.

The twenty-four classical cations can be divided into six different groups of four. Within each group of four, for example cations 190, 196, 202, and 208, the difference results from the stereochemistry and/or place of attachment of the deuteriums. The distinction between groups is a result of the stereochemistry and/or place of attachment of the halogen substitutent. From each group there is one cation that would lose considerable endo-deuterium if 1,3-elimination occurred (this cation is underlined in Scheme 19). The remaining three cations from each group would lose very little or no deuterium when 1,3-elimination occurred. This is because an endo-hydrogen (deuterium) is lost with at least a 15:1 preference over an exo-hydrogen (deuterium). If all twenty-four cations existed, a significant loss of one deuterium would be expected from 2,3-d2-norbornene. This is contrary to the observations, (vide supra). The plausible explanation for these observations together with the detected

# Classical Halonorbornyl Cations of 2,3-D2-norbornene



products in the chlorinations (Tables 2 and 4), brominations (Tables 6 and 8), and iodo monochlorinations (Table 9) is given below. In the chlorination (Scheme 19, the intermediates labelled with "a" mean X=C1, with "b" mean X=Br, and with "c" mean X=I), ion 189a produces cation 190a which undergoes Wagner-Meerwein rearrangement to produce cation 191a. Cation 191a produces cation 192a via 6,2-hydride shift, and cation 192a may or may not react further to produce cation 193a by Wagner-Meerwein rearrangement. If cation 193a is produced, it produces no other cations since there was no detectable amount of endo-2-exo-5-dichloronorbornane which would result from exo-chloride attack on cation 194a. bromination, ion 189b produces cation 190b which undergoes Wagner-Meerwein rearrangement to produce cation 191b. Cation 191b produces cation 192b via 6,2-hydride shift. Cation 192b may or may not react further to produce cation 193b by Wagner-Meerwein rearrangement. Alternatively, cation 190b can undergo 6,2-hydride shift to form cation 213b which undergoes Wagner-Meerwein rearrangement to form cation 212b. iodo monochlorination, ion 189c reacts to produce cation 190c and this undergoes Wagner-Meerwein rearrangement to produce cation 191c which produces no other cations since no anti-7-iodo-exo-2-chloronorbornane was detected.

# ii) Non-classical Ion Interpretation

Scheme 18 shows for each cyclic norbornyl halonium ion  $\underline{45}$ ,  $\underline{38}$ , and  $\underline{137}$ , the non-classical halonorbornyl cations which can be formed via ring opening. Also included are the non-classical cations that would be produced by 6,2-, 6,1-, and/or 1,2-hydride shifts. However, when 2,3- $d_2$ -

norbornene is substituted for norbornene, there are twelve possible  $d_2$ -halonorbornyl cations which are shown in Scheme 20 (the intermediates labelled with "a" mean X=Cl, with "b" mean X=Br, and with "c" mean X=I). These twelve non-classical cations 214-225, can be divided into three groups of four. Within each group, for example cations 214, 217, 220, and 223, each has an equivalent partial positive charge on C-1 and on C-2 (the partial positive charge on each C<sub>2</sub>1 is greater than the partial positive charge on each C-2). The only difference is the result of stereochemistry and/or positioning of the deuterium atom. The distinction between groups arises from the positioning of the partial positive charges.

If 6,1-, 6,2-, and 1,2-hydride shifts occurred at rates which would allow production of equivalent amounts of cations within each group, then a considerable loss of excess one deuterium from 2,3-d<sub>2</sub>-norbornene would result from 1,3-elimination (vide infra). In the group containing cations 214, 217, 220, and 223, the formation of tricyclic product would result in the deuterium on C-6 of cation 220 preferentially being eliminated over the hydrogen on C-6. However, from cation 217, hydrogen would be preferentially eliminated from C-6 over deuterium from C-6; whereas, from cations 214 and 223 only hydrogen can be eliminated from C-6. Similarly, in the group containing cations 215, 218, 221, 224, cation 224 parallels cation 217, cation 221 parallels cation 220, and cations 215 and 218 parallel cations 214 and 223 in their elimination reactions. In the group of cations 216, 219, 222, 225, cations 216 and 225 would lose equal amounts of hydrogen and deuterium; whereas, cations 219 and 222 can only lose hydrogen whenever tricyclic product is formed.

Non-classical Halonorbornyl Cations of 2,3-D2-norbornene

	X of to	223a, b, andc	6,1-H	× ay	6+ 6+ 224a, b, andc	1,2-D $\int_{0}^{\infty} 2,1-D$	Ž.	6+	2,6-H 6,2-H	714a, D, andc
	X d to	220a, b, andc	6,1-D 1,6-D	X	6+ 6+ 221a, b, andc	1,2-H \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	X Q	6+ 222a, b, andc	2,6-Н 6,2-Н	
Br, and I, respectively)	× q · · · · · · · · · · · · · · · · · ·	217a, b, andc	6,1-H   1,6-H	Ž	5+ 6+ 218a,b, andc	1,2-H \( \int 2,1-H \)	¥ \$ \$	219a, b, andc	2,6-H ∰6,2-H	
(in cations a,b, and c, X=Cl,	X The state of the	214a, b, andc	6,1-H 1,6-H	Ž	6+ 6+ D 215a, b, andc	1,2-H \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\	X S	6+ 7	$2,6-D$ $\emptyset$ $6,2-D$	,
Scheme 20 (in	189a 189b 189c		•		•					

As already described for the classical ion interpretation, a 0-2% loss of excess one deuterium (Tables 10,11, and 12) resulted from the formation of tricyclic product. The plausible explanation for these observations together with the detected products (Tables 2,4,6,8, and 9) is given below. In the chlorination (Scheme 20, the intermediates labelled with "a" signify X=C1, with "b" signify X=Br, and with "c" signify X=I), ring opening of ion 189a produces cation 214a. Cation 214a can undergo an endo, endo-6,1-hydride shift to produce cation 215a. the iodo monochlorination(Scheme20), ring opening of ion 189c produces cation 214c which does not undergo any further hydride shift. In the bromination (Scheme 20), ion 189b undergoes ring opening to produce cation 214b. Cation 214b can undergo an endo, endo-6, 1-hydride shift to produce cation 215b. Alternatively, cation 244b can undergo a 6,2-hydride shift to produce cation 225b. Cation 215b can undergo a 1,2-hydride shift to produce cation 216b. Both the 6,2- and 1,2-hydride shifts are exo, exolike which are considerably slower than endo, endo-like shifts. This is supported by the fact that only a small amount of the total addition products resulting from exo-bromide attack on cations 225b and/or 216b, were detected (Table 6). In addition, the amount of product resulting from exo-bromide addition to cation 214b was considerably greater than that for cation 215b; therefore, cation 214b should be produced preferentially to cation 215b. Hence, cation 225b is likely to be produced in a greater amount than cation 216b.

- 3) Exo, exo-5, 6-d2-norbornene and Endo, endo-5, 6-d2-norbornene
- a) Iodo Monochlorinations

# i) Classical Ion Interpretation

The results in Table 12 show that original exo-deuterium loss is preferred to original endo-deuterium loss in the formation of nortricyclyl iodide (128) when the  $d_2$ -norbornenes 105 and 106 are treated with iodo monochloride. It is reasonable to conclude (see classical ion discussion involving 2,3- $d_2$ -norbornene) that ions 137 and 147 are the reactive intermediates when norbornene is the substrate. Cation 147 is formed whenever cation 140 undergoes a Wagner-Meerwein rearrangement (Scheme 17).

Cation  $\underline{140}$  is not included as a reactive intermediate; the reasons are analogous to those of the bromination reaction (see classical ion interpretation for endo, endo-5,6- $d_2$ -norbornene).

When the starting substrate is endo, endo-5,6- $d_2$ -norbornene (106), then ions 226 and 227 are the reactive intermediates. The original endo-

deuterium on C-6 of 106 which remains endo-like in ion 226 becomes exolike in cation 227 because a Wagner-Meerwein rearrangement has occurred..



When the starting substrate is  $exo, exo-5, 6-d_2$ -norbornene ( $\underline{105}$ ), then ions  $\underline{228}$  and  $\underline{229}$  are the reactive intermediates. The original exo-deuterium on C-6 of  $\underline{105}$  which remains exo-like in ion  $\underline{228}$  becomes endo-like in cation  $\underline{229}$  because a Wagner-Meerwein rearrangement has occurred.

If the sole source of tricyclic product is from ions 226 and 228, then one would expect original endo-deuterium to original exo-deuterium loss to be observed with at least a 15:1 ratio; 4,5 whereas, if the sole source of tricyclic product is from classical cations 227 and 229, then one would expect original exo-deuterium to original endo-deuterium loss to be observed with at least a 15:1 ratio. Since the exo:endo deuterium loss ratio is about 50:20 (Table 12), 1,3-elimination occurs preferentially from cation 227 over ion 226 and from cation 229 over ion 228. In conclusion, most 1,3-elimination occurs from the Wagner-Meerwein rearranged cation.

#### ii) Non-classical Ion Interpretation

As already discussed for the classical ion interpretation (vide supra), original exo-deuterium loss is preferred to original endo-deuterium loss (Table 12). One can conclude (see non-classical ion

discussion involving  $2,3-d_2$ -norbornene treated with iodo monochloride) that ions  $\underline{137}$  and  $\underline{143}$  are the reactive intermediates when norbornene is the substrate. Cation  $\underline{143}$  results from ring opening of ion  $\underline{137}$ .

$$\begin{array}{c}
1 \\
137
\end{array}$$

$$\begin{array}{c}
143
\end{array}$$

When the starting substrate is 106, then iodonium ion 226 and non-classical cation 230 are the reactive intermediates. The original endo-deuterium on C-6 of 106 which remains endo-like in ion 226 becomes an almost completely exo-like deuterium in cation 230 because the greater partial positive charge is on C-1 rather than on C-2.

$$\begin{array}{c}
\downarrow \\
D
\end{array}$$

$$\begin{array}{c}
\downarrow \\
D
\end{array}$$

$$\begin{array}{c}
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D
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$$\begin{array}{c}
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D
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$$\begin{array}{c}
\downarrow \\
0\\
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When the starting substrate is 105, then iodonium ion 228 and non-classical cation 231 are the reactive intermediates. The original exo-deuterium on C-6 of 105 which remains exo-like in ion 228 becomes almost completely endo-like in cation 231. The reason for this has been previously discussed for cation 230.

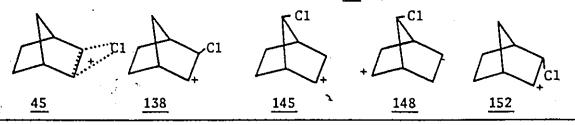
If the sole source of tricyclic product is from 226 and 228, then

one would expect original endo-deuterium to original exo-deuterium loss to be observed with at least a 15:1 preference; whereas, if the sole source of tricyclic product is from non-classical cations 230 and 231, then one would expect a 15:1 preference for original exo-deuterium to original endo-deuterium loss. Since the exo:endo preference is about 50:20 (Table 12), 1,3-elimination occurs preferentially from cation 230 over ion 226 and from cation 231 over ion 228. Significantly, most 1,3-elimination occurs from the first formed non-classical cation.

#### b) Chlorinations

#### i) Classical Ion Interpretation

Original endo-deuterium loss is preferred to original exo-deuterium loss (Table 10) in the formation of nortricyclyl chloride (41) when the  $d_2$ -norbornenes 105 and 106 are treated with chlorine. Intermediates 45, 138, 145, 148, and probably 152 are necessary to explain the products that are formed when chlorine and norbornene are allowed to react (see classical ion discussion involving 2,3- $d_2$ -norbornene). Cation 152 may not be present since all the trans-2,3-dichloronorbornane (43) may be formed solely from



A 15:1 preference for a purely classical ion was determined; probably this is less for non-classical cations 230 and 231 since the endo-hydrogen and endo-deuterium respectively are not completely endo-like.

ion 45 and since all of 41 may be formed from ions 45, 138, 145, and 148.

When the starting substrate is endo, endo-5,6-d<sub>2</sub>-norbornene (106), ions 232, 235, 236, 234, and probably 233 are the reactive intermediates. Ions 232 and 235 on forming tricyclic product would both show at least a 15:1 preference for endo-deuterium to exo-hydrogen loss. Cation 236 would show at least a 15:1 preference for endo-hydrogen to exo-deuterium loss. Cations 234 and 233 can only lose hydrogen because the deuterium is not situated in a position from which it can be lost whenever 1,3-elimination occurs.

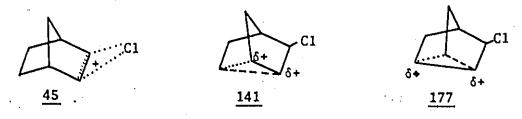
When the starting substrate is exo, exo-5, 6- $d_2$ -norbornene (105), ions 237, 240, 241, 239, and probably 238 are the reactive intermediates. Ions 237, 240, and 238 on forming tricyclic product would show at least a 15:1 preference for endo-hydrogen to exo-deuterium loss. Cations 241 and 239 would show at least a 15:1 preference for endo-deuterium to exo-hydrogen loss.

If cations 233 and 238 were the sole source of tricyclic product, then 106 would lose no deuterium and 105 would lose endo-hydrogen to exodeuterium in a ratio of about 15:1. However, since this is contrary to

the experimental results (Table 10), cations 233 and 238 must contribute wery little or nothing to the observed product ratios. If the sole source of tricyclic product was from "a" (a=ions 232 and 235) and "b" (b=ions 237 and 240), then original endo-deuterium to original exo-deuterium loss would be observed with at least a 15:1 ratio; whereas, if the sole source of tricyclic product was from "c" (c=cations 236 and 234) and "d" (d=cations 241 and 239), then original endo-deuterium to original exo-deuterium loss would be observed with a 1:15 ratio. Since the original exo:endo deuterium loss ratio was about 30:60 (Table 10), "a" produces more tricyclic product that "c" and "b" produces more than "d". In conclusion, 1 3-elimination in norbornene occurs predominantly from the unrearranged intermediates when norbornene and chlorine react.

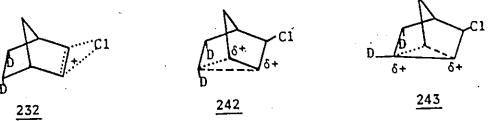
### ii) Non-classical Ion Interpretation

As already discussed for the classical ion interpretation (vide supra), original endo-deuterium to original exo-deuterium loss (Table 10) is preferred. One can conclude (see non-classical ion discussion involving 2,3-d<sub>2</sub>-norbornene) that ions 45, 141, and 177 are the reactive intermediates when norbornene is the substrate. Cation 177 is formed when cation 141 undergoes a endo, endo-6,1-hydride shift.



When the starting substrate is endo, endo-5,  $6-d_2$ -norbornene (106),

then ions 232, 242, and 243 are the reactive intermediates. The original endo-deuterium on C-6 of 106 remains an endo-deuterium in ion 232, but becomes almost completely exo-like in cation 242 because the greater partial positive charge is on C-1 rather than on C-2. On formation of tricyclic product, ion 232 would lose original endo-deuterium to original exo-hydrogen with a preference of at least 15:1, and cation 242 would lose original endo-deuterium to original exo-hydrogen with a ratio of about 1:15. Cation 243 would only lose hydrogen whenever tricyclic product is formed.



When the starting substrate is  $exo, exo-5, 6-d_2$ -norbornene (105), then ions 237, 244, and 245 are the reactive intermediates. The original exo-deuterium on C-6 of 105 which remains exo-like in ion 237 becomes an almost completely endo-like deuterium in cation 244. This is because the greater partial positive charge is on C-1 rather than on C-2. Cation 245 is formed whenever cation 244 undergoes an endo,endo-6,1-hydride shift (a deuteride is shifted in this process, and it remains almost completely endo-like because the greater partial positive charge is on C-6 rather than on C-2). On formation of tricyclic product, ion 237 would lose original endo-hydrogen to original exo-deuterium with a preference of about 15:1, and both cations 244 and 245 would lose hydrogen to original exo-deuterium with a ratio of about 1:15.

If the sole source of tricyclic product was from ions 232 and 237, then the original endo-deuterium to original exo-deuterium loss would be about 15:1. If the sole source of tricyclic product was from cations 242, 243, 244, and 245, a preference for original endo-deuterium to original exo-deuterium loss would be about 1:15. However, since the endo:exo preference (Table 10) was found to be about 30:60, ions 232 and 237 must produce a greater proportion of tricyclic material than from the cations 242, 243, 244, and 245. In conclusion, the cyclic norbornyl chloronium ion produces the major fraction of nortricyclyl chloride (41) whenever norbornene and chlorine are reacted together.

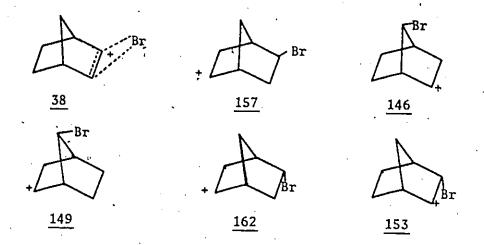
### C. Brominations

# i) Classical Ion Interpretation

The results of Table 11 show that original exo-deuterium loss is preferred to original endo-deuterium loss for the formation of nortricyclyl bromide (28) when the dideuterated norbornenes 105 and 106 respectively are treated with bromine. It is reasonable to conclude (see discussion about classical ion interpretation involving 2,3- $d_2$ -norbornene) that ions 38, 157, 146, 149, 162, and possibly 153 are the reactive intermediates when norbornene is the substrate. Cation 153 may not be a reactive intermediate

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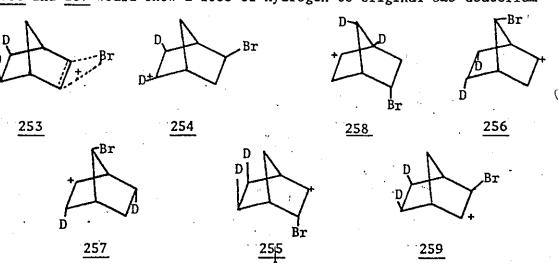
because ion 38 might be the sole source of trans-2,3-dibromonorbornane and ions 38, 157, 146, 149, and/or 162 might be the sole source of 28.



When the substrate is endo, endo-5,6- $d_2$ -norbornene (106), ions 246, 247, 248, 249, 250, and possibly 251 are the reactive intermediates. original endo-deuterium on C-6 of 106 exists as an endo-deuterium in ions 246 and 247, but it becomes an exo-deuterium in cations 248 and 249. formation of tricyclic product, ions  $\underline{246}$  and  $\underline{247}$  would show about a 15:1 preference 4,5 for original endo-deuterium to hydrogen loss, whereas cations 248 and 249 would show about a 15:1 preference for hydrogen to original endo-deuterium loss. Upon undergoing 1,3-elimination, cations 250 and 251 can only lose hydrogen. Cation 252 which is formed directly from ring opening of ion 246, is not included as a reactive intermediate leading directly to products because the addition product that it would produce from exo-bromide attack, the normal mode of addition, was not detected. Even if cation 252 did produce tricyclic product, its effect on the stereochemical outcome of Table 11 would be identical to that of ions 246 and 247; thus any effect that cation 252 might have will be considered indirectly in the discussion of ions 246 and 247.

it still remains as a necessary precursor to all of the other cations.

When the substrate is  $exo, exo-5, 6-d_2$ -norbornene (105), then ions 253, 254, 256, 257, 258, and possibly 255 are the reactive intermediates. The original exo-deuterium on C-6 of 105 remains an exo-deuterium in ions 253 and 255, and it becomes an endo-deuterium in cations 256 and 257. On formation of tricyclic product, ions 253 and 255 would show a loss of hydrogen to original exo-deuterium with a ratio of about 15:1, whereas cations 256 and 257 would show a loss of hydrogen to original exo-deuterium



with a ratio of about 1:15. On formation of tricyclic product, cations  $\underline{254}$  and  $\underline{258}$  can only lose hydrogen. Cation  $\underline{259}$  is not included as a reactive intermediate (see discussion concerning cation  $\underline{252}$ ).

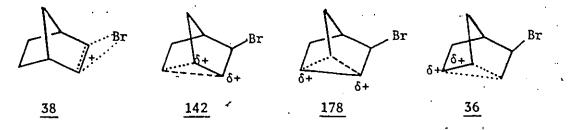
The expected loss of deuterium for the formation of nortricyclyl bromide (28) from the various ions is given below. If the sole source of tricyclic product is from "a" (a = ions 246 and 253), then original endodeuterium to original exo-deuterium loss would be about 15:1: if the sole source was from "b" (b = cations 247 and 254), then most (>90%) of the original endo-deuterium would be lost with all the original exo-deuterium retained; if it was from "c" (c = cations 248 and 258), then only a small percentage (<10%) of original endo-deuterium would be lost with all the original exo-deuterium retained; if it was from "d" (d = cations 249 and 256), then original endo-deuterium to original exo-deuterium loss would be about 1:15; if it was from "e" (e = cations 250 and 257), then most of the original exo-deuterium; if it was from "f" (f = cations 251 and 255), then only a small percentage (<10%) of original exo-deuterium would be lost with all the original endo-deuterium; if it was from "f" (f = cations 251 and 255), then only a small percentage (<10%) of original exo-deuterium would be lost with all the original endo-deuterium retained.

The exo:endo preference for the loss of deuterium in the formation of 28 form 105 and 106 respectively was found to be approximately 50:20 (Table 11). Therefore, more than one set of intermediates from the pairs "a" "b" "c" "d" "e" and "f" must produce tricyclic product. In order to lose 50% of original exo-deuterium, pairs "d" and/or "e" must be the preferred intermediates, whereas in order to lose 20% of original endo-deuterium, pairs "a" and/or "b" must be partially involved. Pairs "c" and

"f" play little or no role in the production of tricyclic product. Since "c" produces only a minor percentage of the total amount of dibromonorbornanes and of tricyclic product, it is likely that "b" also produces only a minor amount of tricyclic product. This is because it is very similiar in structure to the cations is "c", and it only produces a minor percentage of the total amount of dibromonorbornanes. From the above analysis it follows that the major source of tricyclic product arises from pairs "d" and/or "e" and that the minor source arises from pair "a" with pairs "b" "c" and "f" having little role to play.

#### . ii) Non-classical Ion Interpretation

The non-classical cations 142, 178, 36, and the cyclic norbornyl bromonium ion (38) are the reactive intermediates when norbornene and bromine are reacted.



When the substrate is endo, endo-5,6-d<sub>2</sub>-norbornene (106), then ions 246, 260, 261, 262a, and 262b are the reactive intermediates. The original endo-deuterium on C-6 of 106 remains as an endo-deuterium in ion 246, whereas in cation 260 it becomes almost completely exo-like. In cations 262a and 262b the hydrogen and deuterium on each C-2 have partial exo- and endo-like characteristics. If tricyclic product is formed from ion 246, then original endo-deuterium to original exo-hydrogen loss occurs with a

ratio of about 15:1, whereas if tricyclic product is formed from cation 260, then original endo-deuterium to original exo-hydrogen loss occurs with a ratio of about 1:15. On formation of tricyclic product from cation 261, no deuterium is lost, but cations 262a and 262b lose equal proportions of of deuterium and hydrogen.

Similarly, when the substrate is exo, exo-5, 6- $d_2$ -norbornene ( $\underline{105}$ ), then ions  $\underline{253}$ ,  $\underline{263}$ ,  $\underline{264}$ ,  $\underline{265a}$ , and  $\underline{265b}$  are the reactive intermediates. The original exo-deuterium on C-6 of  $\underline{105}$  remains as an exo-deuterium in ion  $\underline{253}$ , whereas in cation  $\underline{263}$  and cation  $\underline{264}$  it becomes almost completely endo-like. If tricyclic product is formed from ion  $\underline{253}$ , then original exo-deuterium to original endo-hydrogen loss occurs with a ratio of about 1:15, whereas if tricyclic product is formed from cations  $\underline{263}$  and  $\underline{264}$ , then the original exo-deuterium to hydrogen loss occurs with a ratio of about 15:1. On formation of tricyclic product, cations  $\underline{265a}$  and  $\underline{265b}$  only lose hydrogen.

If the sole source of tricyclic product is from "a" (a=ions 246 and 253), then original endo-deuterium to original exo-deuterium loss would occur with a ratio of about 15:1. If the sole source of tricyclic product is from "b" (b=cations 260 and 263), then original endo-deuterium to original exo-deuterium loss would occur with a ratio of about 1:15. If the sole source of tricyclic product is from "c" (c=cations 261 and 264), then most (<90%) of the original exo-deuterium would be lost with no original endo-deuterium lost, and if the sole source was from "d" (d= cations 262a, 262b, 265a, and 265b), then the maximum amount of original endo-deuterium which can be lost is 50%. No original exo-deuterium loss is possible from "d".

The exo:endo preference for deuterium loss was about 50:20 (Table 11). Thus route "b" and/or "c" must produce the major amount of tricyclic product, whereas routes "a" and/or "d" must produce a minor amount. Since the greater proportion of dibromonorbornanes results from exo-bromide attack on "b" (cations 260 and 263) as opposed to "c" (cations 261 and 264) and since a similarity in structure among these four cations exists, it can be concluded that "b" produces more tricyclic product than "c". Ions 246 and 253 ("a") are different in structure from cations 262a, 262b, 265a, 265b ("d"); thus it can not be determined from the ratio of dibromonorbornanes whether route "a" or "d" is preferred as the minor route to the tricyclic product. In conclusion, the first formed non-classical cation 142 produces a greater proportion of the tricyclic product than does the bromonium ion 38 and the other non-classical cations in the reaction of nor-bornene and bromine.



#### D. Effect of Solvent

In this investigation, the mechanism of 1,3-elimination has been discussed in terms of "internal" factors (those considered in terms of the carbonium ion framework: substitutent effects are an obvious example) without any reference to "external" factors (those concerned with the interaction of the carbonium ion with the solvent and with the particle carrying the negative charge). Although the "external" factors are largely electrostatic, they are in some measure chemically specific and can affect the chemistry of the carbonium ion moiety so as to influence the nature of the reaction.

Since carbonium ions in solution are accompanied by an equal number of counter-ions, it is impossible to study carbonium ions in solution in isolation. Only by restricting comparisons to systems with the same counter-ions is it possible to investigate the effect of structure on the stability of carbonium ions. The influence of the solvent on the stability or rate of formation of carbonium ions is never a function of its interaction with carbonium ions alone, on the other hand, the chemical effects of solvation, as indicated by the composition or stereochemistry of reaction products derived from the carbonium ion, frequently result from the interaction with the cation only.

In solution, the energy required in organic reactions involving cation formation is offset by interaction between the ions and their surroundings, in particular solvent molecules and other ions. These interactions may be regarded as ways of achieving external dissipation of the

charge on the carbonium ion. If carbonium ion solvation is considered as an electrostatic phenomenon, then the dielectric constant (D) becomes the obvious measure of solvating power. Solvation of carbonium ions can be regarded as a non-directional electrostatic interaction of the ion with the solvent. Carbonium ions will be less stabilized and thus more difficult to form as the dielectric constant of the medium is decreased.

Warnhoff<sup>7,32</sup> et al. found out that solvent polarity as measured by dielectric constant (CH<sub>2</sub>Cl<sub>2</sub>, CCl<sub>4</sub>, and CH<sub>3</sub>CN; D=8.9, 2.2, and 3.8) is not important in determining the ratios of trans addition, hydride shift, and simple Wagner-Meerwein rearrangement although the ratio of hydride shift product (excepting the trans isomer) to the primary Wagner-Meerwein product, 7-syn-2-exo-dibromide, slowly increases with increasing dielectric constant, indicating that the overall hydride shift rate is close to the nucleophile capture rate of the initial parent non-classical cation. This is rationalized as increased stabilization of the non-classical cation by the more polar solvent permitting more hydride shift to occur before capture by a nucleophile.

In this investigation, regardless of the solvents used (CH<sub>2</sub>Cl<sub>2</sub>, CCl<sub>4</sub>, and CH<sub>3</sub>CO<sub>2</sub>H; D=8.9, 2.2, and 6.2 respectively), exo-stereoselectivity was always preferred to endo-stereoselectivity in the brominations (Table 11) and iodo monchlorinations (Table 12) of norbornene. Whereas endo-stereoselectivity was always preferred to exo-stereoselectivity in the chlorination (Table 10). Thus the stereospecificities observed are a result mainly because of "internal" factors.

### E. Effect of Pyridine Concentration

Table 2 shows the effect of pyridine on the product ratios in the reaction of norbornene with chlorine in methylene chloride. The reaction was performed with no pyridine, with a pyridine concentration equal to that of norbornene, and with a pyridine concentration equal to ten times, that of norbornene. Essentially, pyridine has very little effect on the per cent of each product produced. Table 10 shows that for 1,3-elimination, the pyridine concentration for the range described above has no or very little effect on the deuterium loss data.

", Table 6 shows the effect of pyridine on the product ratios in the reaction of norbornene with bromine in methylene chloride. There was a slight increase in tricyclic product as the pyridine concentration increased and a slight decrease in syn-7-exo-2-dibromonorbornane, exo-2-exo-5-dibromonorbornane, and in endo-5-exo-2-dibromonorbornane. The trans-2,3-dibromonorbornane and anti-7-exo-2-dibromonorbornane are affected the most. The former increases as the latter decreases. However, Table 11 shows that for 1,3-elimination, the pyridine concentration has no or very little effect on the deuterium loss data.

In addition, when 2,6-lutidine was substituted for pyridine, the results obtained were similiar to the results obtained when pyridine was used.

CHAPTER 4

EXPERIMENTAL SECTION

#### A. General

A Kofler hot-stage apparatus was used to take melting points which were uncorrected and rounded off to the nearest - 0.1°C. Any boiling points listed are also uncorrected.

Infrared spectra were obtained with a Perkin Elmer 337 Grating Spectrophotometer. Band positions were calibrated and were expressed in reciprocal centimetres (cm<sup>-1</sup>). The spectra of samples were neat unless specified otherwise.

Gas chromatograms were obtained on a Varian Aerograph Gas Chromatograph, Model 204B with a flame ionization detector. The carrier gas was helium with a gas flow rate of 20-30 ml/min. Preparative gas chromatography was carried out on a Varian Aerograph Gas Chromatograph, Model A-90-P with a thermal conductivity detector. The carrier gas was helium with a flow rate of 50-60 ml/min. The injector of the preparative machine was fitted with a glass system. The detector and injector temperatures were 10°C warmer than the column temperature. Relative per cent by weight ratios were determined by a Varian Aerograph Electronic Digital Integrator Model 476. The average of four injections was tabulated. Peak areas were calibrated with a mixture made up of approximately equal weighted amounts of each component. The hydrogen flame ionization detector gave similiar response of weight to area ratio for isomeric compounds, whereas non-identical response was obtained for non-isomeric compounds.

The columns listed below were used for analytical glpc or for preparative glpc work. Chromosorb W (Chromatographic Specialties Ltd.) of mesh size 60/80 was used as the solid phase in all cases.

- I 10% Carbowax 20M TPA, Stainless steel, 12 X 1/8".
- II 5% Silicone gum rubber, Stainless steel, 10 X 1/8.
- III 15% Carbowax 20M TPA, Glass, 10 X 1/4".
- IV 15% Silicone gum rubber, Glass, 10 X 3/16".
- V 15% Silicone gum rubber, Copper, 10 X 1/4".

All mass spectra were taken with a Hitachi Perkin Elmer RMU-6A Spectrometer at 80 electron volts in determining the molecular ion and at 11 electron volts in determining the deuterium content. The deuterium analyses are expressed as atoms of deuterium per molecule in excess of natural abundance deuterium.

Nuclear magnetic resonance (nmr) spectra were obtained on the Varian T-60. An internal standard of tetramethylsilane (TMS) was used. Samples were run neat or dissolved in either carbon tetrachloride or in carbon disulfide as specified. Chemical shifts are reported as '6" values (parts per million downfield from the internal standard).

All spinning band distillations were done using a Nester Faust Auto Annular  $30^{\prime\prime}$  teflon spinning band distillation column.

Microanalysis was done by A. B. Gygli, Microanalysis Laboratories Limited at Toronto, Ontario.

#### B. Reagents

Acetic anhydride (C.I.L. Reagent)
Acetic acid (C.I.L. Reagent)

Acetone (Mallinckrodt, F.W. 58.08)

Bromine (The McArthur Chemical Co. Ltd., [Macco], M.W. 159.83)

T-butanol (Fischer Scientific Co., F.W. 74.12, b.p. 82.1°C)

Calcium chloride (Allied Chemical Canada, Ltd., M.W. 110.99)

Calcium hydride (J. T. Baker Chemical Co., Practical Grade, F.W. 42.1)

Carbon tetrachloride (J. T. Baker Chemical Co., Spectrophometric)

Chlorine (Matheson, M.W. 70.906)

Chloroform (Mallinckrodt, F.W. 119.38)

Cyclopentadiene (Eastmann Organic Chemicals, F.W. 66.10)

Deuterium oxide (Stokler Isotope Chemicals, [S.I.C.], 99.8%D)

Diglyme (Aldrich Chemical Co. Inc., b.p. 161°C)

1,4-Dioxane (J. T. Baker Chemical Co., F.W. 88.11)

Ether absolute (Mallinckrodt, F.W. 74.12)

Helium (Canadian Liquid Air Ltd.,)

Hydrochloric acid (C.I.L. Reagent)

Hydrogen chloride anhydrous (Matheson)

Iodine (Macco, M.W. 126.91)

Iodine Monochloride (Anachemia Chemicals Ltd., M.P. 25-27°C)

Lithium aluminium deuteride (Alfa Inorganics, F.W. 41.95)

Lithium aluminium hydride (Alfa Inorganics, F.W. 37.95)

Magnesium sulfate anhydrous (Shawinigan)

Methanol absolute (Mallinckrodt, F.W. 32.04)

Methylene chloride (Macco, M.W. 89.94)

Nitrogen (Canadian Liquid Air Ltd.,)

Norbornene (Aldrich Chemical Co. Inc., M.W. 94.16)

Norcamphor (Aldrich Chemical Co. Inc., M.W. 110.16)

Pentane (Eastmann, Technical, M.W. 72.15, b.p. 34-36°C)

Potassium (J. T. Baker Chemical Co., A.W. 39.100)

Potassium hydroxide (Macco, M.W. 56.11)

Pyridine (Allied Chemical Canada Ltd., Reagent A.C.S., M.W. 79.10)

Sodium (J. T. Baker Chemical Co., A.W. 22.991)

Sodium acetate (Macco, M.W. 82.04)

Sodium bicarbonate (Macco,)

Sodium chloride (Shawinigan)

Sodium iodide (J. T. Baker Chemical Co., F.W. 149.89)

Sodium thiosulfate (Fisher Scientific Co.,  $Na_2S_2O_3 \cdot SH_2O$ , F.W. 248.18)

Sulfuric acid (C.I.L.)

Sulfuric acid (Fuming 30%) (Allied Chemical, Reagent A.C.S.)

Triphenylphosphine (Aldrich Chemical Co. Inc., M.W. 262.29)

Vinyl bromide (Matheson, M.W. 106.96)

Vinyl chloride (Matheson, M.W. 62.50)

### C. Purification of Solvents and Preparation of Reagents

#### 1) Purification of Acetic Acid

Acetic acid (500ml) and sodium acetate anydrous (20gms) were stirred mechanically in a 1,000ml round bottomed flask. The acetic acid was distilled through a Vigreux (12") column with the fraction having a boiling point of 118°C being collected.

### 2) Preparation of Chlorine in Methylene Chloride

A solution of chlorine in dry methylene chloride was prepared by bubbling chlorine, which was passed through a water trap, a calcium chloride drying tube, and a sulfuric acid trap respectively, into a separatory funnel

containing a known amount of methylene chloride.

#### Purification of Diglyme

Diglyme<sup>73</sup> (1 litre) was stored over small pieces of calcium hydride (10 g.) For twelve hours, then decanted into a distilling flask. Sufficient lithium aluminium hydride was added to ensure excess active hydride; this was followed by distillation of the diglyme under vacuum. The fraction (b.p. 62-63°C) at 15 mm. was collected and stored under dry nitrogen.

#### 4) Purification of 1,4-Dioxane

1,4-Dioxane<sup>73</sup> (100 ml.) and lithium aluminium hydride (lg., 0.0263 mole) were stirred mechanically for one hour in a 250 ml. round bottom flask, and the 1,4-dioxane was distilled. The fraction with a boiling point of 101°C was collected.

#### 5) Purification of Absolute Ether

Absolute ether (1 litre) and lithium aluminium hydride (1 g., 0.0263 mole) were stirred mechanically for one hour in a 2 litre round bottom flask, and the ether was distilled. The absolute ether was purified prior to any experiment requiring the absolute ether.

### 6) Purification of Methylene Chloride

Methylene chloride (500 ml.) was purified by reacting it with bromine in light for two hours. The mixture was worked up by washing it with 5% sodium thiosulfate solution (3X200 ml.), followed by washing with distilled water (3X200 ml.). The methylene chloride was dried for

41°C) was collected. The above procedure was repeated. In order to dry the methylene chloride immediately before any experiment, it was distilled after reacting it with lithium aluminium hydride.

#### Purification of Pentane

Pentane was stirred for 24 hours over 30% fuming sulfuric acid.

The pentane was then washed three times with 10% sodium bicarbonate solution, three times with distilled water, and finally dried with anhydrous magnesium sulfate. The pentane was distilled through a two feet Vigreux column with the fraction having a boiling point of 40-41°C being collected.

### 8) Purification of Pyridine

Pyridine (100 ml) was stored over potassium hydroxide pellets (1 gm) for two days, and then distilled. The fraction of b.p. 115°C was collected.

# 9) Preparation of an Approximately 1M Solution of Potassium t-Butoxide in t-Butanol

t-Butyl alcohol (175 ml) and potassium (1 ct) were reacted at steam bath temperature in a 250 ml round bottomed flask fitted with a condenser and a calcium chloride drying tube. After complete reaction of the potassium, the mixture was distilled with the fraction collected that had a boiling point of 82°C. To the collected t-butyl alcohol (100 ml) was added potassium at steam bath temperature until a saturated solution of potassium t-butoxide in t-butanol was produced.

#### D. Syntheses

### 1) Synthesis of 2,3- $d_2$ -Norbornene

### i) Preparation of $3,3-d_2-2$ -Norbornanone

To deuterium oxide (100 g., 5.55 moles) in a 500 ml. round bottom flask fitted with a condenser and a calcium chloride drying tube was slowly added sodium (3.3 g., 0.144 mole). After the sodium had reacted, norcamphor (7.1 g., 0.0645 mole) dissolved in 1,4-dioxane (60 ml.) was added which resulted in the formation of a two phased system. The mixture was kept at 39°C by an oil bath while being stirred mechanically. Deuterium incorporation was determined every twenty-four hours over a period of eight days, after which the mixture was worked up as follows. The mixture was saturated with sodium chloride, and then it was extracted four times with absolute ether (4X125 ml.). The combined ether extracts were washed with distilled water (2X200 ml.), then dried with anhydrous magnesium sulfate. The ether was removed on a rotatory evaporator. No yield was determined because not all of the 1,4-dioxane could be removed. Mass spectral analysis of the 3,3- $d_2$ -2-norbornanone which was collected by preparative glpc (IV, 150°C), gave a molecular ion at m/e = 112 in agreement with the empirical formula  $C_7H_8D_2O$ , and it showed:  $d_0 = 1.4\%$ ;  $d_1 =$ 2.1%;  $d_2 = 96.5$ %. Analytical glpc (II, 150°C) showed that only one product was present.

ii) Reduction of  $3,3-d_2-2$ -Norbornanone with Lithium Aluminium

Deuteride

To a mechanically stirred slurry of lithium aluminium deuteride (1.35 g., 0.0322 mole) and anhydrous ether (25 ml.) at room temperature in a 100 ml. round bottom flask was added dropwise the  $3,3-d_2$ -2-norbornanone dissolved in anhydrous ether (25 ml.). After stirring for seventy-eight hours, the mixture was worked up by slowly adding distilled water (25 ml.) followed by adding 10% hydrochloric acid (25 ml.). This mixture was extracted with anhydrous ether (4X75 ml.). The combined ether extracts were dried with anhydrous magnesium sulfate followed by removal of the ether. The yield of  $2,3,3-d_3$ -endo-2-norbornanol and its exo-2-isomer (5.8 g., 0.0504 mole) from norcamphor (7.1., 0.0645 mole) was 78%. No accurate deuterium analysis of the alcohols was possible due to the numerous peaks about the very weak molecular ion in the mass spectrum of the two alcohols. An acetylation was performed to determine the deuterium content.

# iii) Acetylation of 2,3,3-d<sub>3</sub>-Endo-2-norbornanol and its Exo-2isomer

Pyridine (42 ml.), acetic anhydride (28 ml.) and 2,3,3-d<sub>3</sub>-endo-2-norbornanol and its exo-2-isomer (0.140 g.) were mechanically stirred at room temperature for twenty-four hours in a 100 ml. round bottom flask. The work up involved adding crushed ice (50 ml.), then extracting the mixture with anhydrous ether (2X40 ml.), washing the combined ether extracts with dilute 5% hydrochloric acid solution (2X40 ml.), washing with dilute 5% sodium bicarbonate solution (2X40 ml.) and washing with distilled water (2X40 ml.). The ether solution was dried over anhydrous magnesium sulfate followed by evaporation of the ether. Mass spectral analysis of both acetates which were collected by preparative glpc (IV, 150°C), showed the

deuterium content as follows:  $d_0 = 0.0\%$ ;  $d_1 = 1.2\%$ ;  $d_2 = 3.5\%$ ;  $d_3 = 96.5\%$ . Analytical glpc analysis (II, 150°C) showed one major peak which contained the two isomeric acetates.

iv) Reaction of 2,3,3-d<sub>3</sub>-Endo-2-norbornanol and its Exo-2-isomer with Triphenylphosphine and Bromine in Diglyme

The procedure in references 27 and 28 was followed. A mixture of  $2,3,3-d_3-endo-2$ -norbornanol and  $2,3,3-d_3-exo-2$ -norbornanol (4.0 g., 0.0348 mole), triphenylphosphine (9.5 g., 0.0378 mole), and diglyme (30 ml.) was stirred magnetically at room temperature in a 100 ml. round bottom flask until a homogeneous solution was achieved. The flask was fitted with a thermometer, an inlet for dry nitrogen, and an equi-pressure separatory funnel with a calcium chloride drying tube. Bromine (5.3 g., 0.0322 mole) in diglyme (20 ml.) was added dropwise with the mixture kept below 15°C as dry nitrogen was bubbled through it. After the addition, the mixture which contained a white precipitate, was stirred for one hour at 15°C followed by the addition of absolute ether (360 ml.). The white precipitate was collected by suction filtration under dry nitrogen. Purification of the precipitate involved dissolving it in methylene chloride (50 ml.), filtering, then adding anhydrous ether (100 ml.) to the methylene chloride. The white precipitate was 2,3,3-d<sub>3</sub>-norbornoxytriphenylphosphonium bromide.

v) Decomposition of 2,3,3-d<sub>3</sub>-Norbornoxytriphenylphosphonium

Bromide

The 2,3,3- $d_3$ -norbornoxytriphenylphosphonium bromide was pyrolyzed under vacuum distillation (0.5-1.0 mm.) yielding a clear colourless dis-

tillate which contained 2,3,3- $d_3$ -exo-2-bromonorbornane and 2,3,3- $d_3$ -endo-2-bromonorbornane. The yield (3.5 g., 0.0196 mole) from the alcohols was 56%.

By comparing the nmr spectrum of exo-2-bromonorbornane with the nmr spectrum (neat) of the mixture of 2,3,3- $d_3$ -exo-2-bromonorbornane (113) and 2,3,3- $d_3$ -endo-2-bromonorbornane (114), it was shown that at least 95% deuterium incorporation occurred at the following positions; endo-C-2-H of 113, exo-C-2-H of 114, exo-C-3-H of 113 and of 114, and endo-C-3-H of 113 and of 114. The nmr spectrum (60 MHz., TMS) of the mixture of 113 and 114 showed the following signals;  $\delta$  3.88(residual multiplet, exo-C-2-H of 114 and endo-C-2-H of 113, both less than 5% 1H), 2.47 (broad singlet, C-1-H, 1H), 2.27(broad singlet, C-4-H, 1H), 2.00(residual multiplet, exo-C-3-H and endo-C-3-H, less than 5% 2H), and 1.83-1.03(norbornyl envelope, exo- and endo-C-5-H, exo- and endo-C-6-H, C-7-H's, 6H).

- vi) Reaction of 2,3,3-d<sub>3</sub>-Exo-2-bromonorbornane and its Endo-2isomer with an Approximately 1M Solution of Potassium t-butoxide in t-Butanol
- $2,3,3-d_3$ -Exo-2-bromonorbornane and its endo-2-isomer (3.5 g., 0.0196 mole) and an approximately 1M solution of potassium t-butoxide in t-butanol were heated on a steam bath in a sealed tube for four days. A white precipitate (potassium bromide) formed during the reaction. The mixture was poured into a 250 ml. round bottom flask containing distilled water (100 ml.). Dry nitrogen was bubbled throughout the flask which led to a water trap, a potassium hydroxide trap, and finally to glass tubes which were cooled by dry ice. The  $2,3-d_2$ -norbornene (107) was sealed in

the glass tubes. The yield of  $2,3-d_2$ -norbornene (0.89 g., 0.0091 mole) was 47%. A sample collected by preparative glpc (IV,  $150^{\circ}$ C) for mass spectral analysis showed a molecular ion at m/e = 96 corresponding to the empirical formula  $C_7H_8D_2$ . The following excess deuterium content was found to exist in 107:  $d_0 = 0.3\%$ ;  $d_1 = 1.7\%$ ;  $d_2 = 93\%$ ;  $d_3 = 5.0\%$ ; or 2.03 excess deuterium atoms per molecule. The nmr spectrum (nmr 1, 60MHz) of 107 showed the following signals;  $\delta$  5.96(residual triplet, C-2-H and C-3-H, less than 5% 2H),  $\delta$  2.83(broad singlet, C-1-H and C-4-H, 2H), 1.80-0.77(norbornyl envelope, exo- and endo-C-5-H, exo- and endo-C-6-H, C-7-H's, 6H).

### 2) Synthesis of Exo- and Endo-5-chloronorbornene

Viny1 chloride (11.7 g., 0.187 mole) and freshly distilled cyclopentadiene (8.8 g., 0.133 mole) were sealed under vacuum at liquid nitrogen temperature in a glass tube. The sealed tube was placed in a steel bomb containing pentane (100 ml.). The reaction was carried out for 15 hours at 220°C. The exo- and endo-5-chloronorbornene were collected by vacuum distillation (b.p. 95-97°C at 54-59 mm.). The yield of exo- and endo-5-chloronorbornene was 60% (10.4 g., 0.0803 mole). Mass spectral analysis showed a molecular ion at m/e = 128, 130 corresponding to the empirical formula C<sub>7</sub>H<sub>9</sub>Cl. Analytical glpc analysis (I, 90°C) showed two major products. The integration of the nmr spectrum of the distilled mixture showed that exo-C-5-H to endo-C-5-H was in the ratio of 7:5 indicating that the ratio of exo-5-chloronorbornene to endo-5-chloronorbornene was 42:58. The nmr spectrum (60 MHz., CCl<sub>4</sub> and TMS) of the mixture showed; 6 6.17(broad multiplet, olefinic-H's of exo- and endo-5-chloronorbornene, 4H), 6 4.42(quintet, J=3.0, 5.0, 4.0, 3.0 Hz., exo-C-

5-H of endo-5-chloronorbornene, 1H), 3.87(triplet with fine splitting, J = 6, 4 Hz., endo-C-5-H of exo-5-chloronorbornene, 1H), 3.23(broad singlet, C-4-H of endo-5-chloronorbornene, 1H), 2.98(broad singlet, C-1-H of endo-5-chloronorbornene, C-1-H and C-4-H of exo-5-chloronorbornene, 3H), 6 2.33 (septet, J = 4.0, 4.5, 3.5, 4.0, 4.5, 3.5 Hz., exo-C-6-H of endo-5-chloronorbornene, 1H), 2.07-1.05(norbornyl envelope, C-7-H's of exo- and endo-5-chloronorbornene, endo-C-6-H's of exo- and endo-5-chloronorbornene, exo-C-6-H of exo-5-chloronorbornene, 7H).

# 3) Synthesis of $E\infty$ - and Endo-5-bromonorbornene

Vinyl bromide (12.0 g., 0.112 mole) and cyclopentadiene (5.0 g., 0.0756 mole) were sealed under vacuum at liquid nitrogen temperature in a glass tube. The glass tube with its contents was heated in a steel bomb containing pentane (100 ml.) for 12 hours at 220°C. The reaction products were distilled under vacuum, and the exo- and endo-5-bromonorbornene were collected at 72-75°C (20 mm.). Mass spectral analysis of the bromides showed a molecular ion at m/e = 172, 174 corresponding to the empirical formula C<sub>7</sub>H<sub>9</sub>Br. Analytical glpc analysis (I, 100°C) showed two major products. The yield of exo- and endo-5-bromonorbornene was 53% (6.93 g., 0.0401 mole). Nmr integration of the nmr spectrum of the products showed that the ratio of exo-C-5-H to endo-C-5-H was 4 : 5 indicating that there was about 44% endo-5-bromonorbornene and 56% exo-5-bromonorbornene. nmr spectrum (60 MHz., TMS) of the distilled products showed:  $\delta$  6.15(broad multiplet, olefinic-H's of exo- and of endo-5-bromonorbornene, 4H), δ 4.27 (quintet, J = 4.0, 4.5 4.5, 4.0 Hz., exo-C-5-H of endo-5-bromonorbornene, 1H), 3.70(broad multiplet, endo-C-5-H of exo-5-bromonorbornene, 1H), 3.05

(broad singlet, C-4-H of exo- and of endo- 5-bromonorbornene, 2H),  $\delta$  2.82 (broad singlet, C-1-H of exo- and of endo-5-bromonorbornene, 2H), and  $\delta$  2.43-1.08(norbornyl envelope, C-7-H's of exo- and of endo-5-bromonorbornene, exo- and endo-C-6-H's of exo- and of endo-5-bromonorbornene, 8H).

#### 4) Synthesis of Exo-2-chloronorbornane

Norbornene (7.0 g., 0.074 mole) and pentane (7 ml.) were added to a 50 ml. round bottom flask and cooled to -78°C by an acetone dry ice bath. To this magnetically stirred solution was bubbled hydrogen chloride for one hour. 35 The work up involved washing with distilled water (2X25 ml.), with dilute sodium bicarbonate solution (2X25 ml.), with distilled water (2X25 ml.) then dried with anhydrous magnesium sulfate. The solvent was distilled off. Yield of exo-2-chloronorbornane was 63% (6.0g.). Mass spectral analysis showed a molecular ion at m/e = 130, 132 corresponding to the empirical formula  $C_7H_{11}C1$ . The nmr spectrum (60 MHz., TMS) of the exo-2chloronorbornane was identical to the nmr spectrum (60 MHz., TMS) of the exo-2-chloronorbornane produced in the large scale reaction of chlorine and norbornene in acetic acid. The nmr spectrum (60 MHz., TMS) of exo-2chloronorbornane showed;  $\delta$  3.83(triplet with fine splitting, J= 5.0, 5.0 Hz., endo-C-2-H, 1H), 2.45-2.20(broad singlet, C-1-H and C-4-H, 2H), and 2.00-0.90 (norbornyl envelope, exo- and endo-C-3-H, exo- and endo-C-5-H, exo- and endo-C-6-H, syn-C-7-H, and anti-C-7-H, 8H).

#### 5) Synthesis of Endo-2-chloronorbornane

2-Chloronorbornene (1.4 g., 0.011 mole), potassium diimide (dipotassium azodicarboxylate, 4.3 g., 0.023 mole), and absolute methanol
(16 ml.) were stirred magnetically in a three necked 50 ml. round bottom

flask. To the yellow slurry was added dropwise acetic acid until a colourless liquid was produced. The methanol was distilled off at 65°C using a Vigreux column (4"). Analytical glpc analysis (II, 150°C) showed one major product. The nmr spectrum (60 MHz.,  $CS_2$  and TMS) of the major product was identical to that reported in the literature for endo-2-chloronorborname, and it showed the following absorptions;  $\delta$  4.10 (broad multiplet, exo-C-2-H, 1H) and 2.40-1.03 (norbornyl envelope, C-1-H, exo- and endo-C-3-H, C-4-H, exo- and endo-C-5-H, exo- and endo-C-6-H, syn-C-7-H, and anti-C-7-H, 10H). The mass spectrum of the major product showed a molecular ion at m/e = 130, 132 corresponding to the empirical formula  $C_7H_{11}C1$ .

#### E. Chlorination of Norbornene

# 1) Large Scale Reaction of Norbornene and Equal Molar Pyridine with Chlorine in Methylene Chloride

Norbornene (35.0 g., 0.372 mole), pyridine (29.4 g., 0.372 mole), and freshly distilled methylene chloride (200 ml.) were dissolved in a three necked 500 ml. round bottom flask. This magnetically stirred solution, with dry nitrogen being bubbled through it, was kept at 0°C by an ice water and salt bath while chlorine dissolved in freshly distilled methylene chloride (200 ml.) was added dropwise in the dark for one hour. After the addition of chlorine, the work up involved washing with dilute sodium thiosulfate solution (3X250 ml.), washing with dilute hydrochloric acid (3X250 ml.), washing with distilled water (3X250 ml.), and drying with anhydrous magnesium sulfate followed by evaporation of the methylene chloride. Analytical glpc analysis (I, 150°C) indicated eight major products were present. The reaction mixture was separated into many frac-

tions by spinning band distillation under vacuum. Since each fraction contained at least two components, preparative glpc (III, 165°C) was used to collect pure fractions for nmr and mass spectral analysis. Only six of the eight products were identified, and they are listed in order of increasing retention time  $(r_t)$  as follows; 3-chloronortricyclene (41)  $(r_t = 1.0 \text{ min.})$ , trans-2,3-dichloronorbornane (43)  $(r_t = 2.4 \text{ min.})$ , anti-7-exo-2-dichloronorbornane (115)  $(r_t = 3.2 \text{ min.})$ , exo,exo-2,3-dichloronorbornane (44)  $(r_t = 6.5 \text{ min.})$ , syn-7-exo-2-dichloronorbornane (42)  $(r_t = 8.0 \text{ min.})$ , and endo,endo-3,5-dichloronortricyclene (116)  $(r_t = 12.1 \text{ min.})$ . The two products at  $r_t = 4.0$  and 14.1 min. were not identified because they were not collected in high enough yield in order to record their spectra.

The nmr spectrum (60 MHz., CCl<sub>4</sub> and TMS) of  $\underline{41}$  showed;  $\delta$  3.93 (singlet, C-3-H, 1H), 2.20(broad singlet overlapping with low field portion of doublet of syn-C-7-H to chloride, C-4-H, 1.36H),  $\delta$  2.10(high field portion of syn-C-7-H to chloride doublet, 0.64H), and 1.60-1.06(broad multiplet, C-1-H, C-2-H, C-5-H, C-5-H, C-6-H, anti-C-7-H to chloride, 6H), and its mass spectrum showed a molecular ion at m/e = 128, 130.

The nmr spectrum (60 MHz.,  $CS_2$  and TMS) of  $\underline{43}$  showed;  $\delta$  4.13(triplet with fine splitting, exo-C-2-H, 1H), 3.57(triplet, endo-C-3-H, 1H), 2.37(broad singlet, C-1-H and C-4-H, 2H), and  $\delta$  2.13-1.06(norbornyl envelope, exo- and endo-C-5-H, exo- and endo-C-6-H, syn-C-7-H, and anti-C-7-H, 6H), and its mass spectrum showed a molecular ion at m/e = 164, 166, 168.

The nmr spectrum (60 MHz.,  $CS_2$  and TMS) of <u>115</u> showed;  $\delta$  4.28 (singlet, syn-C-7-H, 1H), 3.82(a doublet of doublets, endo-C-2-H, 1H), 2.33 (broad singlet, C-1-H and C-4-H, 2H), and  $\delta$  2.20-1.00(norbornyl envelope,

exo- and endo-C-3-H, exo- and endo-C-5-H, exo- and endo-C-6-H, 6H), and its mass spectrum showed a molecular ion at m/e = 164, 166, 168.

The nmr spectrum (60 MHz:, CS<sub>2</sub> and TMS) of  $\underline{44}$  showed;  $\delta$  3.87 (doublet, J = 1 Hz., endo-C-2-H and endo-C-3-H, 2H),  $\delta$  2.38(broad singlet, C-1-H and C-4-H, 2H), and  $\delta$  2.18-1.05(norbornyl envelope, exo- and endo-C-5-H, exo- and endo-C-6-H, syn-C-7-H, and enti-C-7-H, 6H), and its mass spectrum showed a molecular ion at m/e = 164, 166, 168.

The nmr spectrum (60 MHz.,  $CS_2$  and TMS) of  $\underline{42}$  showed;  $\delta$  3.93(sing-let, anti-C-7-H, 1H), 4.07-3.77(broad multiplet overlapped by anti-C-7-H singlet, endo-C-2-H, 1H), 2.67-1.03(norbornyl envelope, C-1-H, exo- and endo-C-3-H, C-4-H, exo- and endo-C-5-H, exo- and endo-C-6-H, 8H), and its mass spectrum showed a molecular ion at m/e = 164, 166, 168.

The nmr spectrum (60 MHz.,  $CS_2$  and TMS) of 116 showed;  $\delta$  4.00 (singlet, endo-C-3-H and endo-C-5-H, 2H),  $\delta$  2.30(broad singlet, C-4-H, 1H), 1.68(doublet, J = 5 Hz., C-7-H and C-7-H both of which are coupled to a cyclopropyl hydrogen, 2H),  $\delta$  1.42(broad singlet, C-1-H, C-2-H, C-6-H, 3H), and its mass spectrum showed a molecular ion at 162, 164, 166.

## 2) Large Scale Reaction of Norbornene with Chlorine in Acetic Acid

In a three necked 500 ml. round bottom flask were added norbornene (6.0 g., 0.640 mole) and dried acetic acid (100 ml.). The flask was surrounded with tin foil and kept at 25°C while a solution of chlorine dissilved in acetic acid (100 ml.) was added dropwise in the dark with dry nitrogen being bubbled throughout the norbornene solution. After the addition, dilute sodium thiosulfate (100 ml.) was stirred in followed by

extraction of the acetic acid and water solution with pentane (3X100 ml.), saturation of the acetic acid and water solution with sodium chloride, then re-extraction with pentane (2X100 ml.). The combined pentane extracts were washed with dilute sodium thiosulfate solution (2X250 ml.), with sodium bicarbonate solution (3X250 ml.), and with distilled water (3X200 ml.). The pentane solution was dried with anhydrous magnesium sulfate, then evaporated off. Analytical glpc analysis (I, 150°C) indicated that there were ten products. The reaction mixture was separated into many fractions by spinning band distillation under vacuum. No fraction contained a pure component; so, preparative glpc (III, 165°C) was used to collect pure components for nmr and mass spectral analysis. Only nine of the ten products were identified, and they are listed in order of increasing retention time  $(r_t)$ ; exo-2-chloronorbornane (120)  $(r_t = 0.8)$ min.), 3-chloronortricyclene (41) (r<sub>t</sub> = 1.0 min.), exo-2-norbornyl acetate (121)  $(r_t = 1.8 \text{ min.})$ , trons-2,3-dichloronorbornane (43)  $(r_t = 2.4 \text{ min.})$ , anti-7-exo-2-dichloronorbornane (115) (r<sub>t</sub> = 3.2 min.), anti-7-chloro-exo-12-norbornyl acetate (122) ( $r_t = 6.9 \text{ min.}$ ), syn-7-exo-2-dichloronorbornane (42) ( $r_t = 8.0 \text{ min.}$ ), syn-7-chloro-exo-2-norbornyl acetate (123) ( $r_t = 9.2$ min.), and endo, endo-3,5-dichloronortricyclene ( $\underline{116}$ ) ( $r_t$  = 12.1 min.). The product at  $r_t$  = 4.0 min. was not identified because it was not collected in high enough yield to record its spectra. There was no nmr spectrum obtained for 116, but it had a similiar retention time to that of endo, endo-3,5-dichloronortricyclene (116) produced from the chlorination of norbornene in methylene chloride. The nmr and mass spectra of 41, 43, 115, 44, and 42 were identical to that of 41, 43, 115, 44, and 42 respectively produced from the chlorination of norbornene in methylene chloride.

The nmr spectrum (60 MHz., TMS) of 120 indicated  $\delta$  3.83(triplet with fine splitting, J = 5.0, 5.0 Hz., endo-C-2-H, 1H), 2.45-2.20(broad singlet, C-1-H and C-4-H, 2H), and  $\delta$  2.00-0.90(norbornyl envelope, exo-and endo-C-3-H, exo- and endo-C-5-H, exo- and endo-C-6-H, syn-C-7-H, and anti-C-7-H, 8H), and its mass spectrum revealed a molecular ion at m/e = 130, 132.

The nmr spectrum (60 MHz., CS<sub>2</sub> and TMS) of 121 indicated;  $\delta$  4.40 (broad multiplet, endo-C-2-H, 1H), 2.18 (broad singlet, C-1-H and C-4-H, 2H),  $\delta$  1.85 (sharp singlet, methyl protons, 3H), and  $\delta$  1.67-0.97 (norbornyl envelope, exo- and endo-C-3-H, exo- and endo-C-5-H, exo- and endo-C-6-H, synC-7-H, and anti-C-7-H, 8H), and its mass spectrum revealed a molecular ion at m/e = 154.

The nmr spectrum (60 MHz., CS<sub>2</sub> and TMS) of 122 indicated;  $\delta$  4.52 (quartet, J = 3.0, 4.0, 3.0, endo-C-2-H, 1H), 4.03(singlet, syn-C-7-H, 1H), 2.23(broad singlet, C-1-H and C-4-H, 2H);  $\delta$  1.92(sharp singlet, methyl protons from acetate, 3H), and  $\delta$  2.08-1.00(norbornyl envelope, exo- and endo-C-3-H, exo- and endo-C-5-H, exo- and endo-C-6-H, 6H), and its mass spectrum revealed a molecular ion at m/e = 188, 190.

The nmr spectrum (60 MHz., CS<sub>2</sub> and TMS) of 123 indicated;  $\delta$  4.50 broad multiplet, endo-C-2-H, 1H), 3.82(doublet with fine splitting, J=1 Hz., anti-C-7-H, 1H), 2.47-2.17(broad singlet, C-1-H and C-4-H, 2H),  $\delta$  1.90(sharp singlet, methyl protons of acetate, 3H), and  $\delta$  2.13-1.03(nor-bornyl envelope, exo- and endo-C-3-H, exo- and endo-C-5-H, exo- and endo-C-6-H, 6H), and its mass spectrum revealed a molecular ion at m/e = 188, 190.

## 3) Chlorination of Norbornene in Methylene Chloride

The procedure was similiar to that of the large scale reaction of norbornene and equal molar pyridine with chlorine in methylene chloride, except no washing with dilute hydrochloric acid was performed. The following quantities were used; norbornene (0.0578 g., 2.45 X 10<sup>-2</sup> M/L) and methylene chloride (2X25 ml.). Analytical glpc analysis (I, 150°C) indicated that there were eight products with identical retention times to the eight products from the large scale reaction in methylene chloride. Six products, therefore, were assumed to be 41, 43, 115, 44, 42, and 116 with two unidentified products.

# 4) Chlorination of Norbornene and Equal Molar Pyridine in Methylene Chloride

The procedure was similiar to that of the large scale reaction of norbornene and equal molar pyridine with chlorine in methylene chloride. The following quantities were used; norbornene (20 mg., 2.18 X  $10^{-2} M/l$ ), pyridine (17.2 mg., 2.18 X  $10^{-2} M/l$ ), and methylene chloride (2X10 ml.). Analytical glpc analysis (I, 150°C) indicated that there were eight products with identical retention times to the eight products from the large scale reaction in methylene chloride. Six products, therefore, were assumed to be 41, 43, 115, 44, 42, and 116 with two unidentified products.

# 5) Chlorination of Norbornene and Ten Times Molar Pyridine in Methylene Chloride

The procedure was similiar to that of the large scale reaction of norbornene and equal molar pyridine with chlorine in methylene chloride.

The following quantities were used; norbornene (20.7 mg., 2.2 X 10<sup>-4</sup> mole), pyridine (174.0 mg., 2.2 X 10<sup>-3</sup> mole), and methylene chloride (2 X 10 ml.). Analytical glpc analysis (I, 150°C) indicated that there were eight products with identical retention times to the eight products from the large scale reaction in methylene chloride. Six products, therefore, were assumed to be 41, 43, 115, 44, 42, and 116 with two unidentified products.

## 6) <u>Chlorination of Norbornene and Equal Molar Pyridine in Carbon Tetra-</u> Chloride

The procedure was similiar to that of the large scale reaction of norbornene and equal molar pyridine with chlorine in methylene chloride. The following quantities were used; norbornene (17.3 mg., 1.80 X 10<sup>-4</sup> mole), pyridine (14.6 µl., 1.80 X 10<sup>-4</sup> mole), and carbon tetrachloride (2 X2.3 ml.). Analytical glpc analysis (I, 150°C) indicated that there were eight products with identical retention times to the eight products from the large scale reaction in methylene chloride. Six products, therefore, were assumed to be 41, 43, 115, 44, 42, and 116 with two unidentified products.

### 7) Chlorination of Norbornene in Acetic Acid

The procedure was similiar to that of the large scale reaction of chlorine with norbornene in acetic acid. The following quantities were used; norbornene (60 mg.,  $12.7 \times 10^{-2} \, \text{M/l}$ ) and dried acetic acid (2X20 ml.). Analytical glpc analysis (I,  $150^{\circ}$ C) indicated that there were eight products with identical retention times to eight out of the ten products from the large scale reaction in acetic acid. Seven of the pro-

ducts in the small scale reaction were assumed to be 41, 43, 115, 122, 42, 123, and 116 because of the similiarity of their reaction times to the corresponding products in the large scale reaction. The eighth product was unidentified in both reactions.

## F. Bromination of Norbornene

# 1) Large Scale Bromination of Norbornene in Acetic Acid

Norbornene (30.5 g., 0.319 mole) and dried acetic acid (200 ml.) were placed in a 500 ml. three necked flask which was surrounded with tin Dry nitrogen was bubbled throughout the mechanically stirred solution which was kept at 25°C, while bromine (58 g., 0.363 mole) dissolved in dried acetic acid (200 ml.,) was added dropwise in the dark for one hour. After the addition, the reaction mixture was worked up by adding dilute sodium thiosulfate solution (100 ml), extracting the acetic acid and water mixture with pentane (3X200 ml.,), saturating the acetic acid and water mixture with sodium chloride, then re-extracting with pentane (2X250 ml.). The combined pentane layers were washed with dilute sodium thiosulfate solution (2X250 ml.), with sodium bicarbonate solution (3X 250 ml.,), and with distilled water (3X250 ml.). The pentane was dried with anhydrous magnesium sulfate. The solvent was removed by a Rotovaporator. Analytical glpc analysis (I, 150°C) showed eight products. The reaction mixture was distilled under vacuum with a spinning band. All the fractions contained at least two components. Since it was impossible to obtain pure compounds by the spinning band distillation, various fractions were selected for separation by preparative glpc (III, 165°C). A nmr spectrum of each collected peak was recorded after analytical glpc (I, I50°C) analysis indicated at least a 95% pure collected component. A mass spectrum of each collected peak was also recorded. There was not enough compound collected of the sixth eluted component to obtain any spectra.

The seven identified products were exo-2-bromonorbornane (27)  $(\mathbf{r_t} = 1.1 \text{ min.})$ , 3-bromonortricyclene (28)  $(\mathbf{r_t} = 1.4 \text{ min.})$ , trans-2,3-dibromonorbornane (29)  $(\mathbf{r_t} = 4.8 \text{ min.})$ , anti-7-exo-2-dibromonorbornane (30)  $(\mathbf{r_t} = 6.1 \text{ min.})$ , anti-7-bromo-exo-2-norbornyl acetate (124)  $(\mathbf{r_t} = 8.1 \text{ min.})$ , syn-7-bromo-exo-2-norbornyl acetate (125)  $(\mathbf{r_t} = 10.5 \text{ min.})$ , and syn-7-exo-2-dibromonorbornane (33)  $(\mathbf{r_t} = 15.2 \text{ min.})$ . The compound at  $\mathbf{r_t} = 8.7 \text{ min.}$  was not identified due to insufficient quantity necessary in order to obtain a nmr spectrum.

The nmr spectrum (60 MHz., TMS) of  $\underline{27}$  showed;  $\delta$  3.88(broad multiplet, endo-C-2-H, 1H), 2.47(broad singlet, C-1-H, 1H), 2.27(broad singlet, C-4-H, 1H), 2.00(broad multiplet, exo- and endo-C-3-H, 2H), and  $\delta$  1.83-1.03(broad multiplet, exo- and endo-C-5-H, exo- and endo-C-6-H, syn-C-7-H, and anti-C-7-H, 6H), and its mass spectrum revealed a molecular ion at m/e = 174, 176.

The nmr spectrum (60 MHz., TMS) of 28 showed; & 3.87(broad singlet, C-3-H, 1H), 2.08(broad singlet overlapping with low field portion of doublet of C-7-H syn to bromide, C-4-H, 1.36H), & 2.00(high field portion of doublet, C-7-H syn to bromide, 0.64H), and 1.60-1.06(broad multiplet, C-1-H, C-2-H C-6-H, C-5-H, C-5-H, and anti-C-7-H, 6H), and its mass spectrum showed a molecular ion at m/e = 172. 174.

The nmr spectrum (60 MHz., TMS) of  $\underline{29}$  indicated;  $\delta$  4.38(multi-

plet, exo-C-3-H coupled to endo-C-2-H (J=3Hz.) and to C-1-H with slight W coupling to exo-C-5-H, 1H), 3.77(triplet, endo-C-2-H coupled to exo-C-3-H (J=3Hz.), 1H), 2.42(broad multiplet, C-1-H and C-4-H, 2H), and  $\delta$  2.15-1.10 (norbornyl envelope, exo- and endo-C-5-H, exo- and endo-C-6-H, exo- and endo-C-7-H, and exo- and exo-C-7-H, exo-

The nmr spectrum (60 MHz.,  $CS_2$  and TMS) of 30 indicated;  $\delta$  4.35 (broad singlet, syn-C-7-H, 1H), 3.88(multiplet, endo-C-2-H, 1H), 2.50 (broad multiplet, C-1-H and C-4-H, 2H), and  $\delta$  2.18-1.10(norbornyl envelope, exo- and endo-C-5-H, exo- and endo-C-6-H, exo- and endo-C-3-H, 6H), and its mass-spectrum revealed a molecular ion at m/e = 252, 254, 256.

The nmr spectrum (60 MHz., CS<sub>2</sub> and TMS) of 124 showed;  $\delta$  4.60 (quartet, J = 4.0, 5.0, 4.0 Hz. coupled to exo- and endo-C-3-H, endo-C-2-H, 1H), 4.12 (broad singlet, syn-C-7-H, 1H), 2.33 (broad singlet, C-1-H and C-4-H, 2H),  $\delta$  1.90 (singlet, methyl protons of acetate group, 3H), and  $\delta$  2.17-0.83 (norbornyl envelope, exo- and endo-C-3-H, exo- and endo-C-5-H, exo- and endo-C-6-H, 6H), and its mass spectrum revealed a molecular ion at m/e = 232, 234.

The nmr spectrum (60 MHz.,  $CS_2$  and TMS) of 125 showed;  $\delta$  4.60 (multiplet, endo-C-2-H, 1H), 3.85 (broad peak, anti-C-7-H, 1H), 2.50 (broad singlet, C-1-H, 1H), 2.37 (broad singlet, C-4-H, 1H), 1.92 (sharp singlet, methyl protons of acetate group, 3H), and  $\delta$  2.20-1.00 (norbornyl envelope, exo- and endo-C-3-H, exo- and endo-C-5-H, exo- and endo-C-6-H, 6H), and its mass spectrum revealed a molecular ion at m/e = 232, 234.

The nmr spectrum (60 MHz., CS<sub>2</sub> and TMS) of 33 showed; 63.93

(singlet, anti-C-7-H, 1H), 3.90(doublet of doublets, endo-C-2-H, 1H), 2.67 (broad singlet, C-1-H and exo-C-3-H, 2H), 6 2.37(broad singlet, C-4-H, 1H), and 2.40-0.97(norbornyl envelope, endo-C-3-H, exo- and endo-C-5-H, exo- and endo-C-6-H, 5H), and its mass spectrum revealed a molecular ion at m/e=252, 254, 256.

#### 2) Bromination of Norbornene in Acetic Acid

The procedure was similiar to that of the large scale bromination of norbornene in acetic acid. The following quantities were used; norbornene (19.7 mg.,  $2.62 \times 10^{-2} \ \text{M/l}$ ) and dried acetic acid (2X8.0 ml.). Analytical glpc (I,  $150^{\circ}$ C) analysis indicated that there were eight products whose retention times were similiar to the products of the large scale reaction. The seven products were assumed to be 27, 28, 29, 30, 124, 125, and 33.

#### 3) Bromination of Norbornene in Methylene Chloride

Norbornene (51.7 mg., 2.2 X 10<sup>-2</sup> M/1) and dried methylene chloride (25 ml.) were placed in a 125 ml. round bottom flask which was surrounded with tin foil. Dry nitrogen was bubbled through the mechanically stirred solution which was kept at about 0°C by an ice, water, and salt bath while bromine (88.0 mg., 2.2 X 10<sup>-2</sup> M/1) dissolved in dried methylene chloride (25 ml.) was added dropwise in the dark for fifteen minutes. After the addition, dried methylene chloride (50 ml.) was added. The mixture was worked up by washing with dilute sodium thiosulfate solution (2X50 ml.), and washing with distilled water (2X50 ml.). The methylene chloride solution was dried with anhydrous magnesium sulfate, followed by removal of

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most of the methylene chloride by a Rotovaporater. Analytical glpc analysis (I, 150°C) showed seven major products. Comparison of retention times with the large scale bromination of norbornene in acetic acid indicated that the first four products in both reactions were identical and that the last product was identical. Each pure component from the large scale reaction was mixed individually with the reaction mixture of the bromination of norbornene in methylene chloride in order to further verify the identity of products. The results were consistent with the above identification. The fifth and sixth eluted products were identified by comparison of reported 32 retention times. The seven products and their retention times are listed in order of increasing retention time; exo-2-bromonorbornane  $(\underline{27})$  (r<sub>t</sub> = 1.1 min.), 3-bromonortricyclene ( $\underline{28}$ ) (r<sub>t</sub> = 1.4 min.), trans-2,3-dibromonorbornane ( $\frac{29}{t}$ ) (r<sub>t</sub> = 4.8 min.), anti-7-exo-2-dibromonorbornane (30) (r<sub>t</sub> = 6.1 min.), endo-5-exo-2-dibromonorbornane (31) (r<sub>t</sub> = 7.8 min.), exo, exo-2,5-dibromonorbornane (32) ( $r_t$  = 8.7 min.), and syn-7-exo-2-dibromonorbornane ( $\underline{33}$ ) ( $r_t = 15.2 \text{ min.}$ ).

# 4) Bromination of Norbornene and Equal Molar Pyridine in Methylene Chloride

The procedure was identical to that of the bromination of norbornene in methylene chloride except that the work up included washing with dilute hydrochloric acid (3X50 ml.) after washing with dilute sodium thiosulfate. The concentrations used were as follows; norbornene (58.0 mg., 2.46 X  $10^{-2}$  M/l), pyridine (54.0 mg., 2.73 X  $10^{-2}$  M/l), bromine (106.0 mg., 2.65 X  $10^{-2}$  M/l), and methylene chloride (2X25 ml.). Analytical glpc analysis (I, 150°C) indicated that there were seven products

with identical retention times to that obtained in the reaction of bromine with norbornene in methylene chloride. The seven products were assumed to be  $\underline{27}$ ,  $\underline{28}$ ,  $\underline{29}$ ,  $\underline{30}$ ,  $\underline{31}$ ,  $\underline{32}$ , and  $\underline{33}$ .

# 5) Bromination of Norbornene and Ten Times Molar Pyridine in Methylene Chloride

The procedure was identical to that of the bromination of norbornene and equal molar pyridine in methylene chloride. The following concentrations were used; norbornene (56.0 mg., 2.38 X  $10^{-2}$  M/Z), pyridine (0.468 g., 23.70 X  $10^{-2}$  M/Z), bromine (120 mg., 2.50 X  $10^{-2}$  M/Z), and methylene chloride (2X30 ml.). Analytical glpc analysis (I, 150°C) indicated that there were seven products with identical retention times to that obtained in the reaction of bromine with norbornene in methylene chloride. The seven products were assumed to be 27, 28, 29, 30, 31, 32, and 33.

## 6) Bromination of Norbornene and Equal Molar Pyridine in Carbon Tetra-Chloride

The procedure was identical to that of the bromination of norbornene and equal molar pyridine in methylene chloride. The following concentrations were used; norbornene (17.5 mg., 1.82 X 10<sup>-4</sup> mole), pyridine (14.4 µl. 1.82 X 10<sup>-4</sup> mole), bromine (29 mg., 1.82 X 10<sup>-4</sup> mole), and carbon tetrachloride (2X10 ml.). Analytical glpc analysis (I, 150°C) indicated that there were seven products with identical retention times to that obtained in the reaction of bromine with norbornene in methylene chloride. The seven products were assumed to be 27, 28, 29, 30, 31, 32,

and 33.

# 7) Bromination of Norbornene and Equal Molar 2,6-Lutidine in Methylene Chloride

The procedure was identical to that of the bromination of norbornene and equal molar pyridine in methylene chloride except 2,6-lutidine was substituted for pyridine. The following quantities were used; norbornene (23.3 mg., 2.48  $\times$  10<sup>-2</sup> Mt), 2,6-lutidine (26.5 mg., 2.48  $\times$  10<sup>-2</sup> M/t), bromine (39.7 mg., 2.48  $\times$  10<sup>-2</sup> M/t), and methylene chloride (2X10 ml.). Analytical glpc analysis (I, 150°C) indicated that there were seven products with identical retention times to that obtained in the reaction of bromine with norbornene in methylene chloride. The seven products were assumed to be 27, 28, 29, 30, 31, 32, and 33.

# G. Reaction of Iodine Monochloride with Norbornene

# 1) Large Scale Reaction of Iodine Monochloride with Norbornene and Equal Molar Pyridine in Methylene Chloride

Norbornene (44.5 g., 0.47 mole), pyridine (38.5 ml.), and methylene chloride (290 ml.) were added to a three necked one litre round bottomed flask which was wrapped with tin foil. The mixture was stirred mechanically and cooled to 0°C by an ice, salt, and water bath. Iodine monochloride (75.8 g., 0.47 mole) in methylene chloride (140 ml.) was added dropwise to the mixture in the dark as dry nitrogen was bubbled throughout the solution. After the addition, the mixture was allowed to sit for twenty minutes followed by a work up consisting of washing with dilute sodium thiosulfate solution (3X200 ml.), washing with dilute hydro-

chloric acid solution (2X200 ml.), washing with distilled water (2X200 ml.), then drying with anhydrous magnesium sulfate. The methylene chloride was removed by distillation through a Vigreux column of lenght one foot. Analytical glpc analysis (I, 150°C) showed products at  $r_t = 3.60$ min. 128,  $r_t = 6.60$  min. 129,  $r_t = 7.30$  min., and  $r_t = 11.0$  min. 130. Vacuum distillation through a vacuum jacketed Vigreux column of lenght 1.5 feet gave fraction 1, b.p. 46-52°C (3.8 mm.) containing 128 plus some minor components; fraction 2, b.p. 56-58°C (3.6 mm.) containing 128 (90% pure by glpc analysis); fractions 3 and 4, b.p. 48-50°C (2.5 mm.) containing 129 and 130; fraction 5, b.p. 50-53°C (2.5 mm.) containing 130 (95% pure by glpc analysis); and fraction 6, b.p. 50-56°C (2.5 mm.) containing 130 (90% pure by glpc analysis). After the distillation, the reddish brown fractions were dissolved separately in ether and washed with dilute sodium thiosulfate solution. The ether was distilled off and the three components of  $r_t = 3.60$ , 6.60, and 11.0 min. were collected by preparative glpc analysis (III, 165°c).

Chemical reactions, nmr spectra, and mass spectra were used to identify the three major products as being 3-iodonortricyclene (128),  $e\infty$ -2-iodo-endo-2-chloronorbornane (129), and  $ext{syn}$ -7-iodo- $ext{co}$ -2-chloronorbornane (130). The nmr spectra 3, 4, and 5 of 128, 129, and 130 respectively are described in the results. The overall yield was 75% (91.2 g., 0.356 mole).

# 2) Reaction of Exo-2-iodo-endo-3-chloronorbornane with Potassium t-butoxide in t-Butanol

Exo-2-iodo-endo-3-chloronorbornane (129) (2.1 g., 90% of 129 and

5% of unknown) was dissolved in an approximately 1M solution of potassium t-butoxide in t-butanol (55 ml.) in a 100 ml. flask fitted with a condenser and a calcium chloride drying tube. The mixture was refluxed and stirred for 3.5 hours at which time analytical glpc analysis (I, 150°C) indicated 98% completion of reaction. The mixture was poured into distilled water (100 ml.) and extracted with pentane (3X50 ml.). The pentane layer was washed with water (4X100 ml.), dried with anhydrous magnesium sulfate, and then the solvent was distilled off. The major peak was collected by preparative glpc (III, 150°C). Mass spectral analysis showed a molecular ion at m/e = 128, 130 corresponding to the empirical formula  $C_7H_9C1$ . From the nmr spectrum and the mass spectrum, the product was determined to be 2-chloronorbornene (131).

The nmr spectrum (60 MHz., CC1<sub>4</sub> and TMS) of <u>131</u> indicated the following absorptions;  $\delta$  5.75(doublet, J = 3.5 Hz., olefinic-H, 1H), 2.85 (broad multiplet, C-1-H and C-4-H, 2H), and  $\delta$  1.88-1.00(norbornyl envelope exo- and endo-C-5-H, exo- and endo-C-6-H, syn-C-7-H, and onti-C-7-H, 6H).

# 3) Lithium Aluminium Hydride Reduction of Exo-2-iodo-endo-3-chloronorbornane

Lithium aluminium hydride (0.13 g., 0.00342 mole) and anhydrous ether (25 ml.) were mechanically stirred in a 100 ml. round bottom flask. To this was added dropwise at room temperature using an equi-pressure separatory funnel, a mixture of products (0.80 g., 0.00313 mole, 90% of 129 and 10% unknown) and anhydrous ether (25 ml.). After the addition, the mixture was stirred for forty-eight hours. Work up involved quenching with water (25 ml.). The ether layer was dried with anhydrous magnesium

sulfate, then it was distilled off. Analytical glpc analysis (I,150°C) indicated that the reaction was 95% complete with one major product (90%). Collection of the major product by preparative glpc (III, 150°C) followed by mass spectral analysis showed a molecular ion at m/e = 130, 132 corresponding to the empirical formula  $C_7H_{11}Cl$ . The nmr spectrum of the major product (60 MHz.,  $CS_2$  and TMS) was identical to that of the nmr spectrum already described of an authentic sample of endo-2-chloronorbornane (132) produced by the reduction of 2-chloronorbornane with diimide. Thus the major product was endo-2-chloronorbornane (132).

# 4) Reaction of Exo-2-iodo-endo-3-chloronorbornane with Tri-n-butyltin hydride

To a mixture containing exo-2-iodo-endo-3-chloronorbornane (129) and some unknown (1.0 g., 90% of 129 and 10% of unknown) was added tri-n-butyltin hydride (1.1 g., 3.8 X 10<sup>-3</sup> mole) in pentane (30 ml.) dropwise at 25°C. After the addition was complete, the pentane layer was washed with water (3X50 ml.), then dried with anhydrous magnesium sulfate. The analytical glpc (I, 150°C) showed that the reaction was 95% complete. The pentane was distilled through a Vigreux column of lenght six inches, and the major product was isolated by preparative glpc (111, 150°C). The nmr spectrum (60 MHz., CCl<sub>4</sub> and TMS) of the major product was identical to that of endo-2-chloronorbornane (132). Some exo-2-chloronorbornane was also present. The nmr spectrum of 132 was previously described when it was synthesized.

# 5) Reaction of Syn-7-iodo-exo-2-chloronorbornane with Potassium t-butoxide in t-Butanol

Syn-7-iodo-exo-2-chloronorbornane (130) (2.1 g., 95% of 130 and 5% of unknown) was refluxed in an approximately 1M solution of potassium tbutoxide in t-butanol (55 ml.). Five aliquots were removed at 3.7, 14.3, 19.5, 25.0, and 35.0 hours and analyzed by analytical glpc (I, 150°C). Three products  $r_t = 2.0$ , 2.6, and 3.0 mim. were present as well as minor components (2%) at  $r_t$  = 1-1.5 and 2.4 min. There was a gradual decrease in intensity of peaks at  $r_t = 10.2 \frac{130}{100}$  and 3.0 min. and an increase in the intensity of the peaks at  $r_t$  = 2.0 and 2.6 min. After 36 hours, the solution was worked up by first adding ice cold water (100 ml.), then the solution was extracted with pentane (3X50 ml.). The combined pentane was washed with water (4X100 ml.), then dried with anhydrous magnesium sulfate followed by evaporation of the pentane. Analytical glpc analysis (II, 150°C) showed that 10% of the starting material remained with the ratio of products at  $r_t$  = 2.0, 2.6, and 3.0 min. being 2 : 1 : 1. The three components were isolated by preparative glpc (V, 130°C). The three major products were identified as anti-7-t-butoxynorbornene (134) ( $r_t = 2.0$ min.), endo-2-t-butoxytricyclo[4.1.0.0 $^{3,7}$ ]heptane (135) (r<sub>t</sub> = 2.6 min.), and syn-7-iodonorbornene (133) ( $r_t = 3.0 \text{ min.}$ ).

Elemental analysis was in agreement with calculated values as shown below.

Compound	Calculated		Found	
	С	н	C•	
134	79.52	10.84	79.59	10.97
135	79.52	10.84	79.66	10.72
133	38.19	4.09	38 <b>.</b> 50	3.92

The nmr spectra (nmrs 6,7,8)of  $\underline{133}$ ,  $\underline{134}$ , and  $\underline{135}$  respectively were already described in the results.

# 6) Reaction of Syn-7-iodo-exo-2-chloronorbornane with Tri-n-butyltin hydride

Syn-7-iodo-exo-2-chloronorbornane (130) (1.3 g., 95% of 130 and 5% of 129) in pentane (32 ml.) was added dropwise to tri-n-butyltin hydride (1.3 g., 4.6 X  $10^{-3}$  mole) in pentane (37 ml.) at 25°C. The solution was washed with water (3X50 ml.), then dried with anhydrous magnesium sulfate. The analytical glpc analysis (I, 150°C) showed one major product (85%), with 10% of 130 and 5% of 129. The major product was isolated by preparative glpc (III, 130°C) after the pentane was removed by distillation through a Vigreux column of lenght six inches. The product was identified as exo-2-chloronorbornane from mass spectral analysis and from nmr analysis. The mass spectrum showed a molecular ion at m/e = 130, 132, and its nmr spectrum (60 MHz., TMS) was identical to the nmr spectrum of exo-2-chloronorbornane (120) previously synthesized by adding hydrogen chloride to norbornene in pentane. The nmr spectrum of 120 was previously described in the experimental.

### 7) Reaction of Syn-7-iodonorbornene with Potassium t-butoxide in t-Butanol

Syn-7-iodonorbornene (133) (0.506 g., 0.00230 mole) and an approximately 1M solution of potassium t-butoxide in t-butanol (15 ml.) were refluxed and stirred magnetically in a 50 ml. round bottom flask. Analytical glpc analysis (I, 130°C) showed two products were formed with retention times similiar to that of the ethers produced in the reaction of syn-7-iodo-exo-2-chloronorbornane with potassium t-butoxide in t-butanol. The

two products were, therefore, assumed to be anti-7-t-butoxynorbornene and endo-2-t-butoxytricyclo[4.1.0.0<sup>3,7</sup>]heptane. Their respective nmr spectra (nmr 7 and 8) were described in the results.

#### 8) Reaction of Iodine Monochloride with Norbornene in Methylene Chloride

Norbornene (62.6 mg., 6.66 X 10<sup>-4</sup> mole) and methylene chloride (25 ml.) were added to a 100 ml. round bottom flask which was surrounded with tin foil. Dry nitrogen was bubbled through the mechanically stirred solution which was kept below 0°C by an ice, water, and salt bath. To the solution was added dropwise in the dark iodine monochloride (108.0 mg., 6.66 X 10<sup>-4</sup> mole) dissolved in methylene chloride (25 ml.). After the reaction, the methylene chloride solution was washed with dilute sodium thiosulfate solution (3X25 ml.), with distilled water (3X25 ml.), and dried with anhydrous magnesium sulfate. The solvent was evaporated. Analytical glpc analysis (I, 150°C) indicated that there were four products with retention times identical to the four products obtained from the large scale reaction of iodine monochloride with norbornene and equal molar pyridine in methylene chloride. Three of the products were thus assumed to be 128, 129, and 130.

# 9) Reaction of Iodine Monochloride with Norbornene and Equal Molar Pyridine in Methylene Chloride

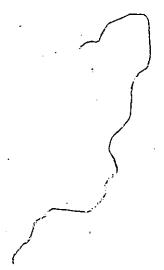
The procedure was identical to that of the reaction of iodine monochloride with norbornene in methylene chloride except that the reaction mixture was washed with dilute hydrochloric acid solution (3X25 ml.) after washing with dilute sodium thiosulfate. The following quantities

were used; norbornene (26.9 mg.,  $2.86 \times 10^{-2} M/l$ ), pyridine (22.6 mg.,  $2.86 \times 10^{-2} Ml$ ), iodine monochloride (73.2 mg.,  $2.86 \times 10^{-2} Ml$ ) and dried methylene chloride (2X10 ml.). Analytical glpc analysis (I, 150°C) indicated that there were four products with retention times identical to those produced in the reaction of iodine monochloride with norbornene in methylene chloride. Three of the products were assumed to be 128, 129, and 130.

# 10) Reaction of Iodine Monochloride with Norbornene in Acetic Acid

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Norbornene (29 mg., 2.08 X  $10^{-2}M/l$ ) and dry acetic acid (15 ml.) were added to a 50 ml. three necked round bottom flask which was wrapped with tin foil. The mixture was stirred mechanically and kept at 25°C. Iodine monochloride (66.0 mg., 2.58  $\times$  10<sup>-2</sup> Ml) in dry acetic acid (16 ml.) was added dropwise to the mixture in the dark as dry nitrogen was bubbled through it. After the addition, dilute sodium thiosulfate solution (15 ml.) was added. The mixture was extracted with pentane (3X50 ml.), then saturated with sodium chloride. The mixture was again extracted with pentane (2X50 ml.). The combined pentane layers were washed with dilute sodium thiosulfate solution (2X50 ml.), then with dilute sodium bicarbonate solution (3X50 ml.), followed by washing with distilled water (3X50 ml.). The pentane was dried with anhydrous magnesium sulfate followed by removal of most of the solvent. Analytical glpc analysis (I, 150°C) indicated the presence of many products. Four of the products had identical retention times to four of the products from the reaction of iodine monochloride to norbornene in methylene chloride. Thus three of the products were assumed to be 128, 129, and 130. Further verification of the assigned structures was performed only on the compound assumed to be 3-iodonortricyclene (128). It was collected by preparative glpc (III, 165°C); its mass spectrum (m/e = 220) was consistent with the empirical formula  $C_7H_9I$ ; its nmr spectrum was identical to that of 3-iodonortricyclene (nmr 3) which was previously described in the results.



CHAPTER 5

REFERENCES

- 2) A. Nickon and N. H. Werstiuk, J. Amer. Chem. Soc., 89, 3915 (1967).
- 3) A. Nickon and N. H. Werstiuk, J. Amer. Chem. Soc., 89, 3917 (1967).
- 4) N. H. Werstiuk, Chem. Common., 1499 (1970).
- 5) N. H. Werstiuk, Can. J. Chem., 53, 26 (1975).
- 6) C. J. Collins and B. M. Benjamin, J. Amer. Chem. Soc., 89, 1652 (1967).
- 7) D. R. Marshall, P. Reynolds-Warnhoff, and E. W. Warnhoff, Can. J. Chem., 49, 885 (1971).
- 8) H. Kwart and L. Kaplan, J. Amer. Chem. Soc., 76, 4072 (1954).
- 9) J. D. Roberts, F. O. Johnson, and R. A. Carboni, J. Amer. Chem. Soc., 76, 5692 (1954).
- 10) M. L. Poutsma, J. Amer. Chem. Soc., 87, 4293 (1965).
- 11) D. D. Tanner and G. C. Gidley, J. Org. Chem., 33, 385 (1968).
- 12) F.-H. Dean, D. R. Marshall, E. W. Warnhoff, and F. L. M. Pattison, Can. J. Ch8m,, 45, 2279 (1967).
- 13) G. J. Karabatsos, C. E. Orzech Jr., J. L. Fry, and S. Meyerson, J. Amer. Chem. Soc., 92, 606 (1970).
- 14) J. C. Gfeever and D. E. Gwyn, Tetrahedron Letters, 813 (1969).
- 15) F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, J. Amer. Chem. Soc., 90, 5298 (1968).
- 16) F. G. Bordwell and B. B. Jarvis, J. Amer. Chem. Soc., 95, 3585 (1973).
- R. G. Pearson and J. Songstad, J. Amer. Chem. Soc., 89, 1827 (1967).
- 18) R. F. Hudson, "Structure and Mechanisms in Organo-Phosesorous Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapters 4 and 5.
- 19) B. B. Jarvis, S. D. Dutkey, and H. L. Ammon, J. Amer. Chem. Soc., 94, 2136 (1972).
- 20) S. J. Cristol, J. K. Harrington, and M. Singer, J. Amer. Chem. Soc., 88, 1529 (1966).
- 21) S. J. Gristol and B. B. Jarvis, J. Amer. Chem. Soc., 88, 3095 (1966).
- 22) S. J. Cristol and B. B. Jarvis, J. Amer. Chem. Esoc., 89, 401 (1967).

- 23) S. J. Cristol, A. R. Dahl, and W. Y. Lim, J. Amer. Chem. Soc., 92, 5670 (1972).
- 24) L. A. Paquette and R. W. Houser, J. Amer. Chem. Soc., 91, 3870 (1969).
- 25) E. J. Corey and E. Block, J. Org. Chem., 34, 1233 (1969).
- 26) R. E. Pincock and E. J. Torupka, J. Amer. Chem. Soc., 91, 4593 (1969).
- 27) J. P. Schaefer and D. S. Weinberg, J. Org. Chem., 30, 2635 (1965).
- 28) J. P. Schaefer and D. S. Weinberg, J. Org. Chem., 30, 2639 (1965).
- 29) N. H. Werstiuk, Can. J. Chem., 48, 2310 (1970).
- 30) S. Masson and A. Thuillier, Bulletin de la Societe Chimique de France, 12, 4368 (1969).
- 31) H. L. Goering and M. J. Degani, J. Amer. Chem. Soc., 91, 4506 (1969).
- 32) D. R. Marshall, P.H.D. Thesis, University of Western Ontario.
- 33) U. E. Diner and J. W. Lown, Cart. J. Chem., 49, 403 (1971).
- 34) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, J. Org. Chem., 30, 2624 (1965).
- 35) L. Schmerling, J. Amer. Chem. Soc., 68, 195 (1946).
- 36) Professor J. A. Berson very kindly provided experimental details.
- 37) N. H. Werstiuk, I. Vancas, J. Warkentin, and F. R. S. Clark, Can. J. Chem., 50, 291 (1972).
- 38) G. Williams, Trans. Faraday Soc., 37, 749 (1941).
- 39) C. K. Ingold and E. H. Ingold, J. Chem. Soc., 2354 (1931).
- 40) S. V. Anantakrishnan and C. K. Ingold, J. Chem. Soc., 984 (1935).
  - 41) S. V. Anantakrishnan and C. K. Ingold, J. Chem. Soc., 1396 (1935).
  - 42) P. W. Roberston, N. T. Clare, K. J. McNaught, and G. W. Paul, J. Chem. Soc., 335 (1937).
  - 43) I. K. Walker and P. W. Roberston, J. Chem. Soc., 1515 (1939).
  - 44) E. P. White and P. W. Roberston, J. Chem. Soc., 1509 (1939).

- 45) I. D. Morton and P. W. Roberston, J. Chem. Soc., 129 (1945).
- 46) B. E. Swedlund and P. W. Roberston, J. Chem. Soc., 131 (1945).
- 47) P. B. D. de la Mare and P. W. Roberston, J. Chem. Soc., 888 (1945).
- 48) I. Hartman and P. W. Roberston, J. Chem. Soc., 891 (1945).
- 49) I. Ting and P. W. Roberston, J. Chem. Soc., 628 (1947).
- 50) B. E. Swedlund and P. W. Roberston, J. Chem. Soc., 630 (1947).
- 51) H. P. Rothbaum, I. Ting, and P. W. Roberston, J. Chem. Soc., 980 (1948).
- 52) P. W. Roberston, R. M. Dixon, W. G. M. Goodwin, I. R. McDonald, and J. F. Scaife, J. Chem. Soc., 294 (1949).
- 53) L. D. Swindale, B. E. Swedlund, and P. W. Roberston, *J. Chem. Soc.*, 812, (1950).
- 54) P. W. Roberston, W. E. Dasent, R. M. Milburn, and W. H. Oliver, J. Chem. Soc., 1628 (1950).
- 55) D. A. Evans and P. W. Roberston, J. Chem. Soc., 2834 (1950).
- 56) I. R. C. McDonald, R. M. Milburn, and P. W. Roberston, J. Chem. Soc., 2836 (1950).
- 57) R. J. Gillespie and M. J. Morton, Quart. Revs., 25, 553 (1971).
- 58) A., Berthoud and M. Mosset, J. Chim. Phys., 33, 272 (1936).
- 59) P. D. Bartlett and D. S. Tarbell, J. Amer. Chem. Soc., 56, 466 (1936).
- 60) J. R. Atkinson and R. P. Bell, J. Chem. Soc., 3260 (1963).
- 61) P. B. D. de la Mare, R. A. Scott, and P. W. Roberston, *J. Chem. Soc.*, 509 (1945). 7
- 62) R. F. Buckles and J. P. Yuk, J. Amer. Chem. Soc., 75, 5048 (1953).
- 63) R. J. Gillespie and J. B. Milne, Inorg. Chem., 5, 1236 (1966).
- 64) R. A. Garrett, R. J. Gillespie, and J. B. Senior, *Inorg. Chem.*, 4, 563 (1965).
- 65) R. J. Gillespie and J. B. Milne, Inorg. Chem., 5, 1577 (1966).
- 66) N. N. Greenwood and H. J. Emeleus, J. Chem. Soc., 987 (1950).

- 67) J. Roberts and G. E. Kimball, J. Amer. Chem. Soc., 59, 947 (1937).
- 68) R. D. Bach and H. F. Henneike, J. Amer. Chem. Soc., 92, 5589 (1970).
- 69) P. v. R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. D. Comisarow, and G. A. Olah, J. Amer. Chem. Soc., 86, 5679 (1964).
- 70) M. Saunders, P. v. R. Schleyer, and G. A. Olah, J. Amer. Chem. Soc., 86, 5680 (1964).
- 71) F. R. Jensen and B. H. Beck, Tetrahedron Lett., 4287 (1966).
- 72) J. A. Berson and P. W. Grubb, J. Amer. Chem. Soc., 87, 4016 (1965).
- 73) Fieser and Fieser, "Reagents for Organic Synthesis," J. Wiley and Sons, Inc., New York · London · Sydney, 1967.