12-1-1991

Deuteriohalogenation of norbornene via organoborane

Bo Han

Follow this and additional works at: http://scholarworks.rit.edu/theses

Recommended Citation

This Thesis is brought to you for free and open access by the Thesis/Dissertation Collections at RIT Scholar Works. It has been accepted for inclusion in Theses by an authorized administrator of RIT Scholar Works. For more information, please contact ritscholarworks@rit.edu.
DEUTERIOHALOGENATION OF NORBORNENE
via ORGANOBORANE

BO HAN

DECEMBER, 1991

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

APPROVED:

Terrence C. Morrill
Project Adviser

Gerald A. Takses
Department Head

Rochester Institute of Technology
Rochester, New York 14623
Department of Chemistry
1. Title of thesis: **Dienerviohalogenation of Norbornene via Organoborane**

   Bo Han hereby **grant permission** to the Wallace Memorial Library of RIT to reproduce my thesis in whole or in part. Any reproduction will not be for commercial use or profit.

   Date: **12-6-91**

2. Title of thesis: ________________________________

   ________________________________ prefer to be contacted each time a request for reproduction is made. I can be reached at the following address.

   ________________________________

   ________________________________

   Date: ________________________________

3. Title of Thesis: ________________________________

   ________________________________ hereby **deny** permission to the Wallace Memorial Library of RIT to reproduce my thesis in whole or in part.

   Date: ________________________________

rev. 1/89
# TABLE OF CONTENTS

Abbreviations........................................................................................................... iv
List of Figures............................................................................................................. v
List of Schemes .......................................................................................................... viii
List of Tables ............................................................................................................... ix
List of Spectra ............................................................................................................. xi
Acknowledgements ................................................................................................... xiii
Abstract ...................................................................................................................... xiv

1. INTRODUCTION ...................................................................................................... 1
   1.1 Hydroboration and Deuterioboration ................................................................. 1
   1.2 Transmercuration .............................................................................................. 6
   1.3 Halogenation of Organoborane ........................................................................ 11
   1.4 The Stereochemistry of the Norbornyl System ................................................... 16
       1.4.1 Carbocation Mechanisms in Norbornene System ....................................... 16
       1.4.2 Free Radical Mechanisms in the Norbornene System ................................. 19
   1.5 The Definition of the Nonclassical Ion ............................................................... 22
   1.6 The Lewis Acidity of Boron Trihalides, BX₃ (X=F,Cl,Br,I) .............................. 25
   1.7 The Objective of the Research ......................................................................... 26

2. RESULTS and DISCUSSION .................................................................................. 30
   2.1 Hydroboration and Deuterioboration ................................................................. 30
   2.2 Transmercuration .............................................................................................. 31
   2.3 Halogenolysis of Organoboranes ..................................................................... 33
       2.3.1 Iodinolysis ................................................................................................ 35
       2.3.2 Brominolysis ............................................................................................ 36
       2.3.3 Chlorinolysis ........................................................................................... 37
       2.3.4 Addition of "HI" or "DI" to Norbornene ...................................................... 38
   2.4 Spectroscopic Analysis ..................................................................................... 40
       2.4.1 ¹H NMR Analysis ................................................................................... 40
       2.4.2 Mass Spectral Analysis .......................................................................... 56
       2.4.3 IR Spectral Analysis .............................................................................. 62

3. CONCLUSIONS ....................................................................................................... 63

4. EXPERIMENTAL ..................................................................................................... 64
   General .................................................................................................................... 64
4.1 Drying and Purification of Tetrahydrofuran (THF) ........................................ 65
4.2 Purification of Boron Trifluoride Diethyl Etherate ........................................ 65
4.3 Purification of Norbornene ................................................................................. 66
4.4 Preparation of Fieser's Solution (for Absorption of Oxygen) ......................... 66
4.5 Preparation of tri-exo-3-Deutero-2-Norbornylborane ........................................ 67
4.6 Preparation of tri-exo-Norbornylborane (Method I) ........................................ 70
4.7 Preparation of tri-exo-Norbornylborane (Method II) ........................................ 70
4.8 Preparation of Authentic Deutério-2-exo-Norbornyl Iodide by Deuteriodination of Norbornene ................................................................. 73
4.9 Attempted Preparation of 3-exo-Deuterium-2-exo-Norbornyl Iodide Via Direct Iodination of tri-exo-3-Deutério-2-Norbornyl Borane Using BI₃ Catalysis ........................................................................ 73
4.10 Preparation of Authentic exo-2-Norbornyl Iodide By Hydroiodination of Norbornene ................................................................. 74
4.11 Preparation of exo-2-Norbornyl Iodide by Direct Iodination of tri-exo-Norbornylborane Using BI₃ Catalysis ................................................................. 74
4.12 Preparation of Authentic Deutério-2-exo-Norbornyl Bromide by Deuteriobromination of Norbornene ................................................................. 75
4.13 Attempted Preparation of exo-3-Deutério-2-Norbornyl Bromide By Direct Brominolysis of tri-exo-3-Deutério-2-Norbornylborane Using Boron Tribromide ........................................................................ 76
4.14 Preparation of Authentic exo-2-Norbornyl Bromide by Hydrobromination of Norbornene ................................................................. 77
4.15 Preparation of exo-2-Norbornyl Bromide By Direct Brominolysis of tri-exo-2-norbornyl Borane Using Boron Tribromide Catalysis ................................................................. 77
4.16 Preparation of Authentic Deutério-exo-2-Norbornyl Chloride by Deuteriochlorination of Norbornene ................................................................. 78
4.17 Preparation of Deutério-exo-2-Norbornyl Chloride By Direct Chlorinolysis of tri-exo-3-Deutério-2-Norbornylborane Using BCl₃ Catalysis ........................................................................ 79
4.18 Preparation of endo-2-Iodonorbornane By Base Promoted Hydroboration-Iodination of Norbornene ................................................................. 79
4.19 Preparation of exo-2-Norbornylmercuric Acetate from Trinorbornylborane Using Boron Tribromide Catalysis ................................................................. 80
4.20 The Preparation of \textit{exo}-2-Norborneol........................................81
REFERENCES ..................................................................................83
APPENDIX .....................................................................................87
Abbreviations

THF: Tetrahydrofuran
LAH: Lithium aluminum Hydride
r.t.: Room Temperature
Δ: Heat
[O]: Oxidation with Alkaline Hydrogen Peroxide
Me: Methyl group
IR: Infrared
d25°: Density at 25°C
R: Alkyl group
NBS: N-Bromosuccinimide
OAc: Acetate (or acetoxy groups)
MeCN: Acetonitrile
(Sia)2BH: Disiamylalkylborane
AO: Atomic orbital
### List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The Structure of Norbornane .......................... 16</td>
</tr>
<tr>
<td>2</td>
<td>The Structure of Norbornene ........................... 16</td>
</tr>
<tr>
<td>3</td>
<td>The Structure of Norbornadiene ....................... 16</td>
</tr>
<tr>
<td>4</td>
<td>Norbornyl Free Radical .............................. 21</td>
</tr>
<tr>
<td>5</td>
<td>Carbocations for which Electron-Deficient Nonclassical Structures Have Been Considered .................... 23</td>
</tr>
<tr>
<td>6</td>
<td>The Availability of ππ Bonding in BF₃ in Contrast to BH₃ ................................................. 26</td>
</tr>
<tr>
<td>7</td>
<td>exo-2-Norbomy Halide .................................. 41</td>
</tr>
<tr>
<td>8</td>
<td>exo-3-d-exo-2-Norbomy Halide .......................... 41</td>
</tr>
<tr>
<td>9</td>
<td>exo-2-Norbomy Halide .................................. 41</td>
</tr>
<tr>
<td>10</td>
<td>exo-3-d-exo-2-Norbomy Halide .......................... 41</td>
</tr>
<tr>
<td>11</td>
<td>Proton NMR Doublet of Doublet of 2-endo Proton in Norbornyl Halide ........................................ 42</td>
</tr>
<tr>
<td>12</td>
<td>Proton NMR Triplet of 2-endo Proton in Norbornyl Halide .................................................... 42</td>
</tr>
<tr>
<td>13</td>
<td>Splitting Pattern of 2-endo Proton in Deuteriated Norbornyl Halide .......................................... 42</td>
</tr>
<tr>
<td>14</td>
<td>NMR Splitting Pattern of 2-endo Proton in Deuteriated Norbornyl Halide while Ignoring the Value of J₂n-7a .................................................. 42</td>
</tr>
<tr>
<td>15</td>
<td>The NMR Signal at δ 3.99, Proton (H₂n) on Carbon Bearing I in Unlabeled Structure (Authentic exo-2-Norborny Iodide) ............................................ 44</td>
</tr>
<tr>
<td>16</td>
<td>The NMR Signal at δ 3.99, Proton (H₂n) on Carbon Bearing I in Unlabeled Stricture. (B₃ Catalyzed Formation of exo-2-Norborny Iodide) ............................ 45</td>
</tr>
<tr>
<td>17</td>
<td>The NMR Splitting Pattern of Proton α to Iodide in Unlabeled Norbornyl Iodide ........................................ 46</td>
</tr>
<tr>
<td>18</td>
<td>The NMR Signal at δ 3.99 of exo-cis-3-d-2-exo-Norborny Iodide ........................................... 46</td>
</tr>
</tbody>
</table>
Figure 19  The NMR Splitting Pattern of Proton $\alpha$ to the Iodide in NMR Spectrum which Two Splitting Patterns were Superimposed ........................................ 46

Figure 20  Signal at $\delta$ 3.99 in NMR Spectrum of Labeled Authentic
exo-2-Norbornyl Iodide................................................................. 47

Figure 21  Signal at $\delta$ 3.99 in NMR Spectrum of BI$_3$ Catalyzed Formation of
Labeled exo-2-Norbornyl Iodide...................................................... 48

Figure 22  NMR Signal at $\delta$ 3.95, Proton (H$_2n$) on Carbon Bearing Br in
Unlabeled Structure. (Authentic exo-2-Norbornyl Bromide)................. 49

Figure 23  NMR Signal at $\delta$ 3.95, Proton (H$_2n$) on Carbon Bearing Br in Unlabeled
Structure (BBr$_3$ Catalyzed Formation of exo-2-Norbornyl Bromide) ...... 49

Figure 24  The NMR Splitting Pattern of Proton $\alpha$ to Bromine in Unlabeled
exo-2-Norbornyl Bromide ............................................................ 50

Figure 25  NMR Signal at $\delta$ 3.95, Proton (H$_2n$) on Carbon Bearing Br in Labeled
Structure (Authentic exo-2-Norbornyl Bromide) ................................ 51

Figure 26  NMR Signal at $\delta$ 3.95, Proton (H$_2n$) on Carbon Bearing Br in Labeled
Structure (BBr$_3$ Catalyzed Formation of exo-2-Norbornyl Bromide) ..... 52

Figure 27  The Splitting Pattern of Proton $\alpha$ to the Bromide in NMR Spectrum
which Two Splitting Patterns were Superimposed ................................ 52

Figure 28  NMR Signal at $\delta$ 3.85, Proton (H$_2n$) on Carbon Bearing Cl in Labeled
Structure (Authentic exo-2-Norbornyl Chloride) ............................... 53

Figure 29  NMR Signal at $\delta$ 3.85, Proton (H$_2n$) on Carbon Bearing Cl in Labeled
Structure (BCl$_3$ Catalyzed Formation of exo-2-Norbornyl Chloride) ...... 54

Figure 30  The Signal at $\delta$ 3.7 in the Proton NMR Spectrum of
the Mixture of exo-cis-3-Deutero-2-exo-Dehydronorbornyl
Chloride (XXXVIII) and syn-7-Deutero-2-exo-Dehydronorbornyl
Chloride (XXXIX)........................................................................ 55

Figure 31  The Signal at $\delta$ 3.7, the NMR Spectrum of Unlabeled
exo-2-Norbornadiene(XL) ................................................................. 55

Figure 32  The Calculation of %D Incorporated in Norbornyl Halide ........... 57

Figure 33  Fundamental Reaction Setup Used for Hydroboration and Halogenation
Reactions with Common Glassware .................................................... 69

Figure 34  The Hydroboration Reaction Apparatus for Preparing
Tri-Norbornylborane ........................................................................ 71

Figure 35  Basic Distillation Apparatus for Air-Sensitive Materials ............. 72
List of Schemes

Scheme 1  The Four-Center Transition State of the Hydroboration Reaction ..........4
Scheme 2  The Free-Redical Mechanism of the Reaction of Organoborane
           with Bromine.................................................................12
Scheme 3  The Mechanism of the Base-Induced Iodination of Tri-Norbomylborane
           with the Inversion of Configuration at the Reaction Center..........13
Scheme 4  The Mechanism of the Iodination of tri-Organoborane
           by Sodium Hydroxide..........................................................14
Scheme 5  A Rapidly Equilibrating Pair of Classical Cations .........................19
Scheme 6  Stereochemical Mechanism of Radical Bromination Reaction of tri-exo-
           Norbornylborane .............................................................19
Scheme 7  The Free-Radical Mechanism of Halogenation of Norbornane.............21
Scheme 8  The Mechanism of the Photoreaction of Norbornane with the
           Molecule (COCl)₂ .................................................................22
Scheme 9.  Deuteriochlorination of Norbornene via A
            Nonclassic Ion Intermediate..................................................27
Scheme 10  The Mechanism of the Autoxidation Reaction of Organoborane .........30
Scheme.11 The Mechanism of the Deuterioboration of Norbornene ..................31
Scheme 12  Possible Mechanism of the Transmercuration Reaction ..................32
Scheme 13  The Mechanism of Halogenolysis of tri-Norbomylborane ................34
Scheme 14. Fragmentation Mechanism for Labeled exo-2-Norbomyl Iodide
           and Bromide .................................................................59
Scheme 15  Fragmentation Mechanism of Deuterium Labeled
           exo-2-Norbomyl Chloride ..................................................60
Scheme 16  Fragmentation Mechanism of Unlabeled exo-2-Norbomyl Iodide......61
Scheme 17  Fragmentation Mechanism of Unlabeled exo-2-Norbomyl Bromide ......62
List of Tables

Table 1  Reaction of tri-exo-2-Norbornylborane or tri-exo-3-d-exo-2-Norbornylborane with Iodine in the Presence of Boron Triiodide ............ 36

Table 2  Reaction of tri-exo-2-Norbornylborane or tri-exo-3-d-exo-2-Norbornylborane with Bromine in the Presence of Boron Tribromide ......... 37

Table 3  Reaction of tri-exo-3-d-exo-2-Norbornylborane with Chlorine in the Presence of Boron Trichloride ........................................ 38

Table 4  Reaction of Norbornene with Deuterium Halide in CH3CN .......... 39

Table 5  Reaction of Norbornene with Hydrogen Halide in CH3CN .......... 40

Table 6  NMR Coupling Constants for Protons of Authentic Unlabeled exo-2-Norbornyl Iodide .................................................. 44

Table 7  NMR Coupling Constants for Protons of Lewis Acid Catalytically formed Unlabeled exo-2-Norbornyl Iodide .................... 45

Table 8  NMR Coupling Constants for Authentic Labeled exo-2-Norbornyl Iodide ................................................................. 47

Table 9  NMR Coupling Constants for Lewis Acid Catalytic Labeled exo-2-Norbornyl Iodide ....................................................... 47

Table 10 NMR Coupling Constants for Authentic Unlabeled exo-2-Norbornyl Bromide ............................................................ 48

Table 11 NMR Coupling Constants for Lewis Acid Catalytic Unlabeled exo-2-Norbornyl Bromide .................................................. 50

Table 12 NMR Coupling Constants for Authentic Labeled exo-2-Norbornyl Bromide ................................................................. 51

Table 13 NMR Coupling Constants for Lewis Acid Catalytic Labeled exo-2-Norbornyl Bromide ...................................................... 51
Table 14  NMR Coupling Constants for Authentic Labeled
\textit{exo}-2-Norbornyl Chloride .............................................. 53

Table 15  NMR Coupling Constants for Lewis Acid Catalytic
Labeled \textit{exo}-2-Norbornyl Chloride........................................... 54

Table 16  NMR Coupling Constants For the Mixture of \textit{exo-cis}-3-Deuterio-2-
\textit{exo}-Dehydronorbornyl Chloride (XXXVIII) and \textit{syn}-7-Deuterio-2-\textit{exo}-
Dehydronorbornyl Chloride (XXXIX) in CDCl$_3$..............................56

Table 17  Total % Deuterium Incorporated in Norbornylhalide .................. 57

Table 18  Principal Peak in Mass Spectra of Labeled \textit{exo}-2-Norbornyl Iodide .... 58

Table 19  Principal Peak in Mass Spectra of Labeled \textit{exo}-2-Norbornyl Bromide .... 58

Table 20  Principal Peak in Mass Spectra of Labeled \textit{exo}-2-Norbornyl Chloride .... 60

Table 21  Principal Peak in Mass Spectra of Unlabeled
\textit{exo}-2-Norbornyl Iodide...................................................... 61

Table 22  Principal Peak in Mass Spectra of Unlabeled
\textit{exo}-2-Norbornyl Bromide...................................................... 62
List of Spectra

1. $^1$H NMR Spectrum of Authentic Labeled exo-2-Norbornyl Iodide ...............88
2. $^1$H NMR Spectrum of 2-endo Proton in Authentic Labeled exo-2-Norbornyl Iodide from "DI" Addition to Norbornene (Expansion) .........................89
3. $^1$H NMR Spectrum of Labeled exo-2-Norbornyl Iodide ..........................90
4. $^1$H NMR Spectrum of 2-endo Proton in Labeled exo-2-Norbornyl Iodide Produced by BI$_3$ Promoted Reaction (Expansion) .................................91
5. $^1$H NMR Spectrum of Authentic Unlabeled exo-2-Norbornyl Iodide ............92
6. $^1$H NMR Spectrum of 2-endo Proton in Authentic Labeled exo-2-Norbornyl Iodide from "HI" Addition to Norbornene (Expansion) .....................93
7. $^1$H NMR Spectrum of Unlabeled exo-2-Norbornyl Iodide ........................94
8. $^1$H NMR Spectrum of 2-endo Proton in Unlabeled exo-2-Norbornyl Iodide Produced by BI$_3$ Promoted Reaction (Expansion) .........................95
9. $^1$H NMR Spectrum of Authentic Labeled exo-2-Norbornyl Bromide ............96
10. $^1$H NMR Spectrum of 2-endo Proton in Authentic Labeled exo-2-Norbornyl Bromide from "DBr" Addition to Norbornene (Expansion) ..............97
11. $^1$H NMR Spectrum of Labeled exo-2-Norbornyl Bromide .......................98
12. $^1$H NMR Spectrum of 2-endo Proton in Labeled exo-2-Norbornyl Bromide Produced by BBr$_3$ Promoted Reaction (Expansion) .....................99
13. $^1$H NMR Spectrum of Authentic Unlabeled exo-2-Norbornyl Bromide ........100
14. $^1$H NMR Spectrum of 2-endo Proton in Authentic Unlabeled exo-2-Norbornyl Bromide from "HBr" Addition to Norbornene (Expansion) .............101
15. $^1$H NMR Spectrum of Unlabeled exo-2-Norbornyl Bromide ....................102
16. $^1$H NMR Spectrum of 2-endo Proton in Unlabeled exo-2-Norbornyl Bromide Produced by BBr$_3$ Promoted Reaction (Expansion) ...................103
17. $^1$H NMR Spectrum of Authentic Labeled exo-2-Norbornyl Chloride ...........104
18. $^1$H NMR Spectrum of 2-endo Proton in Authentic Labeled exo-2-Norbornyl Chloride from "DCI" Addition to Norbornene (Expansion) ............................... 105
19. $^1$H NMR Spectrum of Labeled exo-2-Norbornyl Chloride .......................... 106
20. $^1$H NMR Spectrum of 2-endo Proton in Labeled exo-2-Norbornyl Chloride Produced by BCl$_3$ Promoted Reaction (Expansion) ......................... 107
21. GC/MS Spectrum of Authentic Labeled exo-2-Norbornyl Iodide ................... 108
22. GC/MS Spectrum of Labeled exo-2-Norbornyl Iodide ................................ 109
23. GC/MS Spectrum of Authentic Unlabeled exo-2-Norbornyl Iodide ................ 110
24. GC/MS Spectrum of Unlabeled exo-2-Norbornyl Iodide ............................. 111
25. GC/MS Spectrum of Authentic Labeled exo-2-Norbornyl Bromide ................ 112
26. GC/MS Spectrum of Labeled exo-2-Norbornyl Bromide ............................ 113
27. GC/MS Spectrum of Authentic Unlabeled exo-2-Norbornyl Bromide .............. 114
28. GC/MS Spectrum of Unlabeled exo-2-Norbornyl Bromide .......................... 115
29. GC/MS Spectrum of Authentic Labeled exo-2-Norbornyl Chloride ............... 116
30. GC/MS Spectrum of Labeled exo-2-Norbornyl Chloride ........................... 117
31. IR Spectrum of Authentic Labeled exo-2-Norbornyl Iodide ......................... 118
32. IR Spectrum of Labeled exo-2-Norbornyl Iodide ................................ 119
33. IR Spectrum of Authentic Unlabeled exo-2-Norbornyl Iodide .................... 120
34. IR Spectrum of Unlabeled exo-2-Norbornyl Iodide ................................ 121
35. IR Spectrum of Authentic Labeled exo-2-Norbornyl Bromide ..................... 122
36. IR Spectrum of Labeled exo-2-Norbornyl Bromide ................................ 123
37. IR Spectrum of Authentic Unlabeled exo-2-Norbornyl Bromide ................... 124
38. IR Spectrum of Unlabeled exo-2-Norbornyl Bromide ................................ 125
39. IR Spectrum of Authentic Labeled exo-2-Norbornyl Chloride .................... 126
40. IR Spectrum of Labeled exo-2-Norbornyl Chloride ................................ 127
Acknowledgement

The author is deeply indebted to Dr. T. C. Morrill for his guidance, suggestions and encouragement during the course of the research; to the author's committee members Drs R. A. Clark, A. Langner, R. E. Gilman for their valuable suggestions; to the United Nations and R.I.T for my financial support. Finally, the author wishes to thank chemistry department of R. I. T. for the chemicals and instruments used in this research.
Abstract

A stereospecific pathway for the net addition of deuterium halide to a double bond was investigated using norbornene as the substrate. The polycyclic internal olefin, norbornene, has been chosen as the substrate due to its stereochemical aspects and its ability to reveal mechanistic information.

The combination of hydroboration followed by halogenation in the presence of boron trihalide provides a method for the net anti-Markovnikov hydrohalogenation of alkenes. The Lewis acid-catalyzed halogenation of organoboranes proceeds with mostly retention of configuration at the reaction center as shown by the formation of largely exo-2-halonorboranes from tri-exo-norbornylborane. Deutériohalogenation of norbornene provides NMR evidence that Wagner-Meerwein rearrangement occurs: deuterium scrambling within the norbornyl halide structure shows that rearrangement occurred during the halogenation reaction. This has been done for iodine and bromine as well as chlorine.

Experiments have suggested that the transmercuration reaction of tri-norbornylborane is very sensitive to steric hindrance about the boron atom. The norbornyl group, a secondary alkyl group, is not transferred readily from boron to mercury in spite of the use of Lewis acidic catalysts. This was disappointing since the resulting organomercurial could have been converted to an alkyl halide effecting the same net reaction as described above.
1. INTRODUCTION

1.1 Hydroboration and Deuterioboration

Olefins may be readily converted into organoboranes under mild experimental conditions; this observation was reported in 1956 and 1957, and has provided a major new route to these interesting derivatives.[1,2,3]

$$9RCH=CH_2 + 3 \text{NaBH}_4 + \text{AlCl}_3 \rightarrow 3(\text{RCH}_2\text{CH}_2)_3\text{B} + \text{AlH}_3 + 3\text{NaCl} \quad \text{Eq. 1}$$

$$12RCH=CH_2 + 3 \text{NaBH}_4 + 4\text{BF}_3 \rightarrow 4(\text{RCH}_2\text{CH}_2)_3\text{B} + 3\text{NaBF}_4 \quad \text{Eq. 2}$$

$$6RCH=CH_2 + \text{B}_2\text{H}_6 \rightarrow 2(\text{RCH}_2\text{CH}_2)_3\text{B} \quad \text{Eq. 3}$$

Not only does the boron-hydrogen bond add rapidly and quantitatively to carbon-carbon double and triple bonds, but it adds also with remarkable ease to carbon-oxygen double bonds[4] and to carbon-nitrogen double and triple bonds.[5]

$$\overset{\overline{C}=\overset{\overline{O}+\text{H-B}}{\text{O}}}{} \rightarrow \overset{\overline{H-C-O-B}}{} \quad \text{Eq. 4}$$

$$\overset{\overline{-C=\overset{\overline{N}+\text{H-B}}{\text{N}}}{} \rightarrow \overset{\overline{H-C=\overset{\overline{N}B}}{} \quad \text{Eq. 5}$$

$$\overset{\overline{C=\overset{\overline{C}+\text{H-B}}{\text{C}}}{} \rightarrow \overset{\overline{H-C-C-B}}{} \quad \text{Eq. 6}$$

Consequently, the addition of the boron-hydrogen linkage to multiple bonds between carbon and carbon, oxygen, or nitrogen appears to be a reaction of very wide generality but proceeding under mild conditions.

It has been observed that borane in ether solvent adds with remarkable ease to alkenes, forming organoboranes. It was soon established that this addition proceeds in an anti-Markovnikov manner. Since oxidation of organoboranes with alkaline hydrogen peroxide gives alcohols, hydroboration-oxidation provides a simple means of achieving the anti-Markovnikov hydration of alkenes[6].(Eq.7,8,9)
A review of the hydroboration reaction reveals many interesting features. For example, the reaction involves a syn-addition of the H-B bond. (Eq. 10)

The addition takes place preferentially from the less hindered face of the double bond (Eq. 11).
α-Pinene is converted into isopinocampheol\[^7\] and β-pinene into cis-myrtanol\[^8\].

\[
\begin{align*}
\text{CH}_3 & \quad \text{BH}_3 & \quad \text{CH}_3 & \quad \text{[O]} & \quad \text{isopinocampheol} \\
& \quad \alpha\text{-pinene} & \quad & \quad & \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{BH}_3 & \quad \text{CH}_3 & \quad \text{[O]} & \quad \text{cis-myrtanol} \\
& \quad \beta\text{-pinene} & \quad & \quad & \\
\end{align*}
\]

It is interesting that heat isomerizes the borane from β-pinene to the less hindered tri-trans-myrtanylborane\[^9\] (Eq.14).

\[
\begin{align*}
\text{CH}_2 & \quad \text{BH}_3 & \quad \text{CH}_2 & \quad \text{[O]} & \quad \text{trans-myrtanol} \\
& \quad \beta\text{-pinene} & \quad & \quad & \\
\end{align*}
\]

Oxidation of the isomerized organoborane produces trans-myrtanol\[^2\]. This result clearly demonstrates that the hydroboration stage is controlled by the rate of the reaction and not by the stability of the product.

No rearrangements of the carbon skeleton have been observed, even in molecules as labile as α-pinene (Eq.12). Many functional groups can tolerate hydroboration, so it is possible to synthesize reactive intermediates containing those functional groups and to utilize those intermediates for organic syntheses.

The study by H. C. Brown et al.\[^{10}\] shows that the hydroboration reaction involves a simple four-center transition state, in which the direction of addition is controlled primarily by the polarization of the boron-hydrogen bond \(\text{B}^+\text{H}^-\).
Scheme 1. The Four-centered Transition State of the Hydroboration Reaction.

This four-center transition state is supported by the results of the hydroboration of cyclic olefins\cite{7}. Thus the hydroboration of norbornene proceeds readily to the trialkylborane stage. Oxidation yields a norborneol which by gas chromatographic examination is at least 99\% of the \textit{exo} isomer.

The following examples (Eq.15, 16) also indicates that the addition of diborane to norbornene is a \textit{cis}-concerted reaction (four-centered), a conclusion made by Brown and Zweifel\cite{11}.

The oxidation of \textit{tri}-\textit{exo}-norbornylborane proceeds with retention of configuration.

Deuterioboration, followed by protonolysis of the borane, gives the same product from norbornene as does hydroboration followed by deuteriolysis (Eq.17, 18).
The great majority of simple olefins undergo complete reaction (Eq.19) to form the corresponding trialkylborane. When there is steric hindrance, the reaction appears to proceed rapidly only to the dialkylborane (Eq.20) or monoalkylborane (Eq.21) stage.\(^{[12]}\)

\[
\begin{align*}
3 & \text{CH}_3\text{CH}=\text{CHCH}_3 + \text{BH}_3 & \rightarrow & (\text{CH}_3\text{CH}_2\text{CH}-\text{B})_3\text{B} \quad \text{Eq.19} \\
2 & (\text{CH}_3)_2\text{C}=\text{CHCH}_3 + \text{BH}_3 & \rightarrow & [(\text{CH}_3)_2\text{CH}-\text{C}-(\text{BH}_2)_2\text{BH}] \quad \text{Eq.20} \\
(\text{CH}_3)_2\text{C}=\text{C(\text{CH}_3)}_2 + \text{BH}_3 & \rightarrow & (\text{CH}_3)_2\text{C}-\text{C}-\text{BH}_2 \quad \text{Eq.21}
\end{align*}
\]

The hydroboration-oxidation of the 7,7-dimethylnorbornene yields the *endo* alcohol.

Here the direction of approach of borane to a double bond in Eq.22 is controlled by the steric effect of the *syn* C-7 methyl group\(^{[13]}\).

In summary, the specificity of the addition of borane to an alkene is controlled by both electronic and steric factors.

The discovery of the hydroboration reaction provided a convenient and efficient method for the synthesis of a wide variety of organoboranes from alkenes and alkynes. This ready availability lead to the development of many reactions which are of great value to synthetic chemistry.
More recent studies have shown that organoboranes are extremely versatile intermediates in the synthesis of many other types of organic compounds. Thus, in addition to their conversion to alcohols, carboxylic acids and their derivatives, nitriles, alkyl halides, amines, alkenes and dienes, and various other functional derivatives[6] can also be made. Organoboranes also serve as useful intermediates in the extension of carbon chains and the construction of carbocyclic compounds.

1.2 Transmercuration

Organomercurials are among the oldest organometallics known, having first been reported in 1852 by Frankland[14] (eq.23). In the next sixty years new routes to organomercurials were discovered and many applications in synthesis were reported, particularly in the preparation of other organometallics. However, with the discovery of the versatile Grignard reagent, the interest in organomercurials decreased. In recent years organomercurials have received renewed attention, due in large part to their ability to accommodate essentially all important organic functional groups and the ease with which they undergo transmetallation to form other transition metal organometallics useful in organic synthesis.

Prior to 1956 organoborane compounds were generally prepared from the appropriate Grignard or organolithium reagent. Since most other organometallics could be obtained directly through reaction of these reagents with the appropriate metal salt, there was no advantage to be gained by going through the organoborane intermediate. With the discovery of the hydroboration reaction, a wide variety of organoboranes became readily available for the first time, and this provided the incentive to study the metallation reactions of these compounds.

Organoboranes interact with a variety of metal derivatives to yield organometallic compounds. Reactions occur most readily for the heavier, less electropositive elements, the reactions with mercury derivatives having been most extensively investigated[6].

Organomercurials are stable organometallic compounds that undergo many useful reactions with organic substrates as well as being the source for many other organometallics. The
discovery of hydroboration led to the possibility that routes to organomercurials could be devised that avoided the use of Grignard or organolithium reagents[15].

Organoboranes are more useful for the preparation of organomercurials from an organic synthesis viewpoint [16]. Alkyl, benzylic, vinyl and aryl groups are readily transferred from boron to mercury upon treating organoboranes with a wide variety of mercury salts (Eq.23).

\[ \text{R-B} + \text{HgX}_2 \rightarrow \text{RHgX} \quad \text{Eq.23} \]

Boronic and borinic acids and esters, triorganoboranes and tetraorganoborate salts all undergo this reaction. Since organoboranes are directly available via hydroboration of alkenes and alkynes, this approach takes on added significance (Eq.24-26).

\[
\begin{align*}
\text{RCH}=\text{CH}_2 & \xrightarrow{1. \text{HBR}_2} \text{RCH}_2\text{CH}_2\text{HgCl} \\
& \xrightarrow{2. \text{Hg(OAc)}_2} \\
& \xrightarrow{3. \text{NaCl}} \\
\text{RC}=\text{CH} & \xrightarrow{1. \text{HBR}_2} \text{RC}C=\text{CH}\text{HgCl} \\
& \xrightarrow{2. \text{Hg(OAc)}_2} \\
& \xrightarrow{3. \text{NaCl}} \\
\text{RC}=\text{CH} & \xrightarrow{1. \text{BH}_3} \text{RCH}_2\text{CH}\text{HgCl} \\
& \xrightarrow{2. \text{CH}_3\text{OH}} \\
& \xrightarrow{3. \text{HgCl}_2/\text{NaOH}}
\end{align*}
\]

Eq.24-26

Early results showed that aryl groups from arylidihydroxyboranes (Eq.27)[17] or triarylboranes[18] could be transferred by reaction with mercury(II) chloride in aqueous solution.

\[ \text{PhB(OH)}_2 + \text{HgCl}_2 + \text{H}_2\text{O} \rightarrow \text{PhHgCl} + \text{B(OH)}_3 \quad \text{Eq.27} \]

Trialkylboranes also react with aqueous mercury(II) chloride[19] or with mercury(II) acetate in 1,2-dimethoxyethane[20]. The reaction of tri-primary alkylboranes with mercury(II) acetate in THF is almost quantitative (Eq.28)[21,22] within minutes at 0-20°C, but secondary groups are transferred less readily.
\[
R_3B + 3Hg(OAc)_2 \rightarrow 3RHgOAc + B(OAc)_3 \quad \text{Eq.28}
\]

If the stoichiometry is changed from 1:3 to 2:3 (organoborane : mercuric acetate), and the conditions used are somewhat vigorous, good yields of dialkylmercury compounds can be obtained from tri-primary-alkylboranes (Eq.29)\(^{[23]}\).

\[
2R_3B + 3Hg(OAc)_2 \rightarrow 3R_2Hg + 2B(OAc)_3 \quad \text{Eq.29}
\]

Secondary groups can be transferred if a mercury alkoxide, particularly mercury(I) t-butoxide, in an alcohol solvent, is employed as the reagent, but only two of the three groups on boron are generally utilized\(^{[24]}\).

The transfers are not always stereospecific\(^{[25, 26]}\), possibly because of radical involvement\(^{[24]}\).

Alkenyldicyclohexylboranes selectively and stereospecifically transfer the alkenyl group (Eq.30) to mercury(II) acetate\(^{[27]}\). A similar transfer, also proceeding with retention, occurs with β-alkenylcatecholboranes\(^{[28]}\).

\[
\begin{align*}
\text{(c-C}_6\text{H}_{11})_2\text{B} & \quad \text{H} \\
\text{R} & \quad \text{R}_1 \\
\text{H} & \quad \text{R}_2 \\
\end{align*}
\]

There are other examples of preparing organomercurials via organoboranes as follows:

\[
\begin{align*}
\text{H}_2\text{CH} & \quad \text{BH}_3 \\
\text{H}_2\text{CH}_2\text{HgOAc} & \quad \text{H}_2\text{CH}_2\text{HgCl} \\
\text{NaCl} & \quad 98\% \text{ Yield} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2=\text{CH} & \quad \text{O} \\
\text{CH}_2\text{H}_2\text{CH}_2\text{C}_\text{OCH}_3 & \quad \text{BH}_3 \\
\text{H}_2\text{CH}_2\text{HgOAc} & \quad \text{H}_2\text{CH}_2\text{HgCl} \\
\text{Eq.32} \quad \text{HgOAc} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2=\text{CH} & \quad \text{BH} \\
\text{O} & \quad \text{BCH}_2\text{-CH}_2 \\
\text{Eq.33} & \quad \text{THESIS}
\end{align*}
\]
Organomercurials have been known since the 1850's\textsuperscript{[27,29,30]}. Hundreds or perhaps thousands of these compounds are now known, and many are commercially available. A wide variety of synthetic procedures exist for their preparation. These unique organomercurials possess a number of characteristics making them attractive as intermediates in organic synthesis. They are generally stable to air, solvents, dilute acids and bases, and elevated temperatures, and accommodate essentially all important organic functional groups. Their toxicity is not generally a problem since they are usually high melting, crystalline, relatively non-volatile solids. The main applications of organomercurials are as follows: hydrogen and halogen substitution, synthesis of heteroatom-containing compounds, dimerization, alkylation, alkene and alkyne addition, substitution reactions, carbonylation, acylation, and so on. Some examples are given below:

\[
\begin{align*}
\text{Cl} & \quad \text{H} \quad \text{Cl} \\
\text{H}_2\text{C}=\text{C}=\text{CH}_2 \quad + \quad \text{HCl} \quad \rightarrow \quad \text{H}_2\text{C}=\text{CH}-\text{C}=\text{CH}_2
\end{align*}
\]  
Eq.35

\[
\text{ClICH}=\text{CHHgCl} + \text{DCl} \quad \rightarrow \quad \text{ClICH}=\text{CHD}
\]  
\text{cis or trans} \quad \text{retention} 
Eq.36
The protonolysis or deuterolysis of alkenylmercurials derived from mercury salt additions to alkynes provides a valuable method of preparing stereoisomerically pure alkenes (Eq. 35, 36).

\[
\begin{align*}
\text{AcO}_2\text{C} &= \text{C} = \text{CH}_3 \quad \text{HgCl} \\
+ \text{NaBH}_4 &\rightarrow \text{AcO}_2\text{C} = \text{C} \quad \text{H} \\
\text{C}_6\text{H}_5 &\quad \text{Eq. 37}
\end{align*}
\]

Similarly, sodium borohydride reduction of β-acetoxymercurials derived from alkyne additions can be non-stereospecifically reduced to the corresponding enol acetates[31] (Eq. 37).

The halogenation of organomercurials provides a useful method for the preparation of a wide variety of organic halides, especially those not easily obtained by direct halogenation.

\[
\begin{align*}
\text{CH}_3\text{O}_2\text{C} &\quad \text{Hg(OAc)}_2 \\
\text{CH}_3\text{O}_2\text{C} &\rightarrow \text{Br}_2 \quad \text{H}_2\text{O/NaCl} \\
\text{OH} &\quad \text{C}_5\text{H}_5\text{N} \quad \text{Eq. 38}
\end{align*}
\]

The halogenation reaction can prove useful when employed in combination with the solvomercuration reaction.

\[
\begin{align*}
\text{RCH} &= \text{CH}_2 \quad \text{I}_3(\text{BH}_3) \rightarrow \text{Hg(OAc)}_2 \\
\text{RCH}_2\text{CH}_2\text{Br} &\quad \text{Eq. 39}
\end{align*}
\]

The hydroboration-mercuration of terminal olefins and subsequent in situ bromination affords a convenient method for the anti-Markovnikov hydrobromination of olefins (Eq. 39).

A wide variety of heteroatom-containing compounds can be conveniently prepared via organomercury intermediates. There are some useful approaches to the synthesis of O, S, N and P-containing compounds[15].

\[
\begin{align*}
\text{RHgCl} + \text{S} &\rightarrow \text{R-S-S-R} \quad \text{Eq. 40} \\
\text{HgCl} &\rightarrow \text{O} \quad \text{Eq. 41}
\end{align*}
\]
The dimerization of organomercurials can be effected thermally, photolytically or more commonly by employing transition metal reagents. It provides a convenient entry into 1,3-dienes and biaryls, but has proven less useful for the synthesis of alkanes[15].

\[
2\text{ArHgCl} \xrightarrow{0.5\%[\text{CIRh(CO)}_2]_2} \text{Ar-Ar} \quad \text{Eq.42}
\]

The most obvious approach to the alkylation of organomercurials, the reaction with organic halides (Eq.43), is quite restricted. Almost all successful examples of this reaction have been achieved using triphenylmethyl halides or related benzylic halides.

\[
\text{R}_2\text{Hg} + \text{R'}\text{X} \rightarrow \text{R-R'} + \text{RHgX} \quad \text{Eq.43}
\]

### 1.3 Halogenation of Organoborane

The rupture of the carbon-boron bond by direct reaction of halogens, such as bromine and iodine,[32] with the trialkylboranes has proven to be surprisingly difficult. The trialkylboranes exhibit a peculiar inertness toward the molecular halogens. Bromine reacts only relatively slowly with trialkylborane in the dark in the absence of a solvent. But the reaction is great facilitated by the use of methylene chloride as a solvent and provides a convenient procedure for the anti-Markovnikov hydrobromination of olefins[33] (Eq.44).

\[
\text{R}_3\text{B} + \text{Br}_2 + \text{CH}_2\text{Cl}_2, \text{Dark} \rightarrow \text{RBr} + \text{R}_2\text{BBBr} \quad \text{Eq.44}
\]

\[
(25^\circ, -24\text{hr}, 80-90\%) \quad [\text{R}= \text{n-}, \text{i-}, \text{s-C}_4\text{H}_9; -(\text{CH}_2)_{5-6}; \text{norbornyl}]
\]

Investigation revealed an unexpected feature—the reaction does not involve a simple rupture of the carbon-carbon bond by bromine. Instead, the reaction proceeds through the fast α-bromination of the organoborane and subsequent reaction of the intermediate with the hydrogen bromide[34,35] (Eq.45).
The mechanism of this reaction (Scheme 2) is showed as below:

\[
\text{Br}_2 + R_3B \xrightarrow{\text{Slow}} Br^- + R_2BB + R^+ \quad \text{Eq.45a}
\]

\[
R_2B\text{C}^- + Br^- \rightarrow R_2B\text{C}^- + HBr \quad \text{Eq.45b}
\]

\[
R_2B\text{C}^- + Br_2 \rightarrow R_2B\text{C}^- + Br^- \quad \text{Eq.45c}
\]

Scheme 2: The free-radical mechanism of the reaction of organoborane with bromine.

This free-radical bromination proceeds rapidly, even in the dark\textsuperscript{[36]}. The remarkably high reactivity of organoborane toward attack by bromine radicals\textsuperscript{[37]} is indicated by the observation that even the use of cyclohexane as a solvent results in insignificant diversion of bromine atoms to this possible reactant.

The precise nature of the initiation step is uncertain, but may involve the attack of bromine on the organoborane (Eq.45a)\textsuperscript{[38]}. The hydrogen bromide produced in the substitution step can then react preferentially with \(\alpha\)-bromoorganoborane to form alkyl bromide (Eq.45d), or competitively with an alkyl group on the \(\alpha\)-bromoorganoborane to afford an alkane (Eq.45e).

\[
R_2B\text{C}^- + HBr \rightarrow R_2BB + H\text{C}^- \quad \text{Eq.45d}
\]

\[
R-\text{C}^- + HBr \rightarrow RH + Br-\text{C}^- \quad \text{Eq.45e}
\]
Reactions of organoboranes with bromine and iodine in the presence of sodium methoxide gives the corresponding alkyl bromides and alkyl iodides, respectively in yields of 60-99%\cite{39,40} (Eq.46).

\[
\begin{array}{c}
\text{Br} \\
\text{NaOCH}_3 \\
\end{array}
\quad \text{Br}_2 \\
\quad \text{I}_2 \\
\quad \text{NaOCH}_3 \\
\]

Eq.46

The mainly *endo-* products indicate that the reaction proceeds with inversion of configuration\cite{41}. A mechanism which can account for this remarkable inversion is shown in the Scheme 3. The tremendous acceleration in rate upon addition of base is presumably due to "ate" complex formation(I). This should increase the electron density on carbon, and increase the ease of bond scission upon back-side attack by bromine. Most electrophilic substitutions which result in retention of configuration are thought to involve four-centre transition states\cite{42}. In the "ate" complex, such a four-centre transition state is not possible, so the reaction takes a different mechanistic course resulting in inversion.

Scheme 3. The mechanism of the base-induced iodination of trinorbornylborane with the inversion of configuration at the reaction center.

In the case of trinorbornylborane, only one of the norbornyl groups is converted into the norbornyl halide.

Reaction of trialkylboranes with cupric chloride or cupric bromide in THF-water gives the corresponding alkyl chlorides or alkyl bromides in yields of 43-77% and 75-92% (based on R\textsubscript{3}B) respectively\cite{43}(Eq.47, 48).
The reaction of primary organoborane with iodine is strongly accelerated by sodium hydroxide to give the corresponding alkyl iodide, the reaction being essentially complete in less than 5 minutes at 25° C (Eq.49).

\[
RCH_2CH_2I \xrightarrow{\text{NaOH, I}_2} RCH_2CH_2I
\]

Eq.49

The reaction with secondary alkylboranes is sluggish and gives low yields (30-40%) of the corresponding alkyl iodide\(^{40,44}\).

Brown, et al.\(^{40,44}\), have carried out detailed investigations of the mechanism by which sodium hydroxide accelerates the reaction of organoboranes with iodine.

\[
R_3B + NaOH \leftrightarrow R_3\tilde{BOH} \xrightarrow{\text{Na}^+, I_2} NaI + R_2BOH + RI
\]

Scheme 4: The mechanism of the iodination of triorganoborane by sodium hydroxide.

An indirect method for the conversion of trialkylboranes into alkyl halides involving the mercuration of a trialkylborane, followed by bromodemercuration, has been developed\(^{45}\)(Eq.50).

\[
1/3R_3B \xrightarrow{\text{Hg(OAc)}_2, \text{THF}} RHgOAc \xrightarrow{X_2, \text{Pyr}} 2RX + HgX_2 \quad (X=\text{Br}, \text{I})
\]

Eq.50

This hydroboration-mercuration-halogenation sequence has been used to convert a large number of terminal alkenes into primary bromides and iodides.

Trialkylboranes are readily converted to the corresponding alkylchlorides by a free radical reaction with nitrogen trichloride (NCl\(_3\)). Compared to many other chlorinating agents
examined, NCl₃ is a superior reagent for the effective conversion of organoboranes into alkyl chlorides[46]. The following examples (Eq.51, 52) are showed as below:

\[
\text{(t-Bu)}_3\text{B} + \text{NCl}_3 \rightarrow 3 \text{t-BuCl} + \text{B(NCl}_2\text{)}_3
\]  
Eq.52

It is interesting that the organoborane from norbornene is converted by alkaline hydrogen peroxide into 99.6% exo-norborneol. However, there is a considerable loss of stereochemistry in the reaction with NCl₃. Such loss of stereospecificity is presumably a result of the free radical nature of the reaction.

The use of disiamylborane (bis-3-methyl-2-butylborane, Sia₂BH) as a hydroborating agent increases the yield of iodides from terminal alkene since the primary alkyl groups react in preference to the secondary siamyl groups. Consequently, hydroboration of 1-decene with Sia₂BH, followed by iodination gives a 95% yield of n-decyl iodide (Eq.53).

\[
\text{RCH} = \text{CH}_2 + \text{Sia}_2\text{BH} \rightarrow \text{RCH}_2\text{CH}_2\text{BSia}_2 \xrightarrow{\text{I}_2/\text{CH}_2\text{Cl}_2} \text{RCH}_2\text{CH}_2\text{I} + \text{Sia}_2\text{BOH}
\]  
Eq.53

The procedure does in fact give excellent yields of primary iodides[40].

It is evident that disiamylborane can accommodate a number of common organic functional groups in an alkene under hydroboration conditions[46-48](Eq.54). The functional group tolerance, combined with selectivity in the hydroboration of dienes[49], renders Sia₂BH a valuable reagent for selective hydroiodination of such functionally substituted alkenes and dienes. Some indication of its versatility is provided by the conversion of 4-vinylcyclohexene to the unsaturated primary iodide.
1.4 The Stereochemistry of the Norbornyl System

The norbornane molecule possesses a rigid structure with special steric characteristics. Thus this makes it useful for stereochemical studies. The methylene group (C-7) of norbornane locks the cyclohexane system (C1-6) into a rigid, high-energy boat conformation, and the constraint so produced accentuates the steric crowding within the boat structure (Fig.1).

![Fig.1 The Structure of Norbornane](image)

Due to the strained structure of this system, it can undergo unique reactions which are not observed in the cyclohexane system. Norbornene (Fig.2) and norbornadiene (Fig.3) allow us to investigate many reactions. Ionic and radical reaction mechanisms in the norbornyl system have been studied by determining the stereochemistry of products.

![Fig.2 Norbornene](image)
![Fig.3 Norbornadiene](image)

The use of deuterium provides more information about the stereochemical details of many reactions.

1.4.1 Carbocation Mechanisms in Norbornene System

The addition of hydrogen chloride to norbornene (III) in ethyl ether, methylene chloride, or pentane proceeds rapidly at -78°C to yield *exo*-norbornyl chloride (IV) in isomeric purity of at least 99.5% (Eq.55)

![Eq.55](image)
2-Methylenenorbornane (V) adds hydrogen chloride rapidly to give the tertiary chloride (IV) as the initial product. This is rapidly converted into the secondary chloride (VII) on further treatment with hydrogen chloride (Eq.56).

Similarly, 2-methynorbornene (VIII) is converted initially into the same tertiary chloride (VI) (Eq.57).

Remarkably, 1-methynorbornene (IX) adds hydrogen chloride to give a mixture of 45% of 4-methyl-exo-norbornyl chloride (X) and 55% of the tertiary chloride (XI) (Eq.58).

Finally, the addition of hydrogen chloride to 7,7-dimethynorbornene (XII) yields 90% of 7,7-dimethyl-exo-norbornyl chloride (XIII) and 10% of the Wagner-Meerwein rearranged product, 3,3-dimethyl-exo-norbornyl chloride (XIV) (Eq.59).

The strong directive influence leading to the exclusive formation of the tertiary chlorides from V and VIII are characteristic of carbocation processes. The small discrimination
between protonation at C2 and C3 of IX reveals that the transition state for the protonation reaction involves much smaller development of positive charge than does that for solvolysis, where a 1-methyl group is strongly activating. However, following protonation, the intermediate must be the carbocation in which we are interested. Molecular addition of hydrogen chloride[48] cannot be significant because such an addition would be expected to give the two secondary chlorides from IX. Both secondary chlorides are stable to the reaction conditions. Moreover, molecular addition to XII would be expected to give the endo isomer predominantly[49]. Consequently, it appears clear that these additions of hydrogen chloride proceed via proton transfer from the hydrogen chloride to the olefin with the formation of the 2-norbornyl cation as an intermediate.

The critical experiment involves the addition of deuterium chloride to norbornene (III). A nonclassical ion intermediate XV requires that the tag be equally distributed between the exo-3 (XVI) and syn-7 (XVII) positions (Eq.60).

\[
\text{Exo-3-d (XVI)} + \text{syn-7-d (XVII)} + \text{hydride-shifted products}
\]

The results of a variety of analyses reveal the formation of 57-61% of exo-3-d (XVI), 32-41% syn-7-d (XVII), with 2-7% of hydride-shifted material[51].

These results cannot be accounted for in terms of the sole formation of a nonclassical intermediate (Eq.60). They could be accounted for in terms of the concurrent formation of symmetrical σ-bridged cations (XV) and rapidly equilibrating classical 2-norbornyl cations (Ia ⇄ Ib). However, there appears to be no advantage in introducing this additional complication. The results are most simply accounted for in terms of the formation of a rapidly equilibrating pair of classical cations (Ia ⇄ Ib) which are captured short of full equilibration (Scheme 5).
1.4.2 Free Radical Mechanisms in the Norbornene System

Many nonionic reactions of the norbornyl system exhibit a comparable stereospecificity. The most common free radical additions to norbornene are halogenation additions in the presence of light or other initiators such as NBS, benzoyl peroxide.

In carbon tetrachloride, cyclohexane and methylene chloride, a fast, initially free-radical bromination, followed by a slow cleavage of the resulting α-bromoorganoborane with hydrogen bromide, takes place. Evidence supporting this mechanisms is showed below (Eq.61). Competitive bromination studies reveal that the α-hydrogen in trialkylboranes is highly reactive toward free-radical bromination in the dark reaction.

The bromonorborane obtained via the dark reaction of bromine with tri-norbornylborane is predominantly (99%) exo. This is interpreted (Scheme 6) as indicating that bromine

Scheme 6  Mechanism of Radical Bromination Reaction of tri-exo-Norbornylborane
attacks the α-boronorbornyl free-radical (XX) from the sterically less hindered exo-side to give α-exo-bromoborane (XXI). The subsequent hydrogen bromide cleavage then proceeds with clean retention of configuration to produce stereochemically pure exo-bromonorbornane.

Trialkylboranes react readily with disulfides in the presence of air to give the corresponding sulfides [52](Eq.62).

\[
R_3B + 2CH_3SSCH_3 \xrightarrow{\text{THF, air, r.t. or h}_u, \text{hexane}} 2RSCH_3 + (CH_3S)_2BR
\]

\[
\text{Eq.62}
\]

(R = norbornyl; n, i, s -C_4H_9)

The free radical halogenation of norbornane (norcamphane) with sulfuryl chloride or chlorine reported by Kooymann and Vegter yield the most amount of exo-norbornylchloride[53,54] (Eq.63,64).

\[\text{Norbornane} + \text{SO}_2\text{Cl}_2 \xrightarrow{\text{Peroxide}} \text{Norbornylchloride, 99% exo, 1% endo}\]

\[\text{Eq.63}\]

\[\text{Norbornane} + \text{Cl}_2 \xrightarrow{\text{h}_u} \text{Norbornylchloride, 70% exo, 30% endo}\]

\[\text{Eq.64}\]

Both of these free radical reactions show that the halogenation by bulky groups hinders the attack from the endo position. The mechanism for these reactions is showed below (Scheme 7):

\[\text{Cl}_2 \xrightarrow{\text{h}_u} 2\text{Cl}^\cdot\]
Scheme 7: The Free-radical Mechanism of Halogenation of Norbornane.

Since the norbornyl radical possesses some degree of planarity (Fig.4), the halogen donor can attack from either side. However, the attack from exo side is more favorable for steric reasons, usually leading to a high ratio of exo to endo products.

Another free-radical example is Eq.65.

The following mechanism (Scheme 8) was suggested by Kharasch and Brown[55].

\[(\text{COCl})_2 \xrightarrow{\text{hv}} \cdot \text{COCOCl} + \text{Cl}^\cdot\]  
(Eq.65a)

\[\cdot \text{COCOCl} \rightarrow 2\text{CO} + \text{Cl}^\cdot\]  
(Eq.65b)

\[\text{RH} + \text{Cl}^\cdot \rightarrow \text{R}^\cdot + \text{HCl}\]  
(Eq.65c)

\[\text{R}^\cdot + (\text{COCl})_2 \rightarrow \text{RCOCl} + \cdot\text{COCl}\]  
(Eq.65d)
\[
\text{COCl}^- \rightarrow \text{CO} + \text{Cl}^- \quad \text{(Eq.65e)}
\]

\[
\begin{array}{c}
R^- \ = \ \text{Scheme 8} \\
\end{array}
\]

The mechanism of the photoreaction of norbornane with the molecule \((\text{COCl})_2\).

Again the steric reasons above (Fig.4) cause formation of 95% \textit{exo}-product produced.

It is useful for chemists to study the stereochemistry of reactions in norbornyl system. At present, the much research work about norbornyl system has been done, and thus the details of mechanisms, such as radical, carbocation, are known in the norbornyl system.

1.5 The Definition of the Nonclassical Ion

The study of the rearrangement of camphene hydrochloride into isobornyl chloride (Eq.66) has had major consequences for the development of carbocation theory.

\[
\text{Eq.66}
\]

Meerwein's proposal in 1922 that this rearrangement involves prior formation of a carbocation appears to be the first application of cationic intermediates to account for these molecular transformations. In 1939, C. L. Wilson and his associates suggested that such a rapidly equilibrating pair of ions (Eq.67) might exist instead as the mesomeric species (Eq.66).

\[
\text{Eq.67}
\]
Wilson's proposal caught the fancy of physical organic chemists. The concept was widely adopted and used. Indeed, with the possible exception of the methyl cation, nonclassical structures apparently have been considered for nearly every known aliphatic, alicyclic, and bicyclic carbocation\cite{56}. Representative systems for which nonclassical ions have been considered are shown in Figure 5.

Surprising as it may seem, in view of the vast literature on the subject, there appears to have been no serious attempt by workers in the field to arrive at generally acceptable definition of the term "nonclassical ion." Consequently, it appears appropriate to turn back to the way the term was introduced and used to arrive at an unambiguous definition. The term "nonclassical" was apparently first used by Roberts in referring to his proposed tricyclobutonium structure (XXIII) for the cyclopropylcarbinyl cation (XXII)\cite{57}. 

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Carbocations for which electron-deficient nonclassical structures has been considered.}
\end{figure}
The proposed structure (XXIII) was clearly different from the "classical" structure (XXII) for the intermediate cation. The second time the term was apparently used by Winstein, who refers to the "nonclassical structures" of the norbornyl cation (XXV) and other cations in contrast to their classical structures (XXIV). The third such reference is apparently due again to Roberts: "Recent interest in the structures of carbocations has led to speculation as to whether the ethyl cation is

most appropriately formulated as a simple solvated electron-deficient entity (XXVI), a "nonclassical" bridged ethylene protonium ion (XXVII), or possibly as an equilibrium mixture of the two ions"[58].

Although in the past the term has also been applied to n-bridged species (n: non-bonded electrons), such as the bromonium ion[59] and to π-bridged species, such as the phenonium ion[59], it has been urged by both Bartlett[56] and Sargent[60] that the term "nonclassical" be restricted to delocalizations involving σ-electrons. After all, there is nothing nonclassical about the bromonium ion (XXVIII). It can nicely represented by a single Lewis structure.

Actually, there are major advantages in simplicity in limiting the term "nonclassical carbocation," to cations containing carbon or hydrogen bridging atoms, such as above structures (XXIII), (XXV) and (XXVII). Accordingly, in a collective effect, Paul von R. Schelyer and Brown[62] have developed the following definitions restricted to such cations.
1. A carbocation is a positively charged species in which a significant portion of the positive charge resides on one or more carbon atoms termed the "carbonium" carbon or carbons.

2. A classical carbocation is a positively charged species which can be adequately represented by a single Lewis structure involving only two electron-two center bonds. (typical examples are XXII, XXIV and XXVI) Traditionally, π-conjugated cations, such as allyl and cyclopropenyl, are included in this category.

3. A nonclassical carbocation is a positively charged species which cannot be represented adequately by a single Lewis structure. Such a cation contains one or more carbon or hydrogen bridges joining the two electron-three (or multiple) center bonds including a carbon or hydrogen bridge (typical examples are structures XXIII, XXV and XXVII above).

1.6 The Lewis Acidity of Boron Trihalides, \( \text{BX}_3 \) (X=F,Cl,Br,I){[61]

Consider the family of boron trihalides, \( \text{BX}_3 \) (X=F,Cl,Br,I). Each of these monomers has a trigonal, planar geometry. Each behaves as a Lewis acid, but the acid strength is significantly less than that of BH\(_3\). Moreover, the Lewis acidity of the boron trihalides follows the sequence BF\(_3\)<BCl\(_3\)<BBr\(_3\)<BI\(_3\). This is, perhaps, initially surprising. The electronegativity of the substituents follows the trend F>Cl>Br>I, and simple substituent inductive effects (descreening of the boron nuclear charge by withdrawal of s electron density) would lead you to expect that BF\(_3\) would be the strongest acid of the series and the iodide the weakest. Why, then, is BF\(_3\) the weakest Lewis acid? The answer lies in the ability of the halides, and in particular the fluoride atom, to donate lone pair \( \pi \)-electron density into the empty 2p orbital on the central boron atom. This situation, using BF\(_3\) as the example, is contrasted with that in BH\(_3\) in Fig.6. In BH\(_3\), the hydrogen 1s orbitals have nothing more to offer once the B-H s-bonds have been formed. On the other hand, having formed a B-F s-bond, a fluorine atom still possesses three lone pairs of electrons, one of which resides in a 2p AO oriented parallel to the empty 2p orbital on the boron atom. Delocalization of \( \pi \)-electron density stabilizes the BF\(_3\) molecule, and thus decreases its Lewis acidity. The same is true for BCl\(_3\), BBr\(_3\), and BI\(_3\), but to an ever decreasing degree due to the increasing size of atom. Thus, in going from BF\(_3\) to BI\(_3\), the net Lewis acidity is enhanced.
The Availability of π-π Bonding in BF₃ in Contrast to BH₃.

1.7 The Objective of the Research

We propose to study the scope of the halogenolyses of organoboranes. The key to our results has been the choice of the reaction conditions, especially that of the Lewis acid catalyst. Although some halogenolyses have been reported, we feel that our reaction can occur in higher yield and with a greater understanding of the stereochemistry and mechanism than previously known.

Hydroboration represents an entry to a variety of compounds that are clearly labeled in one stereochemical fashion. For example, deuterioboration of norbornene results in a cis-exo labeled organoborane, which in turn can be converted with retention to the corresponding cis-exo labeled alcohol or amine[62]:

\[
\begin{align*}
\text{BD₃} & \quad \text{THF} \quad \text{BD₃} \\
\end{align*}
\]
The norbornene system undergoes chemical reactions whose stereochemical details often reveal standard mechanistic pathways. An example is the addition of DCl to norbornene which occurs with the well known Wagner-Meerwein rearrangements of carbocations generated in this system (Scheme 9):

![Diagram](image)

**Scheme 9.** Deuteriochloridnation of Norbornene via An Nonclassic Ion Intermediate

Using organoboranes as an entry to synthesize organic halides has been severely limited. It is well known that treatment of alcohols such as XXVIII (see Eq.68) with standard chlorination reagents such as HCl or thionyl chloride would give rise to halides via intermediates Ia and Ib. Thus these reactions would lead to Wagner-Meerwein rearranged products XXXIa and XXXIIb. In like fashion treatment of amines such as XXIX (see Eq.68) to induce diazotization reagents, followed by CuCl coupling conditions would also give rise to Wagner-Meerwein scrambled products.

It is clear that, in this context, the synthesis of halide IIa (bearing cis-vicinal chloride and deuterium in only the exo position) in high yield is a great challenge.

The conversion of terminal olefins, via hydroboration, mercuration and halogenation to the terminal alkyl bromide was reported by Tufariello in 1970 [63]. It was thus thought that a convenient route was available for the regiospecific and perhaps stereospecific preparation of alkyl halides.
Consequently, it occurred to us that a similar reaction sequence (see below) would be carried out in the norbornane system. The net syn addition of deuterium halide to a double bond could be accomplished. This convenient route would be valuable for the conversion of sensitive bicyclic alkenes into alkyl halides without the extensive skeleton rearrangements that occur during hydrogen halide additions. Upon the effective stereospecific addition of deuterium halide to norbornene, conclusions regarding the mechanism involved could be made. It is one goal of this research to carry out the conversion of an internal olefin (norbornene) to an alkyl halide (XXXIII) without rearrangement of the carbon skeleton. The reaction sequence below (Eq.70) shows the results of first part of studies in this research that involved use of an organomercurial intermediate, an approach which was not successful.

Past mercuration work has thus caused our focus of this research to be the synthesis of organic halides by direct halogenolyses of an organoborane (Eq.71, 72) in a higher yield and with greater stereochemical control.
Since it is quite easy for the norbornyl system, a bridged polycyclic system, to undergo rearrangement of the carbon skeleton, use of this system provides a thorough test of the stereospecificity and stereoselectivity of the reaction sequences.
2. RESULTS and DISCUSSION

2.1 Hydroboration and Deuterioboration

The hydroboration was achieved by the dropwise addition of borane:THF complex at 0°C, and then, the solution was stirred an additional hour at room temperature. The reaction system was flushed with dry nitrogen gas until finishing the reaction. The procedure of hydroboration was modified from the one reported by C. F. Lane and H. C. Brown[64, 65].

Deuterioboration was achieved by replacing borane in THF (1.0M) with borane-d3 in THF (1.0M) under the exactly same reaction conditions.

The purities of the isomer (tri-exo-2-norbornylborane and tri-exo-3-d-exo-2-norbornylborane) were checked by oxidation reaction with alkaline-hydrogen peroxide. The isomeric purity checked by NMR was >99% exo-. The yield was >90% (based on norbornene).

In general, organoboranes are very sensitive to oxidation[32, 65, 66], and are normally handled under an atmosphere of nitrogen to prevent autoxidation. The norbornylborane is highly reactive toward oxygen, the mechanism of the autoxidation reaction of organoborane is a free-radical chain reaction showed below (Scheme 10):

\[
\begin{align*}
R_3B + O_2 & \rightarrow R^+ + R_2BO_2 \\
R^+ + O_2 & \rightarrow RO_2^+ \\
RO_2^+ + R_3B & \rightarrow RO_2BR_2 + R^+
\end{align*}
\]

Scheme 10 The Mechanism of the Autoxidation Reaction of Organoborane

Therefore, tri-exo-norbornylborane must be used immediately for the next step after finishing the preparation of hydroboration, or stored in nitrogen-flushed sealed containers.

The other method of hydroboration was that from A. B. Brister's thesis (See Section 4.7). The hydroboration of norbornene was carried out by addition of borane gas, produced by treating Et2O:BF3 with LiAlH4, into the THF solution of norbornene under the protection
of nitrogen gas. The yield was 79% after distillation. This method is not as convenient as the first and the yield is lower.

The hydroboration reaction proved that above 99% exo- isomer can be produced by an anti-Markovnikov syn addition from the less hindered side of the double bond. It appears that the hydroboration reaction involves a simple four-centered transition state, with the direction of addition controlled primarily by the polarization of the boron-hydrogen bond, \( \delta^+ \delta^- \). This is also true for the deuterioboration reaction. The mechanism for deuterioboration of norbornene is shown below (Scheme 11):

![Scheme 11 The Mechanism of Deuterioboration of Norbornene.](image)

The facile hydroboration of norbornene provides the possibility of studying stereochemistry and mechanisms in the norbornyl system.

### 2.2 Transmercuration

In general, organometallic compounds react with halogens with great ease to form the corresponding halides\([67]\). In 1970, R. C. Larock and H. C. Brown reported that organoboranes derived from terminal olefin via hydroboration undergo a quantitative reaction in a matter of minutes with mercuric acetates in essentially quantitative yields\([68]\). The conversion of terminal olefins, via hydroboration, mercuration and bromination to terminal alkyl bromides in excellent yield and under mild conditions was reported in 1970 by Tufariello\([22]\)(Eq.69). The fact that this reaction occurred with regiochemical retention suggested that free radical intermediates that could undergo primary to secondary radical rearrangement did not apply here. So it was thought that a convenient route was available for the stereospecific and stereoselective preparation of alkyl halides.

In view of Tufariello's report, another reaction sequence has devised by changing the substrate of the reaction from a terminal olefin to norbornene, an internal olefin, coupled with the use of deuterioborane, and, eventually, halogenation after the transmetallation
The net syn addition of deuterium halide to a double bond would thus be expected (Eq.70). The possible ionic mechanism for the transmercuration reaction is proposed as follows (Scheme 12):

**Scheme 12**  Possible Ionic Mechanism for the Transmercuration Reaction.

Unfortunately, after attempting Tufariello's sequence of reactions a number of times, transmetallation reaction of tri-exo-norbornylborane with mercury (II) acetate was found to be exceedingly difficult to perform. A yield of less than 5% of alkyl halide by this reaction sequence was obtained. Different reaction conditions such as temperature, solvents, and Lewis acidic catalysts were tried to improve the yield of transmercuration reaction, but there was no improvement in results.
An explanation for this transmercuration result is that tri-exo-norbornylborane containing bulky alkyl groups which surround boron atom makes it difficult for mercury (II) acetate to approach the boron atom under such reasonable conditions.

The literature[69, 66] suggests that mercuration reactions are very sensitive to steric hindrance about the boron atom and hence secondary alkyl groups except the secondary phenyl group fail to react under Tufariello's reaction conditions.

Since the transmercuration can not be easily accomplished by the method we tried, direct halogenation of organoborane was studied (Eq.72).

2.3 Halogenolysis of Organoboranes

As shown by the lack of formation of norbornylmercuric acetate above, the norbornyl group, a sterically-resistant secondary group, did not easily react under Tufariello's reaction conditions. Direct halogenation of organoboranes can, however, be carried out by Lewis acidic catalysis. The deuterium scrambling within the norbornyl halide structure, shown by analyzing the 1H NMR spectrum, indicated that Wagner-Meerwein rearrangement occurs during the halogenolysis of tri-norbornylborane. The carbocation, possibly a nonclassical ion, results in the formation of Wagner-Meerwein product, and this process occurs after norbornyl chloride formation. Assumedly excessive boron trihalide is the scrambling agent.
The following mechanism will rationalize the results of halogenolysis.

Step 1: \[ X_2 + BX_3 \rightarrow \delta^+ \text{X} \rightarrow \delta^- \text{X} \rightarrow \delta^- \text{X} - BX_3 \]

\((X=\text{Cl, Br, I})\)

Step 2:

\[
\begin{align*}
\text{Step 2: } & \quad \text{[Diagram]} \\
& \quad \text{[Diagram]} \\
& \quad \text{[Diagram]} \\
& \quad \text{[Diagram]}
\end{align*}
\]

Step 3:

\[
\begin{align*}
\text{Step 3: } & \quad \text{[Diagram]} \\
& \quad \text{[Diagram]} \\
& \quad \text{[Diagram]}
\end{align*}
\]

Step 4:

\[
\begin{align*}
\text{Step 4: } & \quad \text{[Diagram]} \\
& \quad \text{[Diagram]} \\
& \quad \text{[Diagram]}
\end{align*}
\]

Step 5:

\[
\begin{align*}
\text{Step 5: } & \quad \text{[Diagram]} \\
& \quad \text{[Diagram]} \\
& \quad \text{[Diagram]}
\end{align*}
\]

Step 6:

\[
\begin{align*}
\text{Step 6: } & \quad \text{[Diagram]} \\
& \quad \text{[Diagram]} \\
& \quad \text{[Diagram]}
\end{align*}
\]

Wagner-Meerwein rearrangement products

Scheme 13 The mechanism of halogenolysis of tri-norbornylborane.
Evidence for the Wagner-Meerwein rearrangement will be provided by analyzing $^1$H NMR and GC/MS spectrum as described in Section 2.3.5

2.3.1 Iodinolysis

\[ 3 \text{I}_2 + \text{D}_{3}\text{B} \rightarrow 0.05 \text{BI}_3, \text{CH}_2\text{Cl}_2 \rightarrow 3 \text{D} + \text{BI}_3 \text{ Eq.73} \]

The reaction (Eq.73) was carried out with 1.0 mole of tri-exo-3-d-exo-2-norbornylborane, 3 mole equivalents of iodine (or bromine, or chlorine) and 0.05 moles equivalents of boron triiodide; the results are reported in Table 1 below. The products were identified by $^1$H NMR, IR and GC/MS. The spectra are shown in the appendix. Spectral analysis (see below) shows that Wagner-Meerwein rearrangement occurs after the iodinolysis of tri-norbornylborane. The relevant mechanism is shown in Scheme 13 above. The yield (33%) suggests that only one of the three norbornyl groups attached to boron is converted to iodide. The integration of the $^1$H NMR resonances of $\delta$ 3.95 and 4.20 indicated the isomer mixture consisted of 91% exo- and 19% endo- of products.

Since the catalyst, BI$_3$, is expensive, the preparation of BI$_3$ was tried according to the literature[70]. The reaction shown below (Eq.74) must be carried out under nitrogen in

\[ 3 \text{LiBH}_4 + 8 \text{I}_2 = 3 \text{LiI} + 3 \text{BI}_3 + 4 \text{H}_2 + 4\text{HI} \text{ Eq.74} \]

order to avoid exposure to oxygen. Three traps cooled in liquid nitrogen baths were used to collect the BI$_3$ produced as it was blown from the reaction flask with nitrogen. The impure BI$_3$ was purified by sublimation. The reaction was not smooth because LiBH$_4$ is highly flammable. LiBH$_4$ also easily absorbs water and becomes sticky, and it is dangerous when exposed to air. After two unsuccessful attempts, the preparation of BI$_3$ was abandoned.

The reaction of tri-norbornylborane with iodine to produce endo-2-iodonorbornylborane is accelerated by sodium methoxide. The combination of hydroboration followed by iodination in the presence of a base provides a convenient method for hydroiodination of alkene. The base-induced iodination of exo-norbornylborane proceeds with inversion of configuration at the reaction center (Scheme 3), and results in the formation of endo-2-iodonorbornane from tri-exo-norbornylborane (Eq.75). The purpose of this reaction is to
obtain pure endo product in order to verify the position of an exo proton of endo-2-iodonorborane in 1H NMR spectra. The exo- proton of endo-iodide in 1H NMR is expected to be slightly downfield of the endo-proton of the exo-iodide.

\[
\begin{align*}
\text{B} & + \text{I}_2 \xrightarrow{\text{NaOCH}_3/\text{CH}_3\text{OH}} \text{THF,} \ 0^\circ\text{C, N}_2 \xrightarrow{\text{80\% CH}_3\text{OH/H}_2\text{O}} \text{K}_2\text{CO}_3, \ 3\text{h.} \\
& \text{(exo- + endo-)} \\
\end{align*}
\]

Eq.75

\[\{\text{exo-} + \text{endo-}\}\]

1H NMR analysis shows that the position of exo- proton of endo-2-iodonorborane is at \(\delta 4.20\) (1H, multiplet, C-2 methine) of the 1H NMR spectrum. The yield was 87\% (based on one norbornyl group), and the purity is above 90\%.

**Table 1** Reaction of tri-exo-2-norbomylborane and tri-exo-3-d-exo-2-norbomylborane with iodine in the presence of boron triiodide.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Iodide</th>
<th>Purity (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Yield(%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>R&lt;sub&gt;3&lt;/sub&gt;B(D)&lt;sup&gt;c&lt;/sup&gt; + I&lt;sub&gt;2&lt;/sub&gt; + BI&lt;sub&gt;3&lt;/sub&gt;</td>
<td></td>
<td>98.53%</td>
<td>33%</td>
</tr>
<tr>
<td>R&lt;sub&gt;3&lt;/sub&gt;B&lt;sup&gt;c&lt;/sup&gt; + I&lt;sub&gt;2&lt;/sub&gt; + BI&lt;sub&gt;3&lt;/sub&gt;</td>
<td></td>
<td>86.36%</td>
<td>31.4%</td>
</tr>
</tbody>
</table>

<sup>a</sup>Determined by peak ratios on gas chromatography (GC).<br>
<sup>b</sup>The yield is based on the reaction of R<sub>3</sub>B and is the ratio of observed weight to theoretical weight obtained from column chromatography.<br>
<sup>c</sup>R<sub>3</sub>B(D) is tri-exo-3-d-exo-2-norbomylborane; R<sub>3</sub>B is tri-exo-2-norbomylborane.

### 2.3.2 Brominolysis

\[
\begin{align*}
\text{3 Br}_2 & \xrightarrow{0.5\text{BBr}_3, \text{CH}_2\text{Cl}_2} \text{0\°- r.t., 2 days} \\
& \text{3 Br}_2 + \text{BBr}_3 \\
\end{align*}
\]

Eq.76

Brominolyses (Eq.76) were carried out with 1.0 mole of tri-norbomylborane, 3 mole equivalents of bromine and 0.5 mole equivalents of boron tribromide in an ice-water bath for two hours and then, at room temperature for 2 days. The results are reported in Table 2.
The products were identified by $^1$H NMR, IR and GC/MS (appendix). Spectral analysis shows Wagner-Meerwein rearrangement due to appearance of deuterium scrambling in the products of brominolysis of tri-norbornylborane (see below in this section). It is likely that the boron tribromide causes the formation of a carbocation from the norbornyl bromide leading to Wagner-Meerwein rearrangement (Scheme 13). The yields suggest that one to one and half of the three norbornyl groups attached to boron are converted to alkyl bromide.

**Table 2** Reaction of tri-exo-2-norbornylborane or tri-exo-3-d-exo-2-norbornylborane with bromine in the presence of boron tribromide.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Bromide</th>
<th>Purity (%)$^a$</th>
<th>Yield(%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{R}_3\text{B(D)}^c+\text{Br}_2+\text{BBr}_3$</td>
<td>$\text{Br}^D$</td>
<td>92.57%</td>
<td>47.0%</td>
</tr>
<tr>
<td>$\text{R}_3\text{B}^c+\text{Br}_2+\text{BBr}_3$</td>
<td>$\text{Br}^D$</td>
<td>95.09%</td>
<td>42.82%</td>
</tr>
</tbody>
</table>

$^a$ Determined by peak ratios on gas chromatography (GC). $^b$ The yield is based on the reaction of $\text{R}_3\text{B}$ and is the ratio of observed weight to theoretical weight obtained from column chromatography. $^c$ $\text{R}_3\text{B(D)}$ is tri-exo-3-d-exo-2-norbornylborane; $\text{R}_3\text{B}$ is tri-exo-2-norbornylborane.

**2.3.3 Chlorinolysis**

\[ 3 \text{Cl}_2 + \begin{array}{c} \text{D} \\ \text{CH}_2\text{Cl}_2 \end{array} \begin{array}{c} \text{D} \\ \text{BR} \end{array} 0.1\text{BCl}_3, \text{CH}_2\text{Cl}_2, 30\text{o}-\text{t.}, 2 \text{days} \rightarrow 3 \begin{array}{c} \text{D} \\ \text{Cl} \end{array} + \text{BCl}_3 \]

Eq.77

The reactions (Eq.77) were carried out with 1.0 mole of tri-norbornylbornane, 3 mole equivalents of chloride and 0.1 mole equivalents of boron trichloride in a dry ice-acetone bath for 2 hours and then at room temperature for 2 days. The results are reported in Table 3 and the spectra are shown in the appendix. Analysis by $^1$H NMR, IR and GC/MS shows that Wagner-Meerwein rearrangement indicated by deuterium scrambling in the product norbornyl chloride has occurred (see below). It is likely that the boron trichloride results in the formation of a carbocation (see steps 5-6 in scheme 13). The yields suggest that two or more of the three norbornyl groups attached to boron are converted to the chloride.
It should be noted that the excessive amount of chlorine and boron trichloride will result in many by-products resulting in a low yield of the desired product.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Chloride</th>
<th>Purity (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Crude Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>R&lt;sub&gt;3&lt;/sub&gt;B(D) + Cl&lt;sub&gt;2&lt;/sub&gt; + BCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>74.13%</td>
<td>60.86%</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Determined by peak ratios on gas chromatography (GC). <sup>b</sup>The yield is based on the reaction of R<sub>3</sub>B and is the ratio of observed weight to theoretical weight obtained from column chromatography. c. R<sub>3</sub>B(D) is tri-exo-3-d-exo-2-norbornylborane.

### 2.3.4 Addition of "HI" or "DI" to Norbornene.

When we study the direct halogenolysis of tri-exo-3-d-exo-2-norbornylborane using BX<sub>3</sub> as a catalyst, an important fact we wanted to make clear is whether Wagner-Meerwein rearrangement has occured.

It is well known<sup>[62]</sup> that the deuteriohalogenation of norbornene is always accompanied by Wagner-Meerwein rearrangement resulting in a 1:1 mixture of exo-2-d-exo-3-halobicyclo[2.2.1]heptane and syn-7-d-exo-2-halobicyclo[2.2.1]heptane (Eq.78). The rearrangement mechanism about this reaction is illustrated in Sections 1.5 and 1.7 (see Scheme 9). The deuteriohalogenation of norbornene is easily accomplished when deuterium oxide was used as in Eq.79.

\[
\text{(CH}_3\text{)_3SiCl + NaX + 0.5D}_2\text{O } \xrightarrow{\text{CH}_3\text{CN, r.t., 3h.}} \text{DX + 0.5[(CH}_3\text{)_3Si]_2O + NaCl}
\]  

Eq.79
This procedure offers new and facile synthetic routes to the deuterated compounds which are especially important as labeled compounds. The deuteriohalogenation of norbornene is smoothly carried out using a chlorotrimethylsilane/sodium halide/D2O mixture under mild conditions, and the norbornyl halides are obtained in high yields (Table 4) without troublesome work-up. In addition, the extent of deuterium incorporations is high (Table 17). By this procedure, we obtained standard rearrangement products in a ratio of about one to one of exo-2-d-exo-3-halobicyclo[2.2.1]heptane to syn-7-d-exo-2-halobicyclo[2.2.1]heptane whose 1H NMR spectra can be compared with those obtained from other routes we have studied.

This method offers a novel synthesis of deuterated compounds from olefins by using deuterium oxide, an inexpensive and easy-to-handle deuterium source.

The hydrohalogenation of norbornene could be easily completed when water (H2O) was used in place of D2O in the above reaction (Eq.78 and 79).

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Purity (%)(^a)</th>
<th>Crude Yield(%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>norbornene + &quot;DI&quot;(^c)</td>
<td>(\text{I}^D)</td>
<td>99.94%</td>
<td>98.0%</td>
</tr>
<tr>
<td>norbornene + &quot;DBr&quot;(^c)</td>
<td>(\text{I}^D) (\text{Br}^D)</td>
<td>92.37%</td>
<td>58.0%</td>
</tr>
<tr>
<td>norbornene + &quot;DCl&quot;(^c)</td>
<td>(\text{I}^D) (\text{Cl}^D)</td>
<td>98.66%</td>
<td>94.4%</td>
</tr>
</tbody>
</table>

\(^a\) Determined by peak ratios on gas chromatography (GC). \(^b\) The yield is based on the reaction of norbornene and is the ratio of observed weight to theoretical weight obtained from column chromatography. \(^c\) "DX" came from the following reaction:

\[
\text{Cl} + 0.5\text{D}_2\text{O} \xrightarrow{\text{NaX, CH}_3\text{CN}} \text{DX} + 0.5[\text{(CH}_3\text{)}_3\text{Si}]_2\text{O}
\]

Eq. 80
Table 5  Reaction of norbornene with hydrogen halide in CH₃CN.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Purity (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Crude Yield(%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>norbornene + &quot;HI&quot;&lt;sup&gt;c&lt;/sup&gt;</td>
<td><img src="image" alt="Structure" /></td>
<td>99.77%</td>
<td>97.25%</td>
</tr>
<tr>
<td>norbornene + HBr&lt;sup&gt;d&lt;/sup&gt;</td>
<td><img src="image" alt="Structure" /></td>
<td>99.92%</td>
<td>74.0%</td>
</tr>
</tbody>
</table>

<sup>a</sup>Determined by peak ratios on gas chromatography (GC). b. The yield is based on the reaction of norbornene and is the ratio of observed weight to theoretical weight obtained from column chromatography. c. "HI" came from the following reaction:

\[
(CH_3)_3SiCl + 0.5H_2O \xrightarrow{Nal, CH_3CN \text{ r.t.,3hr.}} HI + 0.5[(CH_3)_3Si]_2O \quad \text{Eq. 81}
\]

<sup>d</sup>HBr is 48% hydrobromic acid.

2.4 Spectroscopic Analysis

2.4.1 <sup>1</sup>H NMR Analysis

In proton analysis of the norbornene system, the values of vicinal coupling constants (J<sub>vic</sub>) always fall into characteristic ranges dependent upon dihedral angles, and with certain characteristic shielding effects, the values of J<sub>vic</sub> afford a means of establishing stereochemistry. Deuterium substitution often results in some simplification of the proton spectrum[71, 72].

We must now analyze carefully the structure of exo-3-d-exo-2-norbornyl halide and exo-2-norbornyl halide and the expected splitting pattern of protons in <sup>1</sup>H NMR spectrum before studying the proton NMR spectrum.

The proton α to the halide atom in norbornyl system is much more downfield than other protons of norbornyl system in the <sup>1</sup>H NMR spectrum due to the electronegativity of halide atom. The conclusion as to whether the Wagner-Meerwein rearrangement happens can be made according to the detailed analysis of splitting pattern of the proton α to the halide in <sup>1</sup>H NMR spectrum.
a) Proton NMR Spectrum of *exo*-2-Norbornyl Halide

If we examine Figs. 8-10, we note that H\(_2n\) can be split by the protons such as H\(_1\), H\(_3n\), H\(_3x\), etc., near it. Due to the vicinal dihedral angle of ca. 0° between H\(_2n\) and H\(_3n\), H\(_2n\) should be split by ca. 8-10 Hz by H\(_3n\), and J\(_{2n-3x}\) should be 3-5 Hz because of the dihedral angle of ca. 110° between H\(_2n\) and H\(_3x\). The dihedral angle of H\(_2n\) with H\(_1\) is ca. 90°, and thus J\(_{2n-1}\) is expected to be the smallest, ~0-2 Hz, according to the Karplus correlation\(^{[71]}\). Thus J\(_{2n-1}\) is very small, and often can be ignored. J\(_{2n-7a}\) in the bicyclo[2.2.1]hexane system is about ~3-4 Hz\(^{[83]}\). This unusually high long-range coupling constant is attributed to the "W-conformation" of the sigma bonds between H\(_2n\) and H\(_7a\):

\[
\begin{align*}
H_2n & \quad C & \quad C & \quad H_7a \\
\end{align*}
\]

Therefore the H\(_2n\) peak split by H\(_3n\) and H\(_3x\) (when the coupling between H\(_2n\) and H\(_7a\) is negligible) will show a doublet of doublets (if first-order) with the relative intensity of
1:1:1:1 (Fig. 11), or if the value of $J_{2n-3x}$ equal to $J_{2n-3n}$, an apparent triplet with the relative intensities of 1:2:1 (Fig. 12) will be observed\textsuperscript{[73]}.  

![Diagram](image1)

**Fig. 11** Doublet of Doublet of 2-endo Proton in Norbornyl Halide.  

![Diagram](image2)

**Fig. 12** Apparent Triplet of 2-endo Proton in Norbornyl Halide.  

b) Proton NMR Spectrum of $exo$-$3$-$d$-$exo$-$2$-Norbornyl Halide  

Deuterium substitution is an extremely useful technique in conjunction with $^1$H NMR spectroscopy, as it often results, as described above, in simplification of spectra. The replacement of proton in 3-exo position with deuterium would remove the coupling of $H_{2n}$ with $H_{3x}$. The splitting pattern will change as follows (Fig. 13 and 14). The $H_{2n}$ signal could be a doublet with the possibility of small additional splitting.  

![Diagram](image3)

**Fig. 13** Splitting Pattern of 2-endo Proton in Deuterated Norbornyl Halide  

![Diagram](image4)

**Fig. 14** Splitting Pattern of 2-endo Proton in Deuterated Norbornyl Halide with Negligible $J_{2n-7a}$.
The value of $J_{2n-7a}$ should still be small or negligible, so a doublet is often observed, and then the splitting pattern is close to Figure 14. In summary, if net *syn* addition of deuterium halide to a double bond could be accomplished, the 2-*endo* proton should have a doublet peak.

c) Proton NMR Spectrum of Wagner-Meerwein Rearrangement Products

The net *syn* addition of deuterium halide to a double bound would show a doublet peak in $^1$H NMR spectrum in $\delta$ 3.85-3.99 region. In fact, $^1$H NMR spectra of all products arising from our BX3-promoted procedure gave more complex multiplets in the $\delta$ 3.85-3.99 area. It is thus apparent that Wagner-Meerwein rearrangement happens, very likely due to the production of a carbocation. Therefore, the conclusion can be made that the reaction of tri-exo-3-d-exo-2-norbornylbornane with halide using their Lewis acid catalysts only produces rearrangement products.

The rearrangement products contain two structures XXXIV and XXXV with a ratio of about 1:1 as below:

Since signal for 2-*endo* proton of structure XXXIV would be expected to possess a substantially "doublet appearance" described above (Section 2.4.1b), and the 2-*endo* proton of structure XXXV will be very close to the splitting pattern for the 2-*endo* proton of structure XXXVI: a triplet or a doublet of doublets (as per above). The signal at $\delta$ (4.0 - 3.8) ($\delta=3.85$ for Cl; $\delta=3.95$ for Br; $\delta=3.99$ for I) for our products is consistent with a sample that is ca. 50% XXXIV and 50% XXXV; the major coupling ($J_{2n-3n}$) is apparently completely retained and the spectrum has the appearance of the triplet of XXXV superimposed upon the doublet of XXXIV in a 1:1 ratio. Thus proton NMR spectroscopic analysis is consistent with XXXVII being a 50:50 mixture of XXXIV and XXXV.
Proton NMR Analysis of Samples

A careful study of the spectra was done as described below:

1) Partial Spectrum of Iodide (Complete Spectrum of Iodide is in Appendix):

Fig. 15

The 3.99 Signal for the Proton on Carbon Bearing I in the Unlabeled Structure. (Authentic cxo-2-Norbornyl Iodide from Addition of "HI" to Norbornene)

The complete 1h NMR spectrum includes (CDCl3): 8 0.8-2.6 (m, 10H), 3.99 (m, C-2 endo-methine, 1H). The coupling constants for H2n are listed in Table 6.

Table 6

<table>
<thead>
<tr>
<th>Coupling Constants for H2n of Authentic Unlabeled exo-2-Norbomyl Iodide Obtained from Addition of &quot;HI&quot; to Norbornene</th>
</tr>
</thead>
<tbody>
<tr>
<td>J Hz</td>
</tr>
<tr>
<td>2n-3n</td>
</tr>
<tr>
<td>2n-3x</td>
</tr>
<tr>
<td>2n-7a</td>
</tr>
</tbody>
</table>

n=endo, \(\Rightarrow\) exo.
Table 7  
Coupling Constants for H$_{2n}$ of Unlabeled *exo*-2-Norbornyl Iodide from Lewis Acid Catalyzed Reaction

<table>
<thead>
<tr>
<th>J</th>
<th>Hz</th>
<th>J</th>
<th>Hz</th>
<th>J</th>
<th>Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>2n-3n</td>
<td>8.04</td>
<td>2n-3x</td>
<td>2.68</td>
<td>2n-7a</td>
<td>2.01</td>
</tr>
</tbody>
</table>

Fig.16 The δ 3.99 Signal Proton (H$_{2n}$) on Carbon Bearing I in the Unlabeled Structure. (*exo*-2-Norbornyl Iodide from Lewis Acid Catalyzed Reaction).

The complete $^1$H NMR spectrum includes (CDCl$_3$): δ 0.8-2.6 (m, 10H), δ 3.99 (m, C-2 *endo*-methine). δ 4.20 (C-2 *exo*-methine). The coupling constants for H$_{2n}$ are listed in Table 7.

The signal at δ=3.99 (Fig.16) was caused by following splitting pattern (Fig.17)
Since the value of $J_{2n-7A}$ is so close to $J_{2n-3x}$ that it can not be ignored at this time, the corresponding signal at $\delta$ 3.99 has a six-line appearance with relative intensities of 1:2:1:1:2:1. The replacement of proton in 3-exo position with deuterium should remove the coupling of $H_{3x}$ with $H_{2n}$. The splitting pattern of proton $\alpha$ to the iodide would then be the superimposition of two kinds of splitting patterns. (Fig. 19) The "doublet appearance" of $exo$-$cis$-$3$-$d$-$2$-$exo$-norbornyl iodide (Fig. 18) superimposed upon the six-line appearance of $syn$-$7$-$d$-$2$-$exo$-norbornyl iodide consists a multiplet peak at $\delta$ 3.99 in proton NMR spectrum (Fig. 19).
The complete $^1$H NMR (CDCl$_3$) shows: $\delta$ 0.8-2.6 (m, 9H), $\delta$ 3.99 (m, C-2 endo-methine, 1H). (No C-2 exo-methine). The coupling constants for H$_2$n are listed in Table 8.

Table 8  Coupling Constants for H$_2$n of Deuterium Labeled Authentic exo-2-Norbornyl Iodide from "DI" Addition to Norbornene.

<table>
<thead>
<tr>
<th>J</th>
<th>Hz</th>
<th>J</th>
<th>Hz</th>
<th>J</th>
<th>Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>2n-3n</td>
<td>8.04</td>
<td>2n-3x</td>
<td>a</td>
<td>2n-7a</td>
<td>1.786</td>
</tr>
</tbody>
</table>

a. Coupling constant distorted by signal overlap.

Table 9  Coupling Constants for H$_2$n of Deuterium Labeled exo-2-norbornyl Iodide Produced by BI$_3$ Promoted Reaction.

<table>
<thead>
<tr>
<th>J</th>
<th>Hz</th>
<th>J</th>
<th>Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>2n-3n</td>
<td>8.04</td>
<td>2n-7a</td>
<td>1.786</td>
</tr>
</tbody>
</table>

The other coupling constants can not be measured.
Fig. 21 Signal at δ 3.99 (H2n) in NMR Spectrum for Deuterium-Labeled exo-2-Norbornyl Iodide Produced by the Bi3 Promoted Reaction.

The complete 1H NMR (CDCl3) shows: δ 0.8-2.6 (m, 9H), δ 3.99 (m, C-2 endo-methine). δ 4.30 (10% C-2 exo-methine). The coupling constants for H2n are listed in Table 9.

2) Spectrum of Bromide (The complete spectrum of the bromide is in the appendix):

<table>
<thead>
<tr>
<th>J</th>
<th>Hz</th>
<th>J</th>
<th>Hz</th>
<th>J</th>
<th>Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>2n-3n</td>
<td>7.14</td>
<td>2n-3x</td>
<td>6.25</td>
<td>2n-7a</td>
<td>1.786</td>
</tr>
</tbody>
</table>
The complete $^1$H NMR (CDCl$_3$) spectrum shows: $\delta$ 0.8-2.5 (m, 10H), $\delta$ 3.95 (m, C-2 endo-methylene 1H). No evidence (exo proton) for the endo product was obtained. The coupling constants for H$_{2n}$ are listed in Table 10.

Fig. 22 Signal at $\delta$ 3.95 for Proton (H$_{2n}$) on Carbon Bearing Br in the Unlabeled Structure.
(Authentic Unlabeled exo-2-norbornyl Bromide from "HBr" Addition to Norbornene)

Fig. 23 Signal at $\delta$ 3.95, for Proton (H$_{2n}$) on Carbon Bearing Br in the Unlabeled Structure.
(Unlabeled exo-2-norbornyl Bromide Produced by BBr$_3$ Promoted Reaction).
Table 11  Coupling Constants for H₂n of Unlabeled exo-2-norbornyl Bromide from Lewis Acid Catalyzed Reaction.

<table>
<thead>
<tr>
<th>J</th>
<th>Hz</th>
<th>J</th>
<th>Hz</th>
<th>J</th>
<th>Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>2n-3n</td>
<td>7.14</td>
<td>2n-3x</td>
<td>6.25</td>
<td>2n-7a</td>
<td>1.786</td>
</tr>
</tbody>
</table>

¹H NMR (CDCl₃): δ 0.8-2.5 (m, 10H), δ 3.95 (m, C-2 endo-methine 1H). There was no evidence (no exo C-2 proton) for endo halide. The coupling constants for H₂n are listed in Table 11.

The signal at δ=3.95 (Fig.22, 23) was caused by the coupling suggested by Fig.24. The protons of the proton NMR spectra of exo-2-norbornyl bromide corresponding to the proton on the carbon bearing bromide give rise to a crude "triplet"(Fig.23).

![Diagram of the Splitting Pattern of Proton α to Bromide in Unlabeled exo-2-Norbornyl Bromide.]

Fig.24 The Splitting Pattern of Proton α to Bromide in Unlabeled exo-2-Norbornyl Bromide.

When deuterium to exo-2-norbornyl bromide by DBr addition, the signal at δ 3.95 of (proton H₂n on carbon bearing Br) in ¹H NMR spectrum is as shown in Fig.25:
Fig. 25 Signal at δ 3.95 Proton (H$_2n$) on Carbon Bearing Br in Labeled Structure. (Authentic Labeled exo-2-norbornyl Bromide from "DBr" Addition to Norbornene)

The complete $^1$H NMR (CDCl$_3$) spectrum shows: δ 0.6-2.5 (m, 9H), δ 3.95 (m, C-2 endo-methine 1H). There is no evidence for an exo proton at C-2 (and thus no evidence for endo product). The coupling constants for H$_2n$ are listed in Table 12.

**Table 12** Coupling Constants for H$_2n$ of Authentic Labeled exo-2-norbornyl Bromide from "DBr" Addition to Norbornene.

<table>
<thead>
<tr>
<th>J</th>
<th>Hz</th>
<th>J</th>
<th>Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>2n-3n</td>
<td>87.14</td>
<td>2n-7a</td>
<td>0.893</td>
</tr>
</tbody>
</table>

**Table 13** Coupling Constants for H$_2n$ of Labeled exo-2-norbornyl Bromide from Lewis Acid Catalyzed Reaction

<table>
<thead>
<tr>
<th>J</th>
<th>Hz</th>
<th>J</th>
<th>Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>2n-3n</td>
<td>7.14</td>
<td>2n-7a</td>
<td>0.893</td>
</tr>
</tbody>
</table>

The other coupling constants cannot be measured in this spectrum due to overlapping signals.
Fig. 26 Signal at δ 3.95, for Proton (H₂n) on Carbon Bearing Br in Labeled Structure.
(Labeled exo-2-norbomyl Bromide from the Lewis Acid Catalyzed Reaction).

The complete ¹H NMR (CDCl₃) spectrum shows: δ 0.6-2.5 (m, 9H), δ 3.90 (m, C-2 exo-methine), δ 4.28 (s, C-2 endo-methine). The endo/exo ratio is 9.2%. The coupling constants for H₂n are listed in Table 13.

The splitting pattern for Fig. 26 is interpreted in Fig. 27:

Fig. 27 The Splitting Pattern of Proton α to the Bromide in NMR Spectrum which two Splitting Patterns were Superimposed.
Wagner-Meerwein rearrangement may very well lead to \( \text{exo-cis}-3\text{-d}-2\text{-exo-norbornyl} \) bromide and \( \text{syn}-7\text{-d}-2\text{-exo-norbornyl} \) bromide. The corresponding signal for the rearrangement product would have the appearance of the triplet of \( \text{syn}-7\text{-d}-2\text{-exo-norbornyl} \) bromide superimposed upon the expected doublet of \( \text{exo-cis}-3\text{-d}-2\text{-exonorbornyl} \) bromide.

3) Spectrum of the Norbornyl Chlorides (The Complete Spectrum of chloride are in appendix):

![Figure 28](image-url)

Fig.28 Signal at \( \delta 3.85 \), Proton \( H_{2n} \) on Carbon Bearing Cl in Labeled Product.

(Authentic Labeled \( \text{exo-2-Norbornyl} \) Chloride from "DCI" Addition to Norbornene)

<table>
<thead>
<tr>
<th>Table 14</th>
<th>Coupling Constants for ( H_{2n} ) of Authentic Labeled ( \text{exo-2-Norbornyl} ) Chloride from &quot;DCI&quot; Addition to Norbornene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( J ) ( Hz )</td>
</tr>
<tr>
<td>2n-3n</td>
<td>8.04</td>
</tr>
</tbody>
</table>

The complete \( ^1\text{H} \) NMR (CDCl3) spectrum shows: \( \delta 0.8-2.4 \) (m, 9H), \( \delta 3.85 \) (m, C-2 \( \text{endo-methine} \)). (There is no evidence for \( \text{endo-halide} \)). The coupling constants based on the spectrum of sample are listed in Table 14.
The signal at δ=3.85 (Fig.28, 29) has a similar appearance to that of labeled bromide, the splitting pattern is a triplet. The results of proton NMR spectrum of exo-3-d-exo-2-norbornyl chloride is also close to the products of addition of deuterium chloride to norbornadiene[74].
The proton NMR spectrum of the mixture of XXXVIII and XXXIX (from the addition of deuterium chloride to norbornadiene) (at δ 3.7) is shown in Fig.30.

Fig.30 The Signal at δ 3.7, the Proton NMR Spectrum of the Mixture of XXXVIII and XXXIX
(The Spectra was Determined on a Perin-Elmer R-20 (60MHz) Instrument.)

Fig.31 The Signal at δ 3.7, the NMR Spectrum of Unlabeled XL[78]
(The Spectra was Determined on a Perin-Elmer R-20 (60MHz) Instrument.)
The NMR spectrum of the mixture of XXXVIII and XXXIX would be expected to be identical (at δ 3.7) with that of unlabeled XL and IV. The corresponding signal for XXXVIII would be expected to possess a substantially "doublet appearance." The proton signal of the NMR spectra of XL (from the addition of hydrogen chloride to norbornadiene) corresponding to the proton on the carbon bearing chloride is shown in Fig.31. This signal, despite its "triplet appearance" in deuteriochloroform, reveals its multiplicity when examined in a variety of solvents\textsuperscript{74}. and the triplet appearance in some cases is thus a "deceptively simple signal"\textsuperscript{71-74,75}. Coupling constants that are pertinent to this signal are listed in Table 16.

<table>
<thead>
<tr>
<th>( J^b )</th>
<th>Hz</th>
<th>( J^b )</th>
<th>Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>2n-3n</td>
<td>5.4</td>
<td>2n-7a</td>
<td>1.6</td>
</tr>
<tr>
<td>2n-3x</td>
<td>4.2</td>
<td>2n-1</td>
<td>1.0</td>
</tr>
</tbody>
</table>

\( a \) These are in agreement with those previously reported in CCl₄.
\( b \) N = endo, X = exo, A = anti, S = syn.

2.4.2 Mass Spectral Analysis

We can calculate the percentage of D incorporated in the norbornylhalide from the GC/MS spectra as described below. The Table 7 lists %D incorporated in norbornyl halide for all labeled products.
Table 17  Total % deuterium incorporated in norbornylhalide

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>%D in the structure of norbornyl halide</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₃B(D) + I₂ + Bi₃</td>
<td>![Image]</td>
<td>100%</td>
</tr>
<tr>
<td>norbornene + &quot;DI&quot;</td>
<td>![Image]</td>
<td>78.13%</td>
</tr>
<tr>
<td>R₃B(D) + Br₂ + BBr₃</td>
<td>![Image]</td>
<td>100%</td>
</tr>
<tr>
<td>norbornene + &quot;DBr&quot;</td>
<td>![Image]</td>
<td>80.95%</td>
</tr>
<tr>
<td>R₃B(D) + Cl₂ + BCl₃</td>
<td>![Image]</td>
<td>77.42%</td>
</tr>
<tr>
<td>norbornene + &quot;DCl&quot;</td>
<td>![Image]</td>
<td>83.33%</td>
</tr>
</tbody>
</table>

The calculation method is shown as Fig.32. Because the molecular ion peak of halides were too small to be measured accurately, m/z 96 and m/z 95 which are the M-X fragments were used in calculations. If no m/z 95 fragment was observed, we assume that %D incorporation was 100%.

\[
C₇H₁₁⁺  \quad \text{m/e 95} \quad \text{C}_7\text{H}_{10}\text{D}⁺  \quad \text{m/e 96}
\]

\[
\begin{align*}
D\% &= \frac{a}{a+b} \times 100\% \\
\end{align*}
\]

Fig.32 The calculation of D% incorporated in norbornyl halide.
Table 18  Principle Peak in Mass Spectrum of Labeled exo-2-Norbornyl Iodide

<table>
<thead>
<tr>
<th>m/z</th>
<th>39</th>
<th>40</th>
<th>67</th>
<th>68</th>
<th>96</th>
<th>127b</th>
<th>223b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak abundance</td>
<td>24</td>
<td>14</td>
<td>28</td>
<td>36</td>
<td>100</td>
<td>10</td>
<td>2</td>
</tr>
</tbody>
</table>

a. The sample came from the procedure involving Lewis acid catalysis.
b. m/z 127 is I⁺; m/z 223 is the molecular ion.

Table 19  Principle Peak in Mass Spectrum of Labeled exo-2-Norbornyl Bromide

<table>
<thead>
<tr>
<th>m/z</th>
<th>39</th>
<th>40</th>
<th>67</th>
<th>68</th>
<th>96</th>
<th>175b</th>
<th>177b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak abundance</td>
<td>28</td>
<td>16</td>
<td>26</td>
<td>32</td>
<td>100</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

a. m/z 177 is the isotopic peak of m/z 175. b. The sample came from the procedure involving Lewis acid catalysis.

If we examine the GC/MS spectra of the bromide and the iodide carefully (the MS spectra are in the appendix), it can be found that these two spectra have a similar fragmentation characteristic. They all have the strongest peak at m/z 96, but their m/z 69 peaks are small. The fragment at m/z 96 is due to the precursor less the halide atom. This can be explained by that fact that I and Br have weaker bonds to carbon than does Cl, and it is thus easier for them to lose halogen. Therefore, the m/z 96 peak is the molecular ion peak. The fragmentation mechanism of them are shown as in Scheme 14:
And

Scheme 14. Fragmentation Mechanism for Labeled exo-2-Norbomyl Iodide and Bromide.

Because the product structure molecule is the product of Wagner-Meerwein rearrangement which contains exo-cis-3-d-2-exo-norbomyl halide (Br, I) and syn-7-d-2-exo-norbomyl halide (Br, I) with a ratio of about 1:1, the fragmentation route will result in different m/z 96 structures, and the rest of smaller fragments arise from the m/z 96 fragment [The product molecular ion of exo-cis-3-d-2-exo-norbomyl halide (Br, I) produced m/z: 96, 68, 67, 40, 39 etc; and the product molecular ion of syn-7-d-2-exo-norbomyl halide (Br, I) produced m/z 96, 68, 40 etc.].
Table 20  Principle Peak in the Mass Spectrum of Labeled *exo*-2-Norbornyl Chloride$^a$

<table>
<thead>
<tr>
<th>m/z:</th>
<th>39</th>
<th>40</th>
<th>67</th>
<th>68</th>
<th>69</th>
<th>96</th>
<th>131</th>
<th>133$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak abundance:</td>
<td>38</td>
<td>20</td>
<td>60</td>
<td>100</td>
<td>54</td>
<td>20</td>
<td>12</td>
<td>4</td>
</tr>
</tbody>
</table>

a. This sample came from Lewis acid catalytic procedure. b. m/z 133 is the $^{37}$Cl peak corresponding to m/z 131.

And

Scheme 15  Fragmentation Mechanism of Deuterium Labeled *exo*-2-Norbornyl Chloride.

By interpreting the GC-MS results, we conclude that norbornyl chloride rearranges as shown in Scheme 15. The two rearrangement products each result in resonance forms of
the molecular ion (m/z 131) which are the sources of the fragments of m/z 67, 68, and 69. There is no chance for the molecular ions from the bromide and iodide in like fashion to form the resonance forms as does the chloride before Br and I leave from their precursor molecule, so the parent peaks of bromide and iodide are at m/z 96. Here the norbornyl chloride gives rise to a larger m/z 68 peak than do the bromide or iodide, because the molecular ion of chloride has the resonance form in which the Cl atom is relatively more stable in the structure than Br or I, the fragment m/z 68 not only comes from the fragment of m/z 96, but m/z 131 (the resonance form of the molecular ion of chloride). If m/z 68 comes only from the fragmentation of m/z 96, the m/z 96 peak would probably be stronger. (the mass spectra are in the appendix)

The unlabeled exo-2-norbornyl bromide and iodide have similar fragmentation patterns to their labeled structure; the parent peak is m/z 95 and that is caused by the lose of I or Br, and the all other fragments result from the further fragmentation of m/z 95. The main peaks of iodide and bromide in GC/MS are listed in Tables 21 and 22, respectively, and the fragmentations are shown in Schemes 16 and 17.

Table 21 Principle Peaks in the Mass Spectrum of Unlabeled exo-2-Norbornyl Iodide

<table>
<thead>
<tr>
<th>m/z:</th>
<th>39</th>
<th>41</th>
<th>67</th>
<th>95</th>
<th>127(^b)</th>
<th>222(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak abundance:</td>
<td>28</td>
<td>24</td>
<td>54</td>
<td>100</td>
<td>10</td>
<td>2</td>
</tr>
</tbody>
</table>

a. The sample came from the Lewis acid procedure. b. m/z 127 is I\(^+\), m/z 222 is molecular ion of iodide.

Scheme 16 Fragmentation Mechanism of Unlabeled exo-2-Norbornyl Iodide.
Table 22   Principle Peaks in the Mass Spectrum of Unlabeled exo-2-Norbornyl Bromide

<table>
<thead>
<tr>
<th>m/z:</th>
<th>39</th>
<th>41</th>
<th>67</th>
<th>79&lt;sup&gt;b&lt;/sup&gt;</th>
<th>95</th>
<th>174&lt;sup&gt;b&lt;/sup&gt;</th>
<th>176</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak abundance:</td>
<td>34</td>
<td>20</td>
<td>40</td>
<td>6</td>
<td>100</td>
<td>1.2</td>
<td>1.2</td>
</tr>
</tbody>
</table>

a. The sample came from the Lewis acid procedure. b. m/z 79 is Br<sup>+</sup>, m/z 174 is the molecular ion of bromide.

![Scheme 17](image)

Scheme 17   Fragmentation Mechanism of Unlabeled exo-2-Norbornyl Bromide.

2.4.3 IR Spectral Analysis

The IR spectra of iodide, bromide and chloride can be compared with the data in the literatures<sup>40, 46, 76, 77, 78</sup> and the spectra are in the appendix. The iodide, bromide and chloride have similar IR spectra. The weak peak at 2190 cm<sup>-1</sup> corresponds to deuterium-carbon stretching.
3. CONCLUSIONS

Undoubtedly the reactions of iodine, bromine, and chlorine with labeled trinorbornylboranes using the corresponding Lewis acid catalyst involves Wagner-Meerwein rearrangement, and norbornyl halide products are formed in yields of 31-61%. The rearrangement is due to a carbocation intermediate, possibly a nonclassical ion, even when the reaction is carried out in CH₂Cl₂ under mild reaction conditions. The halogenation process is likely ionic and it occurs readily to produce \textit{exo-cis}-3-deuterio-2-exo-norbornyl halide and \textit{syn}-7-deuterio-2-exo-norbornyl halide in a ratio of about 1:1. It is reasonable to assume that the boron trihalides (BI₃, BBr₃, BCl₃) are the scrambling agents since they are known to produce carbocations from alkyl halides. Therefore, the Wagner-Meerwein rearrangement happens after initial product formation. Reliable evidence for this ionic mechanism is based on \textsuperscript{1}H NMR, IR and GC-MS. The spectra of iodide, bromide and chloride that came from the BX₃ procedure are nearly the same as the spectra of iodide, bromide and chloride that came from the net addition of deuterium halide to norbornene; thus we can draw the conclusion that both procedures involve similar rearrangements.

Chlorotrimethylsilane/sodium halide in the presence of water has been found to be facile method for the hydrohalogenation of norbornene to form norbornyl halides in good yield under mild conditions. This literature procedure has successfully been extended to the preparation of deuterated norbornyl halides by using deuterium oxide in place of water. The present method offers a novel synthesis of deuterated compounds from norbornene by using D₂O, an inexpensive and easy-to-handle material, as the deuterium source.

Experiments have proved that the transmercuration reaction of tri-norbornyl borane is very sensitive to the steric hindrance about the boron atom. The norbornyl group is not transferred readily from boron to mercury even in the presence of Lewis acid catalysts.

The use of methanolic sodium methoxide in the iodination of \textit{triexo}-norbornyl borane provides norbornyl iodide in considerably higher yields. The iodination in the presence of a base-induced iodination of organoboranes proceeds largely with inversion of configuration at the boron-carbon reaction center, resulting in formation of \textit{endo}-2-iodonorbornane from \textit{tri-exo}-norbornylborane.
4. EXPERIMENTAL

General

The techniques used in handing air-sensitive materials are described elsewhere. All glassware was oven-dried at 140° for at least four hours before use, assembled hot, and cooled under a stream of dry prepurified nitrogen. Air- and moisture-sensitive materials were transferred using oven-dried, nitrogen-flushed hypodermic syringes fitted with stainless steel needles.

Reagent Sources

The reagents used in the research were purchased from Aldrich Chemical Company, Inc., Fisher Scientific Co. J.T. Baker Chemical Co. Boron-d₃:THF complexes in THF solution and boron triiodide were purchased from Cambridge Isotope Laboratory, Inc. and PNB-Pfaltz & Bauer, Inc., respectively.

All products were purified by column chromatography on silica gel (70-230 mesh, 60Å) by eluting successively with hexane. The purity reported were based on the data from GC and GC/MS spectra. The yields were calculated as follows:

\[
\% \text{Yield} = \frac{\text{Weight Purified sample (g)}}{\text{Theoretical weight (g)}} \times 100\%
\]

Analysis Methods

¹H NMR spectra have been recorded on Bruker-NMR SY-200 spectrometer operating at proton frequency of 200 MHz. Tetramethylsilane (TMS) was used as an internal standard (δ=0.00 ppm), and all chemical shifts were recorded in δ (ppm) relative to TMS. Deuteriochloroform (CDCl₃) was used as a solvent. Multiplicity notations are: s, singlet; d, doublet; t, triplet; m, multiplet. The exo:endo isomer ratios of 2-halonorbornane were determined by integration of the C-2 methine protons at δ 3.85-3.99 (endo proton of exo-2-halonorbornane) and δ 4.20-4.22 (exo proton of endo-2-halonorbornane).
GC/MS spectra were obtained on a Hewlett-Packard GC/MS-MSD HP5995 spectrometer at a of capillary column and oven temperature 150° C.

Infrared spectra were obtained on a Perkin-Elmer 1310 spectrophotometer between 4000-600 cm⁻¹. Liquid samples were analyzed as thin film between sodium chloride plates or in sodium chloride liquid cells without using any solvent.

GC spectra were obtained on a Hewlett-Packard HP-GC 5890, Series II instrument. The temperature of capillary column and oven were 150° C.

TLC was completed on silica gel plate using hexane as a solvent. Rf is 0.90; 0.90; 0.85 for exo-iodide; bromide and chloride, respectively.

4.1 Drying and Purification of Tetrahydrofuran (THF)

A 1-l single neck round bottom flask, fitted with a magnetic stirring bar, and a reflux condenser (with drying tube on the top of condenser), was charged with 800 ml of THF and 4 g of lithium aluminum hydride (LAH). A sufficient amount of LAH has been added when a 1-ml aliquot of the solvent shows vigorous hydrogen evolution on hydrolysis with a drop of water. The flask is heated to reflux with heating mantle for 30 min.. The THF is then distilled under the atmospheric pressure and the THF was collected (bp 65-67° C). This THF is kept dry by storing under nitrogen over calcium hydride or 4 Å molecular sieves.

Notes
1. CAUTION: Solutions of LAH in oxygen-containing solvents may decompose explosively at elevated temperature (160° C). Therefore the distillation should never be carried out to dryness, and materials boiling above 100° C should be distilled under reduced pressure.

2. Addition of LAH to THF leads to bubbling even when the THF is dry. Therefore, the best way to test for active hydride is to hydrolyze an aliquot. No more than 1% by weight of LAH should ever be required using this method.

4.2 Purification of Boron Trifluoride Diethyl Etherate
Commercial BF$_3$:Et$_2$O is suitable for most purpose (see Note 1 below). The material may be purified by distillation under an inert atmosphere. Approximately 500 ml of commercial BF$_3$:Et$_2$O, 2 g of CaH$_2$ (Note 1), and 10 ml of Et$_2$O are added to a 1-l flask. The mixture is distilled under vacuum. A moderate forerun (30 ml) is taken, and then pure BF$_3$:Et$_2$O is distilled (60$^\circ$ and 20 mm, Note 2).

Notes
1. Commercial BF$_3$:Et$_2$O may contain acidic impurities, such as arsenic and phosphorus compounds, which are reduced to foul smelling hydrides, PH$_3$ and AsH$_3$, during the preparation of BH$_3$ from undistilled BF$_3$:Et$_2$O. Calcium hydride serves to remove certain of these impurities and it also reduces bumping during the distillation.

2. BF$_3$:Et$_2$O may yellow or darken on standing and should be protected from moisture air and light.

4.3 Purification of Norbornene

Norbornene must be dry and peroxide-free for successful use in the hydroboration reaction. Norbornene may be purified by distillation under nitrogen from small amount of fresh lithium aluminium hydride (LAH). LAH simultaneously removes water and peroxides. If the olefin requires a large amount of LAH for purification, the material should be filtered prior to distillation to lessen the possibility of an exothermic polymerization reaction catalyzed by aluminum salts. If the olefin is suspected of containing large amounts of peroxide, it should be tested for this and the peroxide removed by standard chemical means\cite{79} prior to distillation with LAH. Norbornene is distillated from LAH under reduced pressure (Note) at a b.p. of 96$^\circ$ C. Since vacuum distillation of norbornene from active hydride is often plagued by foaming, a splash guard or a long Vigreaux column should be employed.

Note: The distillation is never allowed to go to dryness!

4.4 Preparation of Fieser's Solution (for Absorption of Oxygen)\cite{80}
The solution is prepared by dissolving 20 g of potassium hydroxide in 100 ml of water in a 150-ml Erlenmeyer flask and adding 2 g of sodium anthraquinone-β-sulfonate and 15 g of sodium hydrosulfite (Na₂S₂O₄) in the warm solution. The mixture is stirred until a clear, blood-red solution is obtained and this is cooled to room temperature. The traces of oxygen in tank nitrogen are removed by passage through this solution. The sulfonated anthrahydroquinone dianion absorbs oxygen with great speed and is continually regenerated by the hydrosulfite. When the color of solution changes to dull red or brown or when a precipitate appears, the solution should be changed. This quantity of solution can absorb about 788 ml of oxygen.

Dry, deoxygenated nitrogen is prepared by bubbling commercial nitrogen through a series of traps: The first contains Fieser's solution for the absorption of oxygen; The second is empty to prevent crossover. The third and fourth traps contain respectively, concentrated sulfuric acid and sodium hydroxide pellets; These last two traps are for the removal of water vapor and sulfuric acid.

4.5 Preparation of tri-exo-3-Deutero-2-Norbornylborane

\[
3 \begin{array}{c}
\text{BD}_3:\text{THF}
\end{array} \xrightarrow{\text{THF} \ 0-5^\circ C} \begin{array}{c}
\text{BD}_3\text{B}
\end{array}
\]

A 250-ml three-necked, round-bottled flask equipped with a reflux condenser, thermometer, magnetic stirring bar, and pressure-equalizing dropping funnel is assembled as in Fig.33. The apparatus is flamed with a Bunsen burner while flushing the system with dry nitrogen (Note 1). The nitrogen stream is introduced through a septum inlet on the dropping funnel using a hypodermic needle which was connected into a nitrogen line. The nitrogen is vented through a mercury or mineral oil bubbler connected to the outlet of the condenser. After cooling to room temperature under a positive nitrogen pressure, the reaction flask is charged with 5.0 g (53.1 mmol) of norbornene by removing the condenser and adding the solid norbornene as quickly as possible under a blanket of nitrogen. The system is then flushed with nitrogen for 1 minute. Tetrahydrofuran, 10 ml, is added via a dry syringe, and the clear, colorless solution is cooled to 5-10°C with stirring in an ice-water bath. The borane-d₃: tetrahydrofuran (BD₃:THF) complex (19.47 ml of a 1.0 M THF solution, 0.0177 moles plus 10% excess) is added to the calibrated dropping funnel via a double-ended needle. Hydroboration is achieved by the slow, dropwise addition of the BD₃:THF solution to the norbornene-THF solution (Note 2). Following the addition, the clear, colorless reaction mixture is stirred at room temperature for 1.0 hour to complete the reaction. Excess hydride is destroyed by the careful addition of 5 drops of water (Note 3). After hydrogen is no longer evolved (in approximately 10 minutes), THF is removed on a rotatory evaporator to give white wax-like solid product. The crude yield is about 100% by weight. this product is used at once for next step reaction.(Note 4)

Notes
1. Alternatively, the apparatus may be dried in an oven at 125°C, assembled hot, and then flushed with nitrogen.

2. The hydroboration reaction is exothermic, proceeding readily to the trialkylborane stage.

3. The addition of water should be controlled so as to avoid a rapid evolution of hydrogen. The hydrogen evolved, approximately 0.133 l, should be safely vented in a hood.

4. The trialkylborane is easily oxidized, so it can not be stored for a long time.
Figure 33  Fundamental Reaction Setup Used for Hydroboration and Halogenation Reactions with Common Glassware.
4.6 Preparation of *tri-exo*-Norbornylborane (Method I)

\[
\begin{align*}
3 \text{norbornene} &+ \text{BH}_3:\text{THF} \xrightarrow{\text{THF}, 0-5^\circ\text{C}} \text{tri-exo-Norbornylborane}
\end{align*}
\]

A 250-ml flask and accessories were assembled as described in section 4.5. The flask was flushed with nitrogen and maintained under a static pressure of nitrogen. The flask was charged with 10 g (106.2 mmole) of norbornene and 50 ml of dry THF and cooled to 0°C. Hydroboration was achieved by the dropwise addition of 38.8 ml of a 1.00 M solution of borane (38.8 mmole BH₃) in tetrahydrofuran at 0°C, followed by stirring at room temperature for 1 hour. Excess hydride was destroyed by addition of several drops of water until hydrogen was no longer produced. Solvent was removed with a rotatory evaporator. The crude yield was about 100% by weight. The product was used immediately for next step reaction.

4.7 Preparation of *tri-exo*-Norbornylborane (Method II)[81]

\[
\begin{align*}
4 \text{Et}_2\text{O}:\text{BF}_3 + 3 \text{LiAlH}_4 + 12 \text{norbornene} &\xrightarrow{\text{THF}, 0^\circ\text{C}} 3 \text{tri-exo-Norbornylborane} + 3 \text{LiAlF}_4 + 4 \text{Et}_2\text{O}
\end{align*}
\]

The apparatus was assembled as in Figure 34. The entire system was flushed with dry, deoxygenated nitrogen. In the first flask were placed 100 ml of dry THF and 6 g of lithium aluminium hydride. The dropping funnel was charged with 36 ml of freshly distilled boron trifluoride etherate. The second flask was charged with 300 ml of dry THF and 108 g (1.147 moles) of bicyclo[2.2.1]hept-2-ene (norbornene). The nitrogen flow was continued during the addition of reagents to the various flasks. The boron trifluoride etherate was added dropwise to LAH-THF mixture with stirring, the borane produced was blown by the nitrogen into the stirred norbornene-THF solution. When addition of the boron trifluoride etherate solution was finished, the first flask was heated to dryness or white fumes were evolved, whereupon heating was stopped. The second flask was then heated to reflux for 1.0 hour. Excess BH₃:THF was destroyed by adding a few drops of water. The reaction mixture was transferred to a dry 500 ml distilling flask that had been flushed with nitrogen. THF was removed. The *tri-exo*-norbornylborane was distilled under a reduced pressure and protection of nitrogen (Figure 35). The product has a white wax appearance. The yield based on norbornene is about 59-79%.
Figure 34. The reaction apparatus for Preparing Tri-norbornylborane.
Figure 35  Basic Distillation Apparatus for Air-Sensitive Materials.
(tri-Norbomylborane)
4.8 Preparation of Authentic Deuterio-2-exo-norbornyl Iodide by Deuteriodination of Norbornene

\[
\text{norbornene} + (\text{CH}_3)_2\text{SiCl} + \text{NaI} + 0.5 \text{D}_2\text{O} \xrightarrow{\text{CH}_3\text{CN}} \text{D-norbornyl} + \text{NaCl} + 0.5 [(\text{CH}_3)_3\text{Si}]_2\text{O}
\]

This procedure and the procedures of those similar reactions below are a modified form of the one reported by S. Irifune et al.\cite{76}

A 250-ml three-necked, round-bottomed flask equipped with a reflux condenser, thermometer, magnetic stirring bar, and pressure-equalizing dropping funnel was assembled. The apparatus was flamed with a burner while flushing the system with dry nitrogen. The reaction was carried out in a steam of nitrogen. To a well stirred solution of dry NaI (36 g, 0.24 mol) in dry CH$_3$CN (150 ml) was slowly added ClSi(CH$_3$)$_3$ (30 ml, 0.24mol) and then D$_2$O (2.4 g, 0.12mol), with continuous good stirring. To the mixture was added norbornene (18.8 g., 0.20 mol) at one time, and the mixture was allowed to react at room temperature for 3 h. The reaction was quenched with water (200 ml) and extracted with ether (150 ml) and dried (MgSO$_4$). After evaporation of ether, the product was subjected to column chromatography on silica gel by eluting with hexane. 43.5 g of purified colorless product was obtained. The yield was 98\% (theory: 44.5 g). The product were identified by NMR, GC-MS and IR. (See Table 4)

4.9 Attempted Preparation of 3-exo-Deuterium-2-exo-Norbornyl Iodide Via Direct Iodination of tri-exo-3-Deuterio-2-Norbornyl Borane Using BI$_3$ Catalysis

\[
\text{norbornyl} + 3\text{I}_2 + 0.05 \text{BI}_3 \xrightarrow{\text{CH}_2\text{Cl}_2, \text{O}^\circ-\text{r.t., 2 days}} 3 \text{D-norbornyl} + \text{BI}_3
\]

A 250-ml flask was assembled with a magnetic stirring bar, an inlet with a rubber septum, a condenser with a calcium chloride drying tube, a funnel, a thermometer and a mercury bubbler. The apparatus was dried and flushed with nitrogen, and a nitrogen atmosphere maintained throughout the iodination stage. The flask was charged with 5.289 g (17.7
mmol) of tri-norbornylborane in 100 ml of methylene chloride. The colorless solution was cooled to 0° C in a water-ice bath, and 13.38 g (52.72 mmol) of iodine was added to the solution all at once through the thermometer inlet under a blanket of nitrogen, and 0.345 g. (0.879 mmol) of BI₃ was followed to add to the solution in a same way. The dark purple solution was stirred at 0° C until the ice melts, then the solution was allowed to warm to the room temperature (the total reaction time lasted 48 h). The reaction mixture was quenched and extracted with methylene chloride (3x50 ml) and the organic layers were washed with 10% Na₂S₂O₃ solution, water and dried over anhydrous magnesium sulfate. Evaporation of the methylene chloride gave a 10.3 g of brown oil product. The norbornyl iodide product was further purified by column chromatography on silica gel by eluting with hexane. The pure product was obtained in 33% yield (3.95 g), the purity is 98.53%. Analysis by TLC showed one spot on the plate. Rf = 0.90. Analyzes by ¹H NMR, GC, GC-MS, and IR were obtained. GC indicated that the purity is above 95%. See Table 1.

4.10 Preparation of Authentic exo-2-Norbornyl Iodide By Hydroiodination of Norbornene

\[
\begin{align*}
&\text{(CH₃)₃SiCl/NaI/H₂O} \\
\text{CH₃CN, r.t., 0.5h.} \\
&\text{I}
\end{align*}
\]

The reaction apparatus was assembled as described above in Section 4.8. The reaction was carried out in a steam of nitrogen. To an efficiently stirred solution of NaI (36 g, 0.24 mol) in MeCN (150 ml) was slowly added ClSiMe₃ (30 ml, 0.24 mol), water (2.16 g, 0.12 mol) and then norbornene (18.8 g, 0.20 mol). The mixture was allowed to react at room temperature for 1 h. The reaction was quenched with water (100 ml) and the product was extracted with ether (3x50 ml). The ether layer was washed with 10% Na₂S₂O₃ solution (200 ml) and dried (MgSO₄). Evaporation of the ether gave 49.85 g of almost pure exo-norbornyl iodide. exo-Norbornyl iodide was further purified by column chromatography on silica gel with hexane (column size: 1.5 x 24 in, DxL; and 6 g of sample), whereupon 43.1 g of colorless oil was obtained in 97.25% yield. TLC showed one spot at Rf = 0.90. GC indicates 99.94% purity. IR, ¹H NMR, GC-MS, and GC analyzes were all obtained. (See Table 5)

4.11 Preparation of exo-2-Norbornyl Iodide by Direct Iodination of tri-exo-Norbornylborane Using BI₃ Catalysis
The oven-dried apparatus consists of a 250-ml three-neck flask fitted with a septum inlet, magnetic stirring bar, reflux condenser, and mercury bubbler. The flask is flushed with nitrogen and maintained under a static pressure of the gas during the following reaction.

The tri-exo-norbornylborane (10.4 g, 35.16 mmol) was prepared exactly as described above (See Section 4.6). After hydroboration was completed, 5 drops of water was added to destroy residual traces of hydride. While flushing the reaction apparatus with nitrogen, the connecting tube was temporarily removed and 100 ml of methylene chloride and 10.4 g of tri-exo-norbornylborane were added and the flask was immersed in an ice-water bath. When the temperature of solution reach to 0°C, 26.76 g (105.44 mmol) of iodine was added all at once with good stirring, and this was quickly followed by addition of 0.689 g (1.758 mmol) of BI₃. The reaction mixture was allowed to react at 0°C for 2h., then the solution was warmed to room temperature and stirred 2 days. This solution was washed with 10% Na₂S₂O₃ (Note) and water. The CH₂Cl₂ layer was dried over anhydrous MgSO₄. When the drying agent was filtered off and solvent removed, a yield of 14.5 g of the brown oil crude product was obtained. After purification by column chromatography, ~7.4 g (theory:23.58 g) of colorless iodide was obtained. Thus the yield was 31.4%. TLC showed one spot on the plate (TLC solvent was hexane). GC indicated the purity is 86.36%. (See Table 1) The spectra are in the appendix.

Note: Na₂S₂O₃ was used to reduced the unreacted I₂ to I⁻ anion, it thus causes the solution to turn from a purple color to colorless.

**4.12 Preparation of Authentic Deuterio-2-exo-Norbornyl Bromide by Deuteriobromination of Norbornene**

\[
\text{CH}_3\text{CN} + (\text{CH}_3)_3\text{SiCl} + \text{KBr} + 0.5 \text{D}_2\text{O} \xrightarrow{\text{r.t., 3h.}} \text{Br} + \text{KCl} + 0.5 [(\text{CH}_3)_3\text{Si}]_2\text{O}
\]
A dry 250-ml flask equipped with a reflux condenser protected by a drying tube, a septum inlet, thermometer, magnetic stirring bar (fitted with a Teflon collar), and mercury bubbler, was flushed with nitrogen and maintained under a static nitrogen pressure. The flask was charged with about 150 ml of dry MeCN and 4.284 g (36.0 mmol) of potassium bromide (KBr). The solution was well stirred and then, slowly 4.5 ml (36 mmol) of ClSiMe₃ and 360 mg (18 mmol) of D₂O were added with continuous stirring. To this mixture was added 2.825 g (30 mmol) of norbornene at one time, and the mixture was allowed to react at room temperature for 3 h. The reaction was quenched with water (~200 ml) and extracted with ether (3x50 ml). The organic layer was washed with 10% NaHCO₃ solution, water, and dried for 4 h (MgSO₄). After removing the ether by evaporation, 3.4 g of brown crude oil-like product was obtained. The product was purified using column chromatography on silica gel by eluting with hexane. The purified product (colorless) was 3.06 g (theory: 5.277 g), a yield of 58%. The product was characterized by ¹H NMR, GC-MS and IR. (See Table 4)

4.13 Attempted Preparation of exo-3-Deuterio-2-Norbornyl Bromide By Direct Brominolysis of tri-exo-3-Deuterio-2-Norbornylborane Using Boron Tribromide

\[
\text{\begin{array}{c}
\text{\begin{tikzpicture}
\node (D3) at (0,0) {D};
\node (B) at (0,-0.5) {B};
\node (3B) at (0,-1) {3};
\node (Br) at (0,-1.5) {Br};
\draw[->] (D3) -- (B) -- (3B) -- (Br);
\end{tikzpicture}}
\end{array}} \rightarrow 0.5 \text{BBr}_3, \text{CH}_2\text{Cl}_2 \rightarrow 3 \text{D} \text{Br} + \text{BBr}_3
\]

The apparatus was assembled as described in Section 4.14 and was dried. A nitrogen atmosphere was maintained throughout the bromination stage. The flask was charged with 5.289 g (17.7 mmol) of tri-norbomylborane in 100 ml of methylene chloride. The colorless solution was immersed in a water-ice bath until the temperature of solution reached 0°C. Then 8.5 g (53.19 mmol) of bromine was transferred into pressure-equalizing dropping funnel and added dropwise to flask. After that, 0.64 ml (1.75 mmol d=2.650, ~1.7 g) of boron tribromide was added to the flask with the aid of a double-ended needle. The solution was stirred at 0°C for two 2 h. The reaction mixture was allowed to warm to room temperature, and then this was stirred for 48 h. The reaction was quenched by adding the solution to 150 ml of water; this was extracted with methylene chloride (3x50 ml). The CH₂Cl₂ layer was washed with 10% NaHCO₃, then water, and then dried over anhydrous MgSO₄. Evaporation of the methylene chloride gave 11.5 g of crude brown oil product. Further purification by column chromatography on silica gel with hexane gave 4.31 g
(yield, 47%) of colorless organic bromide. TLC shows the product has only one spot of 0.9 Rf. The product was characterized by 1H NMR, IR and GC-MS (See Table 2).

### 4.14 Preparation of Authentic exo-2-Norbornyl Bromide by Hydrobromination of Norbornene[^82]

$$\text{norbornene} + \text{HBr(aq)} \rightarrow \text{exo-2-Norbornyl Bromide}$$

A dry 250-ml flask equipped with a septum inlet, pressure-equalizing dropping funnel, magnetic stirring bar, and mercury bubbler. This flask was flushed with nitrogen and maintained under a static pressure of nitrogen gas. The flask was charged with 25 g (265 mmol) of norbornene and 150 ml of dry tetrahydrofuran. The flask was immersed in an ice-water bath and the contents brought to 0°C. The hydrobromination of norbornene was achieved by slowly dropping 90 g (1.11 mol HBr) of 48% hydrobromic acid (a large excess). The temperature was maintained at 0°C during the addition. The clear reaction mixture was permitted to stir for 2.5 h at room temperature to complete the hydrobromination reaction. The reaction solution with a light green color was poured into 200 ml of water, and extracted with CH2Cl2 (3x70 ml). The methylene chloride layer was washed with 10% NaHCO3, and several times with water and dried (MgSO4) (drying over 4 h.). After removing the methylene chloride, 48 g of brown oil-like crude product was obtained. The product was purified on silica gel by eluting successively with hexane. The purified sample (colorless) was 34.3 g in 74% yield (theory: 46.44 g). TLC shows one spot (Rf~0.85). The product was characterized by 1H NMR, GC-MS and IR (See Table 5).

### 4.15 Preparation of exo-2-Norbornyl Bromide By Direct Brominolysis of tri-exo-2-Norbornyl Borane Using Boron Tribromide Catalysis

$$\text{tri-norbornylborane} + 3 \text{BBr}_3 \rightarrow \text{exo-2-Norbornyl Bromide}$$

A 250-ml flask with septum inlet, magnetic stirrer, pressure-equalizing dropping funnel, and mercury bubbler was charged with 35.16 mmol (10.4 g) of tri-norbornylborane, ~150 ml
of dry CH₂Cl₂, and flushed with nitrogen. Then the flask was immersed in an ice-water bath, and the solution was cooled to 0°C. To this was added 105 mmol (16.8 g) of bromine solution by the dropping funnel, in a dropwise fashion to the stirred reaction mixture. After that, 17.58 mmol (1.66 ml, ~4.40 g) of boron tribromide was transferred into flask with the aid of a double-ended needle (Note). The reaction mixture was stirred at 0°C for ~2 h. The solution was then allowed to come to room temperature and stirred another 48 h. The solution was poured into ~200 ml of water, and extracted with CH₂Cl₂ (3x50 ml). The organic layer was washed with 10% NaHCO₃, several times with water, and dried over anhydrous magnesium sulfate. This resulted in 18.1 g of brown oil crude product. The brown product was purified by column chromatography on silica gel (by eluting with hexane) resulting in ~8.0 g (42.8% yield) of pure sample (colorless). TLC shows one spot of Rf ~0.85 (See Table 2). The spectral characteristics of the product are reported in the appendix.

Note: Boron trihalide (B1₃, BBr₃, BCl₃) is a kind of air-sensitive reagent.

4.16 Preparation of Authentic Deuterio-exo-2-Norbornyl Chloride by Deuteriochlorination of Norbornene

\[
\text{Norbornene} + (\text{CH}_3)_3\text{SiCl} + 0.5 \text{D}_2\text{O} \xrightarrow{\text{NaCl, CH}_3\text{CN, r.t., 3 h. under N}_2} \text{Deuterio-exo-2-Norbornyl Chloride} + 0.5 [(\text{CH}_3)_3\text{Si}]_2\text{O}
\]

An oven-dried 250-ml three-necked flask equipped with a septum inlet, a reflux condenser protected by a calcium chloride (CaCl₂) drying tube, thermometer, magnetic stirring bar, and a static pressure of N₂ gas was maintained throughout the reaction. To a well-stirred solution of dry NaCl (14.04 g, 0.240 mol) in dry MeCN (~150 ml) was slowly added ClSiMe₃ (30 ml, 0.24 mol). Then D₂O (2.4 g, 0.12 mol) was introduced into the mixture solution at one time, and the mixture was allowed to react at room temperature for 3 h. The reaction was quenched with ~200 ml water and extracted with ether (3x50 ml). The ether layer was washed with 10% NaHCO₃ solution, water and dried (MgSO₄). After evaporation of the ether, 31 g of crude product with a yellow-green color was obtained. The product was subject to column chromatography on silica gel by eluting with hexane.
Pure product was obtained in 94.4% (24.8 g) yield. The sample was characterized by $^1$H NMR, GC-MS and IR (See Table 4).

### 4.17 Preparation of Deuterio-\textit{exo}-2-Norbornyl Chloride By Direct Chlorinolysis of tri-\textit{exo}-3-Deuterio-2-Norbornylborane Using BCl$_3$ Catalysis

A dry 250-ml flask equipped with a septum inlet, pressure-equalizing dropping funnel, magnetic stirring bar, and mercury bubble was flushed with nitrogen. The flask was charged with 5.289 g (17.7 mmol) of \textit{tri-exo}-3-deuterio-\textit{exo}-2-norbornylborane and 150 ml of CH$_2$Cl$_2$. The flask was immersed in dry ice-acteone bath for 15 min. before addition of 1.77 mmol (1.77 ml of a 1.0 M solution in CH$_2$Cl$_2$, d=1.460) of boron trichloride to this solution with the aid of the double-ended needle. Chlorine gas was then added until the rapid disappearance of the yellow-green color of this gas ceased. A small excess of chlorine was added over a short time, gas addition was stopped, and pressure was released from the flask by a hypodermic needle. The mixture solution was then stirred for 48 h. at room temperature. About 100 ml of 10% NaHCO$_3$ solution was added dropwise to this solution to neutralize the acid solution, and this was followed extraction with CH$_2$Cl$_2$; the organic layer was washed with water, and dried over anhydrous MgSO$_4$. After removing solvent, this sample was purified by column chromatography (same as above), and in this way 8.5 g of crude sample gave 4.25 g of purified product in 60.86% yield. GC indicated 74.13% purity. The product was characterized by IR, $^1$H NMR, GC-MS (See Table 3).

### 4.18 Preparation of \textit{endo}-2-Iodonorborane By Base Promoted Hydroboration-Iodination of Norbornene.

A dry 250-ml flask equipped with a septum inlet, pressure-equalizing dropping funnel, magnetic stirring bar, and mercury bubble was flushed with nitrogen. The flask was charged with 5.289 g (17.7 mmol) of \textit{tri-exo}-3-deuterio-\textit{exo}-2-norbornylborane and 150 ml of CH$_2$Cl$_2$. The flask was immersed in dry ice-acteone bath for 15 min. before addition of 1.77 mmol (1.77 ml of a 1.0 M solution in CH$_2$Cl$_2$, d=1.460) of boron trichloride to this solution with the aid of the double-ended needle. Chlorine gas was then added until the rapid disappearance of the yellow-green color of this gas ceased. A small excess of chlorine was added over a short time, gas addition was stopped, and pressure was released from the flask by a hypodermic needle. The mixture solution was then stirred for 48 h. at room temperature. About 100 ml of 10% NaHCO$_3$ solution was added dropwise to this solution to neutralize the acid solution, and this was followed extraction with CH$_2$Cl$_2$; the organic layer was washed with water, and dried over anhydrous MgSO$_4$. After removing solvent, this sample was purified by column chromatography (same as above), and in this way 8.5 g of crude sample gave 4.25 g of purified product in 60.86% yield. GC indicated 74.13% purity. The product was characterized by IR, $^1$H NMR, GC-MS (See Table 3).
A 1000-ml flask with septum inlet, magnetic stirrer, and connecting tube was charged with 300 mmol (28.2) of norbornene and flushed with nitrogen. Then 200 ml of tetrahydrofuran was added and the reaction mixture cooled to 0°C. Hydroboration was achieved by the dropwise addition of 100 mmol (41 ml of a 2.44 M solution in tetrahydrofuran) of borane. After stirring an additional hour at room temperature, 1 ml of absolute methanol was added to destroy residual trace of hydride (little hydrogen was evolved). The reaction apparatus was completely covered in aluminum foil and cooled to 0°C. Iodine (220 mmol 56g) was added all at once under a blanket of nitrogen, and 220 mmol (46.5 ml of a 4.72 M solution of methanol) of sodium methoxide was added dropwise over 10 min. with a syringe. Immediately, 100 ml of saturated aqueous sodium thiosulfate was added to decolorize excess iodine. The reaction mixture was then extracted with 3x50-ml pentane and the organic layers dried over anhydrous potassium carbonate and removed. To remove the small amount of exo-isomer, the crude product was treated as follows: The mixture of 2-iodonorbornane isomers was refluxed for 3 h. in 80% aqueous methanol (v/v) containing 5 g of potassium carbonate. (The exo-isomer was converted to 2-methoxynorbornane.) Then 100 ml of pentane was added and the organic layer removed and dried over anhydrous potassium carbonate. Evaporation of the pentane gave 40 g of crude product (brown oil). After purification by column chromatography on silica gel with hexane, 19.22 g of colorless product was obtained. The yield was 87% (based on one norbornyl group). Analysis by $^1$H NMR indicated that the crude material before methanolysis was above 80% endo-iodide. The compound shows an endo H-C-I resonance at δ4.2 (1H, multiplet, C-2 methine). The mass spectrum shows the parent ion at m/z 222. The infrared spectra is nearly identical to the exo-isomer. (The mechanism is in the results and discussion).

**4.19 Preparation of exo-2-Norbornylmercuric Acetate from Trinorbornylborane Using Boron Tribromide Catalysis**
Trinorbornylborane (10.47 g, 35.4 mmol) was dissolved in tetrahydrofuran (100 ml) and this solution added through a septum cap to a nitrogen-flushed flask fitted with an efficient stirring bar in an ice-water bath. Solid, dry mercuric acetate (33.84 g, 106.2 mmol) (Note 1) was added in one lot to the well-stirred solution, followed by addition of boron tribromide (1.77 ml of 1.0M solution in CH2Cl2, 1.77 mmol); the solution was kept for 1 day, and it was noted that crystals of Hg(OAc)2 still were visible. The reaction solution was quenched with water, and extracted with CH2Cl2. The organic layer was dried over anhydrous MgSO4, and solvent was removed by rotatory evaporator. The desired alkyl mercuric acetate was not obtained! Modifications are discussed below in Note 2.

Note:
1: The solid mercury (II) acetate may be added rapidly to the reaction through an opened entry port. Alternatively, a bent side arm can be charged with the mercury (II) acetate and rotated at the appropriate time to tip the salt into the reaction mixture.

2: This reaction was done a number of times and the results were apparently all unsuccessful. Other Lewis acid catalysts such as FeCl3, BCl3, BBr3 were used, but they also did not lead to the correct final product.

4.20 The Preparation of exo-2-Norborneol

\[
\text{3B} + 3\text{H}_2\text{O}_2 + \text{NaOH (aq.)} \xrightarrow{40^\circ\text{C}} \text{3 OH} + \text{NaB(OH)}_4
\]

The tri-exo-2-norbornylborane solution (obtained by hydroboration of 18.8 g of norbornene) was added 25 ml of 3N aqueous NaOH. 25 ml of a 30% aqueous H2O2 solution was introduced into the dropping funnel and added dropwise to the stirred reaction mixture. (The temperature did not exceed ~40°C) After completing the addition of H2O2, the reaction mixture was heated and maintained at 50°C for to in sure complete oxidation. Then, the reaction solution containing 2-phases was added ~70 ml of ethyl ester, and then was poured into a separatory funnel to extract the ether layer. The organic layer was washed with water and saturated NaCl solution, and dried over anhydrous MgSO4. After
filtered and concentrated on a rotary evaporator, 20.0 g of white solid, m.p. 124-126°C was given. The yield is above 90%. The isomeric purity is >99% exo- by ¹H NMR.
REFERENCES

36. The reaction with bromine is greatly facilitated by light.
   C. F. Lane, Ph.D. Thesis, Purdue University, (1972).
72. L. M. Jackman and S. Sternhell, Applications of Nuclear magnetic Resonance Spectroscopy in Organic chemistry.
APPENDIX

$^1$H NMR, GC/MS and IR Spectra
NMR Spectrum of Authentic Labeled exo-2-Norbornyl Iodide from "DI" Addition to Norborne
$^1$H NMR Spectrum of 2-endo proton in Authentic Labeled exo-2-Norbornyl Iodide from "DI" Addition to Norbornene (Expnsion)
NMR Spectrum of Labeled exo-2-Norbornyl Iodide
Produced by B13 promoted Reaction
\(^1\text{H NMR Spectrum of 2-endo proton in Labeled exo-2-Norbornyl Iodide Produced by BI}_3\text{ promoted Reaction (Expansion)}\)
$^1$H NMR Spectrum of 2-endo proton in Authentic Unlabeled exo-2-Norbornyl Iodide from "$^1$H" Addition to Norborne (Expansion)
NMR Spectrum of Unlabeled exo-2-Norbomyl Iodide
Produced by B\textsubscript{1}\textsubscript{3} Promoted Reaction
$^1$H NMR Spectrum of 2-endo proton in Unlabeled exo-2-Norbornyl Iodide Produced by $\text{Bl}_3$ Promoted Reaction (Expansion)
NMR Spectrum of Authentic Labeled exo-2-Norbornyl Bromide from "DBr" Addition to Norbornene
$^1$H NMR Spectrum of 2-endo Proton in Authentic Labeled exo-2-Norbornyl Bromide from "DBr" Addition to Norbornene (Expansion)
NMR Spectrum of Labeled exo-2-Norbomyl Bromide
Produced by BBr₃ Promoted Reaction
$^1$H NMR Spectrum of 2-endo Proton in Labeled exo-2-Norbornyl Bromide Produced by BBr$_3$ Promoted Reaction (Expansion)
NMR Spectrum of Authentic Unlabeled exo-2-Norbomyl Bromide from "HBr" Addition to Norbronene
$^1$H NMR Spectrum of 2-endo Proton in Authentic Unlabeled exo-2-Norbornyl Bromide from "HBr" Addition to Norbronene (Expansion)
NMR Spectrum of Unlabeled exo-2-Norbornyl Bromide
Produced by BBr$_3$ Promoted Reaction
NMR Spectrum of Authentic Labeled exo-2-Norbornyl Chloride from "DCI" Addition to Norbornene
$^1$H NMR Spectrum of 2-endo Proton in Authentic Labeled exo-2-Norbornyl Chloride from "DCI" Addition to Norbornene (Expansion)
NMR Spectrum of Labeled exo-2-Norbornyl Chloride
Produced by BCl₃ Promoted Reaction
$^1$H NMR Spectrum of 2-endo Proton in Labeled exo-2-Norbornyl Chloride Produced by BCl$_3$ Promoted Reaction (Expansion)
GC/MS Spectrum of Authentic Labeled exo-2-Norbornyl Iodide
from "DI" Addition to Norbornene
GC/MS Spectrum of Labeled exo-2-Norbornyl Iodide

Produced by BI₃ Promoted Reaction
GC/MS Spectrum of Authentic Unlabeled exo-2-Norbornyl Iodide
from "HI" Addition to Norbornene
GC/MS Spectrum of Unlabeled exo-2-Norbornyl Iodide

Produced by B13 Promoted Reaction
GC/MS Spectrum of Authentic Labeled exo-2-Norbornyl Bromide

from "DBr" Addition to Norbornene
GC/MS Spectrum of Labeled exo-2-Norbornyl Bromide

Produced by BBr3 Promoted Reaction.
GC/MS Spectrum of Authentic Unlabeled exo-2-Norbornyl Bromide
from "HBr" Addition to Norbornene
GC/MS Spectrum of Unlabeled exo-2-Norbornyl Bromide

Produced by BBr₃ Promoted Reaction
GC/MS Spectrum of Authentic Labeled exo-2-Norbornyl Chloride from "DCI" Addition to Norbornene
GC/MS Spectrum of Labeled exo-2-Norbornyl Chloride

Produced by BCl₃ Promoted Reaction
IR Spectrum of Authentic Labeled exo-2-Norbornyl Iodide
from "DI" Addition to Norbornene
IR Spectrum of Labeled exo-2-Norbornyl Iodide
Produced by BI₃ Promoted Reaction
IR Spectrum of Authentic Unlabeled exo-2-Norbornyl Iodide from "HI" Addition to Norbornene
IR Spectrum of Unlabeled exo-2-Norbornyl Iodide
Produced by BI₃ Promoted Reaction
IR Spectrum of Authentic Labeled exo-2-Norbomyl Bromide from "DBr" Addition to Norbornene
IR Spectrum of Labeled exo-2-Norbornyl Bromide
Produced by BBr₃ Promoted Reaction
IR Spectrum of Authentic Unlabeled exo-2-Norbornyl Bromide from "HBr" Addition to Norbornene
IR Spectrum of Unlabeled exo-2-Norbornyl Bromide
Produced by BBr$_3$ Promoted Reaction
IR Spectrum of Authentic Labeled exo-2-Norbornyl Chloride from "DCI" Addition to Norbornene
IR Spectrum of Labeled \textit{exo}-2-Norbornyl Chloride produced by BCl$_3$ Promoted Reaction