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AUGUST 1978

XENON DIFLUORIDE FLUORINATION. MECHANISM
AND SELECTIVITY OF BORON TRIFLUORIDE ETHERATE
CATALYSIS IN THE NORBORNENE MODEL

Capt Scott A. Shackelford
PROJECT 2303

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UNITED STATES AIR FORCE
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This technical report has been reviewed and is approved for publication.

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**ABSTRACT**

The boron trifluoride etherate initiated fluorination of norbornene with xenon difluoride in dichloromethane solvent selectively produces the novel 2-exo-5-exo-difluoronorbornane and its analogous 2-endo 5-exo-difluoronorbornane represent approximately half the directly fluorinated reaction products, and the well-known anti- and syn-2,7-difluoronorbornane isomers comprise the remainder. Subsequently the boron trifluoride etherate catalyzes selective isomerization of both 2,7-difluoronorbornanes to produce a nearly exclusive...
yield of the 2-exo-5-exo- and 2-endo-5-exo-difluoronorbornane isomers. A change to diethyl ether solvent yields the normal anti- and syn-2,7-difluoronorbornane isomers as the major difluoride products and quenches the boron trifluoride etherate isomerization. Substitution of lithium tetrafluoroborate for the boron trifluoride etherate in diethyl ether solvent again provides the unique 2,5-difluoronorbornanes as the major difluoride products. The 2,5-difluoronorbornane isomers were unambiguously identified by the direct fluorination of deuterated norbornene. The deuterated norbornene also permitted the initial fluorination mechanism and the selective isomerization pathway in dichloromethane solvent to be studied.
XENON DIFLUORIDE FLUORINATION
MECHANISM AND SELECTIVITY OF BORON TRIFLUORIDE ETHERATE CATALYSIS
IN THE NORBORNENE MODEL

By
Scott A. Shackelford

TECHNICAL REPORT FJSRL-TR-78-0008
August 1978

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Directorate of Chemical Sciences
Frank J. Seiler Research Laboratory
Air Force Systems Command
US Air Force Academy, Colorado 80840
PREFACE

This report documents work conducted under Work Unit 2303-F3-03, Chemistry of Xenon Difluoride, between 18 August 1975 and 15 January 1978. Research is continuing in the areas mentioned in this report and will be documented as additional technical reports and journal articles. Captain Robert A. Hildreth provided constructive discussions and technical assistance. Constructive discussions and support were received from Lt Colonel Ben A. Loving, Dr. Melvin L. Druelinger, and Lt Colonel Lowell A. King. Mr. J. Lloyd Pflug provided technical assistance and performed all nmr and mass spectral analyses. Mrs. B. Plonsky typed the report. Mr. Fred C. Kibler provided extensive technical assistance and necessary glassblowing support.
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XENON DIFLUORIDE FLUORINATION.
MECHANISM AND SELECTIVITY OF BORON TRIFLUORIDE ETHERATE CATALYSIS IN THE NORBORNENE MODEL

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A previously reported benchtop procedure demonstrated xenon difluoride to be a convenient direct fluorinating reagent for aliphatic alkenes. This convenient procedure employed boron trifluoride etherate to catalytically initiate direct alkene fluorination in a dichloromethane suspension. It required only such standard items as a drybox for storing and weighing the xenon difluoride and a benchtop fumehood in which to conduct the fluorinations using standard chemical glassware. When norbornene was fluorinated by this procedure, an unprecedented high yield synthesis of 2-exo-5-exo-difluoronorbornane 1 and its analogous 2-end0-5-exo-isomer 2 occurred. This result was in distinct contrast with previously reported halogen and interhalogen additions to norbornene that selectively produced the anti- and syn-2,7-dihalonorbornane isomers through an ionic mechanism, or the 2-exo-3-exo- and 2-end0-3-exo-dihalonorbornanes from a radical pathway. Two past norbornene fluorinations produced three major products common to each reaction. Fluorination with lead tetraacetate/hydrogen fluoride in a Freon 112 dichloromethane solvent, and a more recent fluorination using difluoroiodobenzenes with a dichloromethane/hydrogen fluoride solvent both afforded the ionically rearranged 2-ex0-7-anti-difluoronorbornane 3 and 2-ex0-7-syn-difluoronorbornane 4, plus nortricyclyl fluoride 11 as the major products. In both cases the syn-2,7-difluoronorbornane 4 proved to be the
predominant species. A more recent hydrogen fluoride initiated reaction between norbornene and xenon difluoride in dichloromethane solvent provided the nortricycl fluoride \( \text{11} \) as its major product. The \( 2,7-, 2,5-, \) and \( 2,3- \)-difluoronorbornane isomer sets comprised the six additional isolated products. \( \text{11} \)

The boron trifluoride ethereal catalyzed fluorination of norbornene with xenon difluoride represents the first selective synthesis of \( 2\text{-exp-5-exp-difluoronorbornane} \) \( \text{1} \) and \( 2\text{-endo-5-exp-difluoronorbornane} \) \( \text{2} \) in high yield. \( \text{3} \)

When this reaction was conducted over a 20-20 hour period, the two combined 2,5-isomers represented 93 percent or more of the difluoride products (Table I, 87-91% of the total reaction products). The \( 2\text{-exp-7-anti-difluoronorbornane} \) \( \text{3} \) is the only other difluoride detected as a minor product. \( \text{12} \)

When a portion of this same reaction is quenched after only one hour and fifteen minutes, four initial difluoride products were found (Equation 1). The \( 2\text{-difluoronorbornane} \) isomers \( \text{1} \) and \( \text{2} \) comprised slightly more than one half of the fluorinated reaction products. The \( 2,7\text{-difluoronorbornanes} \) \( \text{3} \) and \( \text{4} \), commonly the major products in nearly all other norbornene fluorinations, halogenations, and interhalogenations, were identified as the remaining two products. \( \text{13} \)

Analysis of the unquenched portion of this reaction after 20-22 hours again revealed \( \text{1} \) and \( \text{2} \) to be nearly exclusive difluoride products (Table I). This result suggested that the \( 2,7\text{-difluoronorbornane} \)

- INSERT EQUATION 1 -

isomers were selectively isomerized into additional \( 2,5\text{-difluoronorbornane} \) products during the extended 20-22 hour reaction time. This stereospecific
Table I. Difluoronorbornane Isomer Product Distribution From Boron Trifluoride Etherate Catalysis in CH₂Cl₂ Solvent.

<table>
<thead>
<tr>
<th>Run</th>
<th>Conditions</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>(Combined 98.5)</td>
<td>1.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>D</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>A</td>
<td>45</td>
<td>17</td>
<td>38</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>D</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>A</td>
<td>66.5</td>
<td>30</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>D</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>A</td>
<td>64</td>
<td>29</td>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>D</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>A (dark)</td>
<td>65</td>
<td>31</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>D</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>B&lt;sup&gt;a&lt;/sup&gt;</td>
<td>58</td>
<td>26</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>13</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>C&lt;sup&gt;b&lt;/sup&gt;</td>
<td>24.5</td>
<td>26</td>
<td>43</td>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>B&lt;sup&gt;c&lt;/sup&gt;</td>
<td>62</td>
<td>26</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>C&lt;sup&gt;d&lt;/sup&gt;</td>
<td>40</td>
<td>17</td>
<td>31</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>C&lt;sup&gt;e&lt;/sup&gt;</td>
<td>22</td>
<td>26</td>
<td>42</td>
<td>9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>(A No Catalyst)</td>
<td>19</td>
<td>28</td>
<td>37</td>
<td>5</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>ref 11</td>
<td>(HF Catalyst)</td>
<td>11</td>
<td>20</td>
<td>19.5</td>
<td>6</td>
<td>2</td>
<td>3.5</td>
<td>0</td>
<td>38</td>
</tr>
</tbody>
</table>

A. -78°C to room temperature, 20-22 hr.  B. -46°C to room temperature, 20-22 hr.  C. -4°C to -39°C, 1 1/4 hr.  D. Not determined.

<sup>a</sup> Product percentages change to 1 (66), 2 (30), and 3 when unknown 7 is not considered.

<sup>b</sup> -43°C to -39°C during XeF₂ consumption.

<sup>c</sup> Product percentages change to 1 (68), 2 (28), and 3 (3) when unknown 7 is not considered.

<sup>d</sup> -46°C during XeF₂ consumption.

<sup>e</sup> -41°C during XeF₂ consumption.
isomerization is initiated by the boron trifluoride etherate; no isomerization results in the absence of this fluorinated Lewis acid under identical reaction conditions (Table I).

This paper describes the employment of deuterium labeling and catalyst/solvent variation to study the mechanism and product selectivity afforded by this boron trifluoride etherate initiated xenon difluoride/norbornane fluorination. Additionally, the deuterium labeling provides an unambiguous chemical identification of the unique 2,5-difluoronorbornane isomers.\(^\text{11,14}\)

Interesting isomeric product reversals were obtained during the catalyst and solvent variation studies. Such isomeric product reversals could prove significant in correlating reaction condition options with desired product control when using this convenient, direct fluorination procedure.

**RESULTS AND DISCUSSION**

Deuterium Labeling Study. Depending upon the reaction conditions imposed, direct xenon difluoride fluorination of norbornene by boron trifluoride etherate initiation in a dichloromethane suspension produced either three or four difluoronorbornane compounds 1, 2, 3, and 4. The identity of 3 and 4 proved to be the previously reported 2-exo-7-anti- and 2-exo-7-syn-difluoronorbornane isomers respectively;\(^\text{9}\) however, compounds 1 and 2 represented an unreported isomeric pair.\(^\text{14}\) The symmetrical pattern displayed by the \(^1\)H and \(^19\)F nmr's of 1 suggested this new difluoride to be either 2-exo-5-exo-difluoronorbornane or the analogous 2-exo-3-exo-isomer.\(^\text{15}\)

Compound 2 was presumed to be a corresponding endo-exo-isomer. Its somewhat similar geminal-HF pmr splitting pattern to that exhibited by the minor 2-endo-5-exo-dibromonorbornane product previously isolated, further
supported this assignment. A dehydrofluorination of 1 yielded a fluoro-norbornene which by itself failed to conclusively differentiate between the 2-exo-5-exo-difluoronorbornane or the 2-exo-3-endo-isomer. Spectral characterization to identify 1 and 2 was also inadequate since a comparison of all four potential isomers was not possible from this reaction system. Therefore, deuterium labeling of the norbornene was used to verify the isomeric identity of 1 and 2.

Fluorination of 2-deuterionorbornene was conducted under the same reactions used with unlabelled norbornene. A portion of this reaction was quenched after one hour and fifteen minutes so the initially formed reaction products could be isolated and analyzed. The absence of a proton magnetic resonance (pmr) signal from the deuterium atom incorporated in products 1 and 2 afforded an unambiguous identification between the 2,5-difluoro- and 2,3-difluoronorbornane isomeric pairs. A radical fluorination mechanism would produce the unrearranged, deuterated 2-exo-3-exo- and 2-endo-3-exo-difluoronorbornane isomers for 1 and 2 respectively (Equation 2).  

- INSERT EQUATION 2 -

These compounds would reveal a geminal-HF pmr signal one-half the integrated value (one proton) of their analogous unlabeled compounds (Table II). Clearly the pmr results outlined in Table II reveal the 2-exo-3-exo and 2-endo-3-exo-difluoronorbornanes are not produced. Instead fractional geminal-HF pmr values appear for both the 1 and 2 isomers (Table II). Such fractional values must be produced from a norbornyl structural arrangement.
that is characteristic of an ionic reaction mechanism. Thus, 1 and 2 represent 2-exo-5-exo-difluoronorbornane and 2-endo-5-exo-difluoronorbornane, respectively, which only can form by rearrangement within the norbornyl structural skeleton. The initial formation of both ioniically generated 2,7-difluoronorbornane isomers 3 and 4 in addition to 1 and 2, the successful fluorination of a nitrated aliphatic alkene,\(^2\) and the total absence of any 2,3-difluoronorbornanes 5 and 6,\(^3\) all strongly support an exclusive ionic fluorination mechanism. This ionic fluorination's novel selectivity in producing substantial amounts of 1 and 2 was studied further with deuterium labeling.

Additional \(\text{pmr}\) analysis of all four initial products from the 2-deuterionorbornene/xenon difluoride fluorination provided an excellent method for tracing the progress of this selective ionic reaction and for investigating its resultant preferential isomerization pathway. Scheme 1 represents an ionic mechanism consistent with the rearranged deuterium atom of all four initially formed products 1, 2, 3, and 4. The amount of deuterium rearrangement predicted by scheme 1 is recorded in Table II. Excellent agreement is obtained between that predicted and found from \(\text{pmr}\) analysis of the initially formed 1, 2, 3, and 4 difluoride products. The slightly low \(\text{gem-HF}\) and high norbornyl skeleton integration for 1 possibly results from a higher degree of initial fluorination at the deuterium labeled vinyl carbon. An initial 5,3-hydride migration eventually produces both the 2,5-difluoronorbornanes 1 and 2. Alternatively, both 2,7-difluoride isomers 3 and 4 result from an initial sigma bond 4,3-shift (scheme 1).
Table II. Predicted and Actual Initial Product ppm Signals from 2-Deuterononorbornene/XeF$_2$ Fluorination.

<table>
<thead>
<tr>
<th>Product</th>
<th>Gem-HF</th>
<th>Bridgehead</th>
<th>Bridge$^a$</th>
<th>Norbornyl Skeleton</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 Calc.</td>
<td>1.0</td>
<td>2.0</td>
<td>-</td>
<td>6.0</td>
</tr>
<tr>
<td>5 Calc.</td>
<td>1.0</td>
<td>2.0</td>
<td>-</td>
<td>6.0</td>
</tr>
<tr>
<td>4 Calc.</td>
<td>1.5</td>
<td>1.5</td>
<td>-</td>
<td>6.0</td>
</tr>
<tr>
<td>Actual$^b$</td>
<td>1.5</td>
<td>1.5</td>
<td>-</td>
<td>6.0</td>
</tr>
<tr>
<td>3 Calc.</td>
<td>1.0</td>
<td>1.5</td>
<td>0.5</td>
<td>6.0 (6.06)</td>
</tr>
<tr>
<td>Actual$^b$</td>
<td>1.0</td>
<td>1.5</td>
<td>0.5</td>
<td>6.1 (6.06)</td>
</tr>
<tr>
<td>2 Calc.</td>
<td>1.5</td>
<td>2.0</td>
<td>-</td>
<td>5.5</td>
</tr>
<tr>
<td>Actual$^b$</td>
<td>1.5</td>
<td>2.0</td>
<td>-</td>
<td>5.5</td>
</tr>
<tr>
<td>1 Calc.</td>
<td>1.5</td>
<td>2.0</td>
<td>-</td>
<td>5.5</td>
</tr>
<tr>
<td>Actual$^b$</td>
<td>1.4</td>
<td>2.0</td>
<td>-</td>
<td>5.6</td>
</tr>
</tbody>
</table>

$^a$Only the 2-exo-7-anti-difluorononorbornane isomer 3 possesses a chemical shift which allows separate evaluation of the bridge proton(s).

$^b$Reaction Conditions: $-43$ to $-30^\circ$C, 1 1/4 hr., all XeF$_2$ consumed.
The ionic fluorination mechanism outlined in scheme 1 also reveals three possible factors that contribute to the highly selective production of both 2,5-difluoronorbornane isomers 1 and 2 as compared to other norbornene halogenations. The first factor involves formation of the very stable 9 type carbonium ion species. The fluorinated carbonium ions 9a and 9b that produce the 2-5-difluoronorbornane isomers 1 and 2 respectively, rearrange from the initial 8 species to place the positive charge density the farthest possible distance from the fluorine bonded carbon atom. In the case of the 9 type fluorinated carbonium ion species, the positive charge density is three carbon centers away. The 10 type fluorinated carbonium ion that yields both 2,7-difluoronorbornanes possesses its positive charge closer to the fluorine bearing carbon atom just two centers away. The extremely high electron withdrawing properties of the bonded fluorine atom in 8 must be sufficiently long range to require the additional stabilization provided by the 9 type species over the 10 type carbonium ions. Such additional stabilization apparently is not required in norbornene additions with the other less electronegative halogens. A second factor contributing to the high degree of 1 and 2 product formation could be attributed to a favorable steric attack by the fluoride ion. The fluoride ion attack in both 9 species occurs from a direction that minimizes repulsive electronic interactions between the high electron density of the bonded fluorine atom and the attacking fluoride ion. This same electronic interaction minimization is also found in the 10a species that provides product 3. Interestingly products 1, 2, and 3 constitute ninety percent or more of the initial fluorinated products, while the minor product 4
is generated from species \( 10a \) where possible fluorine-fluorine interactions are not minimized. Other norbornene halogenations have often produced the analogous syn-2,7-isomer as the major dihalide product.\(^4\)\(^-\)\(^6\),\(^8\),\(^9\) The third factor involves the role of the boron trifluoride etherate catalyst. All four initial fluorination products are formed from \( 9 \) or \( 10 \) type rearranged carbonium ion species which are generated from \( 8 \) through sigma bond and hydride migrations. Formation of \( 9 \) and \( 10 \) from the initially produced \( 8 \) carbonium ion species results from the energetically unfavorable situation encountered in electrophillic additions when a positive charge resides adjacent to a fluoride bonded carbon atom.\(^1\)\(^8\) A concomitant tetrafluoroborate anion formation during the fluorination (scheme 1) could promote the selective rearrangement of \( 8 \) to the most stable \( 9 \) species by providing the stable boron tetrafluoroborate counter ion. This tetrafluoroborate anion provides a site for the second fluoride atom from \( \text{XeF}_2 \) to reside during the time required for rearrangement. Naturally the attacking fluoride ion upon species \( 9 \) and \( 10 \) can be any one of the fluoride atoms comprising the tetrafluoroborate anion and is not necessary the same fluoride originally bonded in the xenon difluoride reactant. Evidence for the tetrafluoroborate anion formation and participation is discussed and verified in the catalyst/solvent variation study outlined herein.

The tetrafluoroborate anion also appears to participate in the selective isomerization of the anti-2,7-difluoronorbornane \( 3 \) mostly to 2-exo-5-exo-difluoronorbornane \( 1 \) and some to 2-endo-5-exo-difluoronorbornane \( 2 \). A review of Table I illustrates that runs 1-6, 7B, and 8B are very consistent.

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in the percentage of 1, 2, and 3 products initially produced; however, run 3 provided an exception. Since neither varying the concentration of the boron trifluoride etherate catalyst (runs 1, 4, and 5) nor varying the amount of light exposure (runs 5 and 6) significantly altered the isomeric product percentages, an acid catalyzed isomerization of the initially formed products was suspected. Two reactions were conducted where one half of the reaction solution was aliquoted and quenched 1 1/4 hours after the addition and disappearance of the XeF₂ reagent (runs 7C and 8C). The remainder of the reaction solutions were allowed to proceed for a total of 20-22 hours (runs 7B and 8B) under the experimental conditions of runs 1-6. A comparison of run 7B to 7C and of 8B to 8C reveals that all but three to four percent of 3 isomerized mostly to 1 and some to 2. Further verification that boron trifluoride etherate effected the isomerization of 3 to 1 and 2 was achieved by stirring pure anti-2,7-difluoronorbornane 3 in dichloromethane with boron trifluoride etherate under the time and temperature conditions employed in runs 1-6. Analysis of glpc revealed unisomerized 3 (4%), 1 (65%), 2 (29%), and the unidentified isomer 7 with a high glpc retention time. The XeF₂ fluorination of 2-deuteronorbornene (Table II) was conducted under the same experimental conditions of runs 7 and 8 (Table I). By dividing this reaction solution and comparing the initial and isomerized reaction products of 1, the increase or decrease of pmr signals at specific deuterated positions allowed a more detailed study of the isomerization pathway of 3 to 1.
Table III. Proton Magnetic Resonance Analysis of Deuterium Atom Changes in 1 by BF₃O(CH₂CH₃)₂ Assisted Isomerization.

<table>
<thead>
<tr>
<th>Reaction Conditions</th>
<th>Gem-HF</th>
<th>Bridgehead H</th>
<th>Norbornyl Skeletal H</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 1.25 hr (-43 to -39°C)</td>
<td>1.4</td>
<td>2.0</td>
<td>5.6</td>
</tr>
<tr>
<td>B 21.25 hr (-43 to r.t.)</td>
<td>1.5</td>
<td>1.9</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Predicted Change (A to B) increase decrease no change

Reaction condition A (Table III) represents the ppm integration of the initially formed 1 isomer listed in Table II and predicted in scheme 1. Reaction condition B displays the change in ppm integration of 1 after isomerization. Isomer 1 was chosen for this comparison since it is the predominant isomer produced in this selective isomerization of species 3. Comparing both 1 isomers initially produced (scheme 1) with the two 1 isomers predicted by the scheme 2 isomerization pathway, reveals that the selective isomerization of 3 to 1 should decrease the ppm signal at the bridgehead position where no deuterium atom initially existed. Additionally the geminal-HF ppm signal should increase by producing two new 1 isomers (scheme 2) with no deuterium atom incorporated at this position, and no change should occur in the ppm signal in the remaining 2-exo-5-exo-difluoronorbornane structural skeleton. These changes outlined by scheme 2 agree with those actually found (Table III). Nonselective isomerization of difluoronorbornane isomers in the presence of the Lewis acid hydrogen fluoride has been reported¹¹ and was attributed to an analogous process which effects an ionic hydrogen fluoride catalyzed hydrolysis of benzyl fluoride.¹⁹

Just
as the Lewis acid hydrogen fluoride apparently seeks out a highly concentrated nonbonded electron pair on the fluorine atom, the vacant p-orbital of the boron atom in the boron trifluoride Lewis acid species could be expected to behave similarly. Formation of the stable tetrafluoroborate anion would provide a stable species to transport the fluoride ion during isomerization, and once again, allows formation of the same stable 9 monofluoronorbornyl cation (scheme 1) which places the positive charge density three carbon atoms from the fluorine bonded carbon. Continual overnight room temperature isomerization through species 9 (scheme 2) promotes the selective ionic isomerization that produces the major 1 isomer under the longer term reaction conditions. The loss of the initially formed isomer 4 could also be attributed to this boron trifluoride etherate initiated isomerization.

Catalysis/Solvent Studies. Boron trifluoride etherate catalysis selectively provides 2-exo-5-exo-difluoronorbornane 1. Comparison of catalyzed reactions 1-9 (Table I) with a blank XeF₂/norbornene fluorination (Reaction 10) shows the greatest amount of isomer 1 is afforded by the selective boron trifluoride etherate assisted isomerization. However the boron trifluoride etherate catalyzed reactions 7C, 8C, and 9C display some increased selectivity of 1 over that exhibited by the noncatalyzed reaction 10. Scheme 1 invokes formation of the boron tetrafluoroborate anion and its subsequent use as a secondary fluorinating species to explain in part the selectivity toward 2,5-difluoronorbornane isomers. To verify the proposed participation of the tetrafluoroborate anion during initial fluorination, a xenon difluoride fluorination of norbornene was catalyzed directly with the tetrafluoroborate anion in the absence of boron trifluoride.
etherate. The tetrafluoroborate anion was introduced into the reaction as the lithium salt, and diethyl ether solvent was employed for improved solubility of the lithium tetrafluoroborate catalyst. Table IV reveals that the presence of the tetrafluoroborate anion effects production of the

Table IV. XeF₂/Norbornene Fluorination Product Percentages: Catalyst and Solvent Variation Data

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>CH₂Cl₂</td>
<td>19</td>
<td>28</td>
<td>37</td>
<td>5</td>
<td>0</td>
<td>4</td>
<td>8</td>
<td>0</td>
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<tr>
<td>Blank</td>
<td>Diethyl Ether</td>
<td>9</td>
<td>11</td>
<td>48</td>
<td>16</td>
<td>0</td>
<td>3</td>
<td>12</td>
<td>3</td>
</tr>
<tr>
<td>LiBF₄</td>
<td>Diethyl Ether</td>
<td>27</td>
<td>15</td>
<td>18</td>
<td>7</td>
<td>0</td>
<td>0</td>
<td>17</td>
<td>15</td>
</tr>
<tr>
<td>BF₃O(CH₂CH₃)₂</td>
<td>Diethyl Ether</td>
<td>14</td>
<td>12</td>
<td>44</td>
<td>21</td>
<td>0</td>
<td>0</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>BF₃O(CH₂CH₃)₂</td>
<td>Diethyl Ether</td>
<td>16</td>
<td>13</td>
<td>43</td>
<td>19</td>
<td>0</td>
<td>0</td>
<td>6</td>
<td>3</td>
</tr>
</tbody>
</table>

\( ^a \)Difference from 100% are due to the unidentified product.\(^{12}\)

\( ^b \)Compound 12 identified as 2-exo-fluoronorbornane.

\( ^c \)This reaction additionally gave 1.1% of an unknown compound (See ref. 29).

\( ^d \)Less than 1% (0.3%)

\( ^e \)-44°C to room temp., 11 hr.

\( ^f \)-44°C to room temp., 24 hr.

2-exo-5-exo-difluoronorbornane 1 as the major difluoride. The combined 2,5-difluoronorbornanes 1 and 2 predominated over the more common 2,7-di-difluoronorbornanes 3 and 4. However, absence of the tetrafluoroborate anion in diethyl ether solvent produced product 1 as the minor difluoride, and
the 2,7-difluoronorbornanes 3 and 4 significantly predominated over both 2,5-difluoronorbornanes 1 and 2. This comparative result strongly supports tetrafluoroborate anion formation as being one significant factor in the selective synthesis of the 2-exo-5-exo-difluoronorbornane product 1. It follows further that the tetrafluoroborate anion of the catalytic lithium salt introduces the second fluorine atom into the two types of monofluoronorborny1 cation species 9 and 10 in an analogous manner to that illustrated in scheme 1. The tetrafluoroborate anion continually would be replenished by the xenon difluoride reagent as it simultaneously introduces the first fluorine atom into the norbornene molecule to generate species 8, 9 and 10.

Significant in the diethyl ether solvolyzed xenon difluoride fluorination of norbornene is the drastic product reversal that resulted when the catalytic species was varied or omitted entirely (Table IV). Reaction with the lithium tetrafluoroborate favored production of the 2,5-difluorides 1 and 2; however, the uncatalyzed fluorination effected a large selectivity for the 2,7-difluoride products 3 and 4. Such potential isomeric control in this fluorination procedure is surprising and could be a consequence of at least two factors. A greater solvating power of diethyl ether solvent over dichloromethane toward ionic species would stabilize species 8 and 10 more effectively and render a decreased necessity for species 9 formation. This would permit the observed increase of products 3 and 4 from species 10. The appearance of nortricyclo fluoride 11 as a fluorination product in diethyl ether solvent also supports this effect. The enhanced ionic stabilization provided by diethyl ether toward species 8 triggers the emergence of a competing fluorination - elimination pathway. Equation 3
illustrates a plausible fluorination - elimination pathway that incorporates very well into the common mechanistic process outlined in scheme 1.

- INSERT EQUATION 3 -

Upon formation of species 8, the second fluoride species from XeF₂ may fluorinate the rearranged catonic species 9 and 10 as they form from species 8, or alternatively, the second fluoride species can effect an elimination upon species 8 to form nortricycyl fluoride 11. Analogous eliminations previously have been reported with xenon difluoride/alkene fluorinations that produce monofluoroalkenes² or other halogenated alkenes.²⁰ The possible formation of trace amounts of hydrogen fluoride from this elimination pathway could also enhance a lack of product selectivity in the diethyl ether solvent. Secondly, the role of the tetrafluoroborate anion is greatly diminished in the diethyl ether solvent unless the tetrafluoroborate anion is directly introduced. Use of boron trifluoride etherate in diethyl ether solvent continues to favor production of the 2,7-difluoride isomers 3 and 4 (Table IV). Boron trifluoride etherate effects little change in the products obtained when compared to the uncatalyzed fluorination in diethyl ether. Apparently the infinitely high concentration of diethyl ether solvent molecules continuously complexes the boron trifluoride molecules and negates any appreciable tetrafluoroborate anion concentration from forming. The lack of any appreciable 3 and 4 product isomerization to products 1 and 2 (Table IV) also illustrates the inability of complexed boron trifluoride to convert to a tetrafluoroborate anion as outlined in scheme 2.
CONCLUSION

The boron trifluoride etherate initiated fluorination of norbornene with the xenon difluoride reagent initially produces four difluoride addition products. Whether dichloromethane or diethyl ether solvent is employed, 2-exo-5-exo-difluoronorbornane 1, 2-exo-5-exo-difluoronorbornane 2, 2-exo-7-anti-difluoronorbornane 3, and 2-exo-7-syn-difluoronorbornane 4 are the four initial difluoronorbornane isomers obtained; however, an interesting product reversal occurs depending upon which solvent is used. With dichloromethane solvent the two unique 2,5-difluoronorbornane isomers collectively predominate, while the normal 2,7-isomers, produced in other halogenation and interhalogenation additions, are selectively synthesized in diethyl ether. Extended reaction times in dichloromethane solvent affords the 2,5-difluoronorbornanes in nearly exclusive yield through a selective isomerization catalyzed by boron trifluoride etherate.\textsuperscript{3} Analogous direct fluorination in dichloromethane without the boron trifluoride etherate resulted in a less selective distribution; however, a slightly higher selectivity for the 2,5-difluoronorbornane formation was still observed.

A boron trifluoride etherate initiated XeF\textsubscript{2} fluorination of 2-deuterionorbornene in a dichloromethane suspension unambiguously established the identity of the unique 2,5-difluoronorbornane isomers through \textit{mms} integration. This identification effectively complements their identification obtained solely from spectroscopic assignments.\textsuperscript{11} Proton magnetic resonance product integrations also provided a detailed elucidation of this convenient direct ionic fluorination reaction (scheme 1). The production of 2,7-difluoronorbornane products through structural rearrangement strongly suggested
a mechanism with ionic character. Additional evidence pointing to an ionic character was obtained in a separate photochemical induced XeF₂ fluorination of norbornene which provided only the 2-exo-3-exo- and 2-endo-3-exo-difluoronorbornanes 5 and 6 as pure difluoronorbornane addition products under reaction conditions designed to proceed through a radical pathway.²¹ Further analyses of the extended time reaction products in dichloromethane solvent suggested that the selective isomerization of the 2,7-difluoronorbornanes 3 and 4 to the unusual 2,5-difluoronorbornanes 1 and 2 proceeds through Lewis acid catalysis. This catalysis (scheme 2) produces the same stable ionic precursor species 9 necessary for the initial 2,5-difluoronorbornane isomer selectively (scheme 1).

The boron trifluoride etherate performs an important function in the preferential synthesis of the 2-exo-5-exo- and 2-endo-5-exo-difluoronorbornanes in dichloromethane solvent. While it provides some selectivity toward initial 2,5-difluoronorbornane isomer formation, it also initiates the selective isomerization responsible for a nearly exclusive yield of these two 2,5-isomers. In both the initial fluorination (scheme 1) and the selective isomerization (scheme 2) mechanisms, formation of the stable tetrafluoroborate anion represents a key step. The tetrafluoroborate anion provides a stable anion within which the second fluorine atom from XeF₂ can reside while the monofluoronorbornyl cation 8 can rearrange to its most stable species 9. Subsequent secondary fluorination by the tetrafluoroborate anion of the most stable monofluoronorbornyl cation 9 with its charge situated three carbon centers from the fluorine bonded carbon atom, affords the unique 2,5-difluoronorbornanes and regenerates the boron.
trifluoride catalyst. Verification of the tetrafluoroborate anion's participation comes from a diethyl ether solvolyzed fluorination which produced the two normal 2,7-difluoronorbornanes as major products. The infinitely high concentration of diethyl ether molecules continually hold boron trifluoride molecule in its etherate complex and no significant tetrafluoroborate anion can form. However, direct introduction of the tetrafluoroborate anion as LiBF$_4$ into the diethyl ether reaction system, in place of the boron trifluoride etherate, produced a dramatic product reversal where the 2,5-difluoronorbornanes collectively predominated over the analogous 2,7-isomers (Table IV). This continual complexation is also responsible for the lack of any significant selective isomerization when using diethyl ether solvent.

Diethyl ether solvent employed in place of dichloromethane provided a large decrease in the formation of both 2,5-difluoronorbornane products. Instead the 2,7-difluoronorbornane compounds greatly predominated over all other reaction products. Interestingly, they represent analogs of the 2,7-dihalononorbornane compounds that are normally formed as the major products in other halogenation and interhalogenation additions. Compared to the dichloromethane solvent, diethyl ether solvolysis offers a higher degree of stabilization to the monofluoronorbornyl cation species 8 and 10 (scheme 1) and sufficiently diminishes the necessity of the stable species 9 formation by the competing hydride-5,3-migration pathway. The formation of nortricyclyl fluoride 11 from species 8 in diethyl ether solvent, but not with dichloromethane solvent, provides additional evidence to this effect. The dichloromethane solvent enhances the 2,5-difluoronorbornane selectivity
in the \( \text{XeF}_2 \) fluorination of norbornene by maximizing the long range electron withdrawing destabilization effects of the fluorine atom upon the intermediate monofluoronorbornyl cation species. This effect promotes the competing reactant pathway that enhances formation of the most stable monofluoronorbornyl cation species \( \text{9} \) (scheme 1). Subsequent fluorination of species \( \text{9} \) affords the unique 2,5-difluoronorbornanes in high yield. The inability of other less electronegative halogens in norbornene halogenations to produce a substantial proportion of 2,5-dihalonorbornanes is taken as additional evidence for operation of long range fluorine effects in dichloromethane solvated \( \text{XeF}_2 \) fluorination of norbornene. This same factor must also cause the formation of this same stable intermediate species \( \text{9} \) which is necessarily generated during the highly selective isomerization of the 2,7-difluoronorbornanes into their 2,5-isomeric analogs (scheme 2).

The elucidated boron trifluoride etherate initiated ionic fluorination mechanism plus the catalyst and solvent effects upon this direct fluorination procedure, begin to outline the key chemical considerations necessary in predicting and planning future synthetic efforts. The ionic fluorination mechanism, and its propensity to effect the rearrangement of initially formed monofluoronorbornyl ions to more stable forms, can be extended to explain the different major products observed when 1,2-dibromoethene and 1-decene each were fluorinated with the \( \text{XeF}_2 \) reagent.\(^2\) The demonstrated ability to reverse and control the formation of major difluoronorbornane products through solvent or chemical catalyst variation also defines several important parameters within which selective fluorinations might be obtained. Correlation and integration of these catalyst and solvent
variations within this ionic fluorination mechanism provides an intriguing perspective within which to predict and maximize the reaction conditions necessary for improved, high yield, selective syntheses of novel and important fluoroorganic compounds.
EXPERIMENTAL SECTION

General. In all cases the detailed reaction procedures described herein under "Method A" were followed while conducting the fluorinations. Specifically this applies to the storing, weighing, and transferring of the solid XeF$_2$ and to the addition method used to introduce the norbornene, catalyst, and solvent into the reaction system.

The acetone used to rinse and dry all items for this direct fluorination procedure was Burdick and Jackson "Distilled in Glass" and was used as received. The water employed in all operations was taken directly from the laboratory's distilled water line. The dichloromethane solvent was Matheson, Coleman and Bell Spectroquality. Prior to use it was distilled over NaOH pellets and stored over 4Å molecular sieves in a Fischer Scientific Company Isolator/Lab drybox (Ser. No. 287) with a modified drying train. The drybox provided a dry N$_2$ atmosphere under which the solid XeF$_2$ reagent was also stored in a teflon screw top bottle. The diethyl ether solvent was Mallinkrodt AR. Immediately prior to use, it was refluxed over Na metal until a trace amount of benzophenone indicator turned blue to signify dryness. The boron trifluoride etherate catalyst (Eastman Organic Chemicals, Practical Grade) was vacuum distilled to a pure colorless liquid; it was redistilled whenever discoloration appeared during storage. The LiBF$_4$ (PCR, Inc.) was used as received, but the norbornene (Aldrich Chemical Company) was fractionally distilled to a waxy colorless solid prior to use. The XeF$_2$ displayed 100% purity in mass spectral analysis on an instrument possessing a 99.9% detection limit. Care must be taken to use only pure XeF$_2$ in the procedure described. Samples
of XeF₂ that are contaminated with trace amounts of XeF₄ will be explosive if the XeF₄ contaminant air hydrolyzes to XeO₃.²

All glassware, capillary pipets, teflon coated magnetic stir bars, and teflon coated spatulas²³ were cleaned by a similar technique to that previously described.²⁴ The items were soaked in a seven liter stainless steel beaker charged with distilled water and a small amount of Alconox soap. The solution was heated to a mild boil; then, the items were individually removed with tongs and immediately rinsed in succession with distilled H₂O, acetone, distilled H₂O, and acetone. After atmosphere drying, the 35 ml single-necked round bottom flask, teflon coated magnetic stir bar, 14/20 ground glass stopper, spatula (for weighing out the XeF₂), and the graduated cylinder (for measuring out the reaction solvent) were all placed into the Fischer Isolator/Lab drybox to stand overnight. The remaining glassware and equipment remained exposed to the atmosphere on a clean absorbant paper drain pad until needed.

Melting points were obtained in sealed glass capillaries with a Mel-Temp melting point apparatus and are uncorrected. Mass spectra were obtained on either a Hewlett Packard 5990A GC/MS spectrometer equipped with a 5992A GC/MS terminal system or on a DuPont 21-491 dual beam mass spectrometer. With the latter instrument, the product volatility required direct injection using methanol (M⁺ = 32) solvent. Nuclear magnetic resonance (¹H and ¹⁹F) analyses were accomplished with a Varian T-60 spectrometer in DCCl₃ solvent. The ¹H nmr spectra were always referenced to TMS. A Varian Aerograph Moduline Series 2700 dual column chromatograph was used to separate, isolate, and identify the fluorinated products using a 10 ft. by
1/4 in. 10% Carbowax 20M on 80/100 mesh Chromasorb W column with a variable column temperature range from 95°C to 195°C. All products isolated from this g.l.p.c. column were condensed in small glass traps (constructed in this laboratory) that were submerged in a liquid N₂ bath. Isomer product percentages were determined from disk recorder integration scans. There were some unresolvable tars formed in the fluorination reaction which came off the column at fairly high retention times. However, the percent of all isolated products contained in Table I and IV represent 86 to 94% of the total fluorinated products in the boron trifluoride etherate catalyzed CH₂Cl₂ solvated reactions (95% uncatalyzed), 87 to 92% in the boron trifluoride etherate catalyzed diethyl ether solvated reaction (63% uncatalyzed), and 83% in the LiBF₄ catalyzed diethyl ether solvolyzed fluorination. All elemental analyses were accomplished by Gailbreth Laboratories, Knoxville, TN.

Direct Fluorination of Norbornene with Xenon Difluoride in CH₂Cl₂ Solvent. (Method A). Inside an isolator drybox under a dry N₂ atmosphere, a 35 ml 14/20 single-necked round bottom flask was charged with a teflon coated magnetic stir bar and 0.35 g (2.07 mmol) XeF₂. A small powder funnel with a 14/20 ground glass joint was used to help transfer the XeF₂ with a spatula into 35 ml reaction flask. The 35 ml flask was then immediately stoppered with a 14/20 ground glass stopper. (Note: Neither the flask nor the stopper were treated with any silicone vacuum grease.) Next the spatula and funnel, used to transfer the XeF₂, were rinsed with CH₂Cl₂ at room temperature to destroy any residual XeF₂.²⁵ Seven ml of the treated CH₂Cl₂ solvent was poured into a 50 ml graduated cylinder, and the drybox
was then purged three successive times with fresh N\textsubscript{2}. The spent N\textsubscript{2} was pumped directly into a fume hood exhaust. Next, the stoppered 35 ml reaction flask and the CH\textsubscript{2}Cl\textsubscript{2} containing graduated cylinder were removed from the drybox, hand-carried to a benchtop fume hood, and were placed into the hood. The 35 ml reaction flask was submerged into a dry ice/acetone coding bath (ca. -78°C) to reduce the vapor pressure of the XeF\textsubscript{2} prior to the ground glass stopper removal. Within 15 sec the stopper was removed and was immediately replaced with a 15 ml pressure equalized addition funnel fitted with a Dreirite containing drying tube. This apparatus was assembled prior to the XeF\textsubscript{2} weighing in the drybox. All joints in this apparatus assembly were sealed with silicone vacuum grease including the male joint of the 15 ml addition funnel. The entire apparatus was placed into the 35 ml reaction flask as one unit. Next, 0.18 g (2.14 mmol) norbornene was weighed into 2 ml of the treated CH\textsubscript{2}Cl\textsubscript{2} solvent; then, the solution was transferred with a rubber bulb fitted capillary pipet into the 15 ml addition funnel. The drying tube was removed from the addition funnel during this transfer and was then immediately replaced. The norbornene solution was added dropwise to the solid XeF\textsubscript{2} over a 5-10 min period, and the resulting heterogeneous suspension was stirred as soon as mechanically possible. A small amount of pure CH\textsubscript{2}Cl\textsubscript{2} (ca. 0.5 ml) was used to rinse the inside of the additional funnel; this was also added to the reaction suspension at the same rate. Subsequently 0.10 g (0.17 mmol) boron trifluoride etherate\textsuperscript{26} was weighed into 2 ml treated CH\textsubscript{2}Cl\textsubscript{2} solvent; then, this solution was transferred in like manner into the 15 ml addition funnel. Within 5-10 min after the norbornene solution addition, the BF\textsubscript{3}OET\textsubscript{2}
solution was added dropwise to the stirred norbornene/XeF₂ suspension. Again a small amount (ca. 0.5 ml) of pure CH₂Cl₂ was used to rinse the inner walls of the addition funnel, and this wash was allowed to drop into the reaction suspension. The reaction was stirred at -78°C for 5.5 to 6.5 hr; the reaction was extremely slow. The dry ice/acetone cooling bath then was packed once more and insulated with wrapped towels. Over the following 15-16 hours, the bath was allowed to warm to room temperature, and all solid XeF₂ disappeared leaving a dark brown solution. A 30 ml separatory funnel was charged with 10 ml distilled H₂O and 0.25 g NaF to tie up any possible HF formed. The reaction solution was then transferred into the separatory funnel. The 35 ml reaction flask was rinsed with 2 ml CH₂Cl₂, and this rinse was added to the separatory funnel. The CH₂Cl₂ solution was washed with the aqueous NaF solution and separated. The aqueous wash was then extracted with 2 ml CH₂Cl₂, and this was combined with the first CH₂Cl₂ portion. The combined CH₂Cl₂ portions were dried over anhydrous MgSO₄ and filtered to provide a golden solution. In several cases in vacuo solvent removal was accomplished and afforded 0.10 to 0.18 g of a dark brown waxy solid product mixture. Usually, the CH₂Cl₂ solvent was not removed, and the solution was introduced directly to glpc separation and purification. Analysis with the Carbowax 20M column afforded products 1, 2, 3, and 7. They were isolated from the glpc column in the following order: 2-exo-7-anti-difluoronorbornane 3, volatile white solid (mp 109.5 - 111.5°C, lit. 109 - 111°C); ¹H nmr (CDCl₃) δ 5.12 (doublet of broadened singlets, Jd = 58 cps, 1H), 4.58 (doublet of multiplets, Jd = 58 cps, 1H), 2.46 (doublet of multiplets, Jd = 12 cps, 2H), 2.20-0.90 (multiplets, 6H); ¹⁹F nmr
\[(\text{DCl}_3) + 50.8 \text{ ppm from C}_6\text{F}_6 \text{ or } + 163.6 \text{ ppm from CFCl}_3 \text{ (doublet of multiplets, } J_d = 58.7 \text{ cps); mass spectrum } M^+ 132 \text{ (base peak 81); Elem. Anal. Calcd. for C}_7\text{H}_{10}\text{F}_2; C, 63.6; H, 7.64; F, 28.7. \text{ Found: } C, 63.8; H, 7.44; F, 28.8; 2\text{-endo-5-exo-difluoronorbornane 2, volatile white solid (mp 105.0 - 107.0°C); } ^1\text{H nmr} \text{ (DCl}_3) \delta 4.94 \text{ (doublet of multiplets, } J_d = 56 \text{ cps, 1H)}, 4.80 \text{ (doublet of broadened doublets, } J_d = 56 \text{ cps, 1H}), 2.62 \text{ (multiplet, 2H), 2.30-0.60 (multiplets, 6H); } ^19\text{F nmr} \text{ (DCl}_3) + 30.6 \text{ ppm from C}_6\text{F}_6 \text{ (doublet of multiplets, } J = 58.6 \text{ cps); mass spectrum } M^+ 132 \text{ (base peak either 85 or 86); Elem. Anal. Calcd. for C}_7\text{H}_{10}\text{F}_2; C, 63.6; H, 7.64. \text{ Found: } C, 61.8; H, 7.32; 2\text{-exo-5-exo-difluoronorbornane 1, volatile white solid (mp 106.0 - 107.2°C); } ^1\text{H nmr} \text{ (DCl}_3) \delta 4.48 \text{ (doublet of multiplets, } J = 56 \text{ cps, 2H), 2.46 (multiplet, 2H), 2.20 - 1.10 (multiplets, 6H); } ^19\text{F nmr} \text{ (DCl}_3) + 3.0 \text{ ppm from C}_6\text{F}_6 \text{ (multiplet resembling a quintet); mass spectrum } M^+ 132 \text{ (base peak either 85 or 86); Elem. Anal. Calcd. for C}_7\text{H}_{10}\text{F}_2; C, 63.6, H, 7.64; F, 28.7. \text{ Found: } C, 63.3; H, 7.45; F, 29.1; product 7.}

(Method B). All procedures outlined in Method A were repeated with two exceptions. A chlorobenzene/dry ice cooling bath (ca. -43°C) was used in place of the acetone/dry ice bath; and secondly, one half of the reaction solution was removed early, quenched and analyzed. The remainder of the reaction solution was allowed to proceed as in Method A. Depending upon the amount of dry ice used, the temperatures in the chlorobenzene/dry ice bath varied from -46°C to -41°C. In one case (Table I), a reaction at -43°C gradually warmed to -39°C during the 15-20 minutes that the XeF\textsubscript{2} was consumed; two other reactions were held at -41°C and -46°C during consumption of the XeF\textsubscript{2}. One hour and fifteen minutes after the addition of the
BF$_3$OEt$_2$ solution was first added, approximately one half of the reaction solution (ca. 3 ml) was removed and placed into 10 ml aqueous NaF solution. The quenched aliquot was worked up and g.l.p.c. analyzed. Four products were isolated off the Carbowax 20M in the following order: 3, 2, 1, and 4.

- 2-exo-7-syn-difluoronorbornane 4, volatile white solid; $^1$H n.m.r. (DCCl$_3$) $\delta$ 4.80 (doublet of broadened singlets with shoulders, J$_d$ = 56 cps, 2H), 2.46 (doublet of multiplets, J$_d$ = 12 cps, 2H), 2.12 - 0.66 (multiplets, 6H); mass spectrum M$^+$ 132 (base peak 81). Note: Method B was used in the XeF$_2$ fluorination of the 2-deuterionorbornene sample.

(No BF$_3$OEt$_2$ Catalysis). All procedures outlined in Method A were followed identically with one exception. No boron trifluoride etherate catalyst was added. Instead a 2 ml blank of pure CH$_2$Cl$_2$ solvent was added to the stirred norbornene/XeF$_2$ reaction suspension in place of the BF$_3$OEt$_2$/CH$_2$Cl$_2$ 2 ml solution. At the end of the reaction period, the homogeneous reaction solution was a clear gold. Analysis with the Carbowax 20M g.l.p.c. column afforded six products in the following order: 11, 6, 3, 2, 1, and 4.

- 2-nortricyclyl fluoride 11, very volatile white solid; $^1$H n.m.r. (DCCl$_3$) $\delta$ 4.68 (doublet of broadened singlets, J$_d$ = 60 cps, 1H), 1.98 (doublet of broadened singlets, J$_d$ = 12 cps, 2H), 1.28 (broadened singlet, 7H); mass spectrum M$^+$ 112 (base peak 97); 2-endo-3-exo-difluoronorbornane 6, volatile white solid; mass spectrum M$^+$ 132 (base peak 67 with 68 as 82%); g.l.p.c. retention time on Carbowax 20M column identical to major product of a photochemical initiated XeF$_2$/norbornene fluorination which was identified as 2-endo-3-exo-difluoronorbornane by $^1$H n.m.r. and mass spectrum analysis.
Direct Fluorination of Norbornene with Xenon Difluoride in Diethyl Ether Solvent. Initial preparations and procedures were conducted identically with those outlined for Method A in the CH₂Cl₂ solvolyzed reactions except that diethyl ether solvent was used in place of CH₂Cl₂.

(Boron Trifluoride Etherate Catalysis). A 35 ml single-necked round bottom flask, containing a teflon coated magnetic stir bar, was charged with 0.35 g (2.07 mmol) XeF₂. The XeF₂ containing reaction flask was submerged into a chlorobenzene/dry ice cooling bath (-44°C), and the final reaction apparatus was assembled as previously described (Method A). Next, 0.23 g (2.44 mmol) norbornene was weighed into 2 ml Et₂O, and this solution was added dropwise over 4 min to the XeF₂ containing reaction flask. Stirring was begun as soon as mechanically possible. Nine minutes after addition of the norbornene ethereal solution, 0.1 g BF₃OEt₂ was weighed into 2 ml Et₂O, and this solution was added dropwise over 5 min to the stirred reaction suspension. After 2.33 hr, a reaction aliquot was analyzed by GLPC/MS, and no difluoride products were found. A CCl₄/dry ice bath, and a homogenous then substituted for colder chlorobenzene/dry ice bath, and a homogenous solution gradually resulted. Some fluorinated products were found after 4.75 hr reaction time. After 6.66 hr, 1 ml additional Et₂O was added to the reaction solution to replenish some volatile solvent loss. After 10.5 hr the cold bath had warmed to -5°C, and the bath was removed. At 11.0 hr half the reaction (ca. 2 ml) was removed for work up and analysis. The CCl₄/dry ice cold bath was again placed around the reaction flask, then was repacked with dry ice and insulated with towels. Again 1 ml Et₂O was added.
to the reaction to replenish evaporated solvent, and the remaining solution was left to react further. Meanwhile the aliquoted solution was washed with 10 ml distilled H$_2$O containing 0.22 g NaF, 0.20 g KI, and 2 capillary pipet drops of 2N H$_2$SO$_4$. $^{27}$ The ethereal layer was separated, and 1.5 ml of fresh Et$_2$O was used to extract the aqueous solution. The two ethereal portions were combined, dried over anhydrous MgSO$_4$, and were filtered. The nearly colorless (slightly yellow) solution was analyzed by glpc, and the products eluted from the Carbowax 20M column in the following order: 11, 3, 2, 1, and 4.

(No Boron Trifluoride Etherate Catalysis). All reaction preparations and procedures were conducted in a similar manner to that discussed in the analogous BF$_3$OEt$_2$ catalyzed reaction; however, this uncatalyzed reaction proceeded much more slowly. The 35 ml single-necked round bottom flask was charged with a teflon coated magnetic stir bar and 0.35 g (2.07 mmol) XeF$_2$. After cooling this reaction flask in an acetone/dry ice bath, a 2 ml Et$_2$O solution containing 0.20 g (2.13 mmol) norbornene was added dropwise to the XeF$_2$ containing reaction flask over a 5 min period. Stirring was initiated as soon as mechanically possible. Seven minutes after addition of the norbornene solution, 2 ml Et$_2$O was added dropwise to the stirred reaction suspension over a 3 min duration. After 4.75 min solid XeF$_2$ remained in a colorless solution. The acetone/dry ice bath was repacked, insulated with towels, and was permitted to warm to room temperature over the next 16 hr. At this point the reaction was recooled in an acetone/dry ice bath, and a white solid formed on the flask's inner wall just above the solution. The
cold bath was removed, and 1 ml Et₂O was added dropwise over 1.5 min to cover the solid formed on the inner wall. All solid dissolved as the colorless reaction solution returned to room temperature. At 28.5 hr the reaction solution began to turn yellow. After 44 hr the reaction was dark brown, and at the 46.5 hr point, the reaction solution was worked up and glpc analyzed as described in the analogous BF₃·OEt₂ catalyzed reaction. The reaction products were isolated from the Carbowax 20M glpc column in the following order: 12, 11, 6, 3, 2, 1, and 4; 2-fluoronorbornane 12, very volatile white solid; ¹H nmr (CDCl₃) δ 4.62 (doublet of sharp multiplets, J_d = 57 cps, 1H); 2.44 (doublet of multiplets, J_d = 11 cps, 2H); 2.06-0.80 (multiplet, 8H)²⁸; mass spectrum M⁺ 114 (base peak 68).

(Lithium Tetrafluoroborate Catalysis). All reaction preparations and procedures were conducted in similar manner to that already described. A 35 ml single-necked round bottom containing a teflon coated magnetic stir bar was charged with 0.35 g (2.07 mmol) XeF₂ and was then placed into a chlorobenzene/dry ice (−44°C) cooling bath. Next, 0.20 g (2.13 mmol) norbornene was weighed into 4 ml Et₂O. The norbornene solution was added dropwise to the XeF₂ containing reaction flask over a 9 min period, and stirring was begun as soon as mechanically possible. Within 4.5 min after addition all the norbornene solution, 0.20 g LiBF₄ solid was added directly to the stirred reaction suspension with the aid of a 30 ml powder funnel that possessed a 14/20 male ground glass joint. After 7.5 hr solid XeF₂ was still present in the reaction suspension. The chlorobenzene/dry ice cold bath was repacked, insulated, and was left to warm to room temperature. After 23 hr, the dark brown reaction solution was poured into 10 ml distilled
H₂O that contained 0.4 g NaF. The ethereal layer was washed and separated. An additional 5 ml H₂O was added to the aqueous wash, and the aqueous wash was then extracted with 2 ml fresh Et₂O. The two Et₂O portions were combined, dried over anhydrous MgSO₄, filtered, and were analyzed by glpc. Seven products were separated and isolated from the Carbowax 20M glpc column in the following order: 12, 11, unk²⁹, 3, 2, 1, and 4.

**Dehydrofluorination of 2-Exo-5-Exo-Difluoronorbomane.** Using a previously reported dehydrofluorination procedure that provided 7-anti-fluoronorbomene from 3 and 7-syn-fluoronorbomene from 4 respectively⁹, 5-exo-fluoronorbomene was synthesized from 2-exo-5-exo-difluoronorbomane 1.

The dry DMSO solvent was prepared by refluxing it 2 hr over CaH₂ and then vacuum distilling the DMSO at 29-30°C/0.04 mm onto 3Å molecular seives. Under a dry N₂ atmosphere a 10 ml single-necked round bottom flask was charged with a teflon coated magnetic stir bar, 3 ml DMSO, 0.103 g (0.777 mmol) 2-exo-5-exo-difluoronorbomane, and 0.106 g (0.946 mmol) potassium t-butoxide. While still under an N₂ atmosphere, the reaction flask was fitted with a water-cooled reflux condenser topped with a Drierite containing drying tube. The reaction solution was heated between 95-107°C a total of 17 hours; prior to the last 7 hr of heating, an additional 1 ml DMSO was added to the reaction flask under a stream of dry N₂. After cooling to room temperature, 10 ml H₂O was added to the reaction, and the aqueous DMSO reaction solution was continuously extracted 9 hr with 10 ml CH₂Cl₂. The aqueous DMSO layer was then discarded, and CH₂Cl₂ extract was washed with 8 ml H₂O. This H₂O layer was separated, and then was continuously extracted 3 hr with a few
ml (minimum amount needed to form an organic layer, ca. 2 ml) of fresh CH₂Cl₂. This CH₂Cl₂ portion was separated and combined with the first CH₂Cl₂ extract, and the combined CH₂Cl₂ extracts were washed with another 8 ml portion of H₂O. This H₂O wash was then continuously extracted 3 hr with a few ml of fresh CH₂Cl₂ as before. This third CH₂Cl₂ extract was combined with the previous CH₂Cl₂ extracts. These combined CH₂Cl₂ portions were washed with 7 ml fresh H₂O. Again a few ml fresh CH₂Cl₂ was used to extract this 7 ml H₂O wash as before and this fourth CH₂Cl₂ extract was combined with the other CH₂Cl₂ extracts. The combined CH₂Cl₂ extracts were dried over anhydrous MgSO₄, filtered, and were concentrated by careful fractional distillation through a Vigreax column to about 1.5 ml. Analysis by glpc with the Carbowax 20M column provided three peaks using a 85°C column temperature for 5 min after the air peak followed by a 195°C column temperature for a total of 26 min. The first peak proved to be the volatile 5-exo-fluoronorbornene while the second peak was unreacted I. The third peak was DMSO. The glpc analysis revealed that 42% of I was converted to the dehydrofluorinated product. The 5-exo-difluoronorbornene was isolated off the glpc column using a liquid N₂ bath; it was a volatile white solid; ¹H nmr (CDCl₃) δ 6.32 (multiplet, 1H); 5.88 (multiplet, 1H); 4.72 (doublet of multiplets, Jd = 58 cps, 1H); 2.96 (unsymmetrical multiplet, 2H); 1.94 - 1.02 (multiplets, 4H); mass spectrum M⁺ 112 (37%) with M/e = 97(53), 86(66), 84(1.00), 73(84), and 66(82).

Synthesis of 2-Deuterionorbornene.³⁰ A 100 ml three-necked round bottom flask was charged with 22.1 g (0.384 mol) of one micron 40% Na dispersion (Gray Chemical, Inc.) in petroleum and mineral oil. The flask
was fitted with an N₂ stopcocked inlet and identical outlet, plus an overhead mounted mechanical stirrer apparatus. Next, 20 ml "Distilled-in-Glass" hexane treated with neutral alumina (pH = 6.3) was added to the reaction flask. The flask was submerged into a CC₄/dry ice cooling bath (-23°C) and cooled with vigorous stirring. This cooled suspension was stirred at high speed while 12.0 g (0.130 mol) n-chlorobutane in 10 ml hexane was added dropwise over 1.3 hr. The n-chlorobutane was dried over 4Å molecular sieves and passed through neutral alumina (pH = 6.3) prior to its combination with the hexane solvent and introduction into the sodium suspension. After all n-butylchloride was added, the CC₄/dry ice cooling bath was replaced with an ice bath for 35 min. Next, the CC₄/dry ice bath was again placed around the reaction flask, and 8 min. later 12.0 g (0.128 mol) norbornene in 15 ml hexane was added dropwise to the stirred reaction suspension over 10 min. The cooling bath was removed and the reaction solution was stirred at ambient temperature for 22.5 hr. The CC₄/dry ice bath was then placed around the reaction flask for 10 min. and the system was opened to the atmosphere. Next 8.9 g 98% D₂O was very cautiously added dropwise to the rapidly stirred suspension using a disposable capillary pipet. The reaction exothermed slightly after the first few drops of D₂O were added, but all material was contained in the reaction flask. After all the D₂O was added, the cooling bath was removed, and the reaction was stirred at ambient temperature 4.5 hr. The reaction solution was transferred into a separatory funnel; then 75 ml H₂O and 10 ml hexane were also placed into the funnel. The distinct organic layer was separated, and the remaining emulsion was extracted six times with three 20 ml hexane portions
followed by three 40 ml diethyl ether portions. All hexane and ethereal extracts were combined and dried over anhydrous MgSO₄. After filtration, the solvent was removed by fractional distillation. The undistilled portion was then distilled through a microwave short path apparatus, and only the material that condensed in the water cooled condenser was retained. Proton nmr analysis revealed this material to be 2-deuterionorbornene. An attempt to further deuterate this 1.9 g sample met with failure; however, the 2-deuterionorbornene sample (0.7 g) was recovered by short path distillation. This sample afforded the following nmr analysis: \( ^1H \text{nmr (CDCl}_3 \) δ 6.04 (sharp multiplet, 1H); 2.86 (sharp multiplet, 2H); 1.86 - 0.66 (multiplets 6H); mass spectrum M+1 = 96 (5.6), M+ = 95 (12.7), M-1 = 94 (7.5) with m/e = 68 (43.0), 67 (100), and 66 (56.5).

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REFERENCES AND NOTES

1. Currently a USAF/APSC Exchange Scientist and presently located at DFVLR/ 
Lampoldshausen, D7101 Hardthausen am Kocher, Federal Republic of Germany.


12. Under these extended 20–22 hr. reaction conditions, an unidentified 
compound 7 was isolated which comprised only 9–13% of the total reaction 
products. Its mass spectrum afforded M+ = 110 (base peak = 67), and its 
{}^1 H NMR gave no gem–HF signal. This unknown's retention time was greater 
than 1, 2, or 3.

13. Additional investigation after reference 3 revealed that the 2-exo-7-syn– 
difluoronorbornane 4 initially forms a minor product (7–12%) but dis-
appears under the extended 20–22 hr. reaction conditions.

14. Subsequent to completing the deuterium labeling study described herein 
and in reference 3, Zupan, Gregoricic, and Pollak reported the spectro-
scopic characterization of both 2,5-difluoronorbornane isomers 1 and 2. 
Both the spectroscopic characterization (reference 11) and this comple-
mentary deuterium labeling study agree.

15. A pictorial ¹H NMR of compound 1 is presented in reference 3.

16. Pictorial ¹H NMRs of compound 2 and of 2-endo-5-exo-difluoronorbornane 
are presented in references 3 and 8 respectively.
17. An example of another long range influence involving this fluorine atom, which covers more than two atomic centers, can be seen in the 

nmr spectrum of 5-fluoronorborn-2-ene where the two vicinal protons differ in chemical shift by 24 cps.


23. Initially only teflon coated stainless steel spatulas were used to handle, transfer, and weigh out the XeF₂ reagent. Later it was found that ordinary clean, dry stainless steel spatulas were satisfactory.


25. At room temperature a 0.35 g XeF₂ sample reacted with pure CH₂Cl₂ within 5 min. and was totally consumed within 10 min. S.A. Shackelford, unpublished results.

26. In runs 3, 5, and 6 (Table I) 0.20 g (1.41 mmol) BF₃OEt₂ was employed. Runs 1 and 4 contained 0.10 g (0.71 mmol) BF₃OEt₂.

27. The acidified KI was employed as a protective measure should any XeO₂ form from an undetected contaminant in XeF₂. Acidic KI converts XeO₂ immediately to Xe and O₂.


29. This unknown trace product afforded a mass spectrum with M⁺ 112 (base peak 84). This mass spectrum is similar to that obtained for 5-fluoronorbornene.

synthesize the 2-deuterionorbornene proved to be hazardous and quite unpredictable. In one case, the reaction was cooled too much (-70°C) while the n-butyl chloride was added dropwise to the stirred sodium metal suspension. At this cold temperature an immediate conversion to n-butyl sodium apparently did not occur causing a build-up of unreacted n-butyl chloride in the sodium metal suspension. Once reaction began, it quickly exothermed uncontrollably and exploded violently. Proper shielding and precautions should be instituted when attempting the described metalation reaction.
\[
\text{F} \xrightarrow{\text{Xe}} \text{F} \quad \text{F}_3\text{B} \xrightarrow{\text{O}(\text{CH}_2\text{CH}_3)_2} \text{Xe} \quad \text{BF}_4^- + \text{O}(\text{CH}_2\text{CH}_3)_2
\]

**Scheme 1**

1. \(\text{F} \xrightarrow{\text{Xe}} \text{F} \)
2. \( \text{F} \)
3. \( \text{F} \)
4. \( \text{F} \)

**Steps:**
- \( \text{BF}_4^- \) migration
- \( \text{H}-5,3 \)-migration
- \( \sigma-4,3 \)-shift
- \( \text{H}-5,4 \)-migration
If initial $1$ product (SCHEME 1)

initial $2$ product (SCHEME 1)

isomerized 1 product

initial $1$ products (SCHEME 1)

initial $3$ product (SCHEME 1)

isomerized 1 product

initial $2$ product (SCHEME 1)

initial $3$ product (SCHEME 1)