tional Institutes of Health (Grant GM 15997) for financial support.

Registry No. 1, 3031-15-0; 2, 36230-30-5; 3, 18623-61-5; 4, 71185-22-3; 5, 71185-23-4; 6, 71185-24-5; 7, 71185-25-6; 8, 71185-26-7; 9 isomer 1, 71185-27-8; 9 isomer 2, 71185-28-9; 10, 71185-29-0; 11, 71185-30-3; 12, 71185-31-4; 13, 71185-32-5; 14, 2717-39-7; 15, 71185-33-6; 16, 71185-34-7; methyl iodide, 74-88-4; trimethylchlorosilane, 75-77-4; 6,7-bis(bromomethyl)-1,2,3,4,5,8-hexamethylnaphthalene, 62571-66-8; 6,7-bis(deuteriomethyl)-1,2,3,4,5,8-hexamethylnaphthalene, 71185-35-8.

Xenon Difluoride Fluorination. 3. Mechanism and Selectivity of Boron Trifluoride Etherate Catalysis in the Norbornene Model

Scott A. Shackelford[1]

Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory (AFSC), USAF Academy, Colorado 80840

Received December 5, 1978

The boron trifluoride etherate initiated fluorination of norbornene with xenon difluoride in dichloromethane solvent selectively produces the novel compound 2-*exo*,5-*exo*-difluoronorbornane and its analogues 2-*endo*,5-*exo*-difluoronorbornane isomer. Initially the two 2,5-difluoronorbornanes represent about half of 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 and produces 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 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.

A previously reported open-system, bench-top procedure proved xenon difluoride to be a safe direct fluorinating reagent for aliphatic alkenes.[2] This convenient procedure employed boron trifluoride etherate to catalytically initiate direct alkene fluorination in a dichloromethane suspension. It was conducted in standard chemical glassware and required only such general items as a drybox for storing and weighing the xenon difluoride plus a bench-top fume hood. When norbornene was fluorinated by this procedure, an unprecedented high yield of 2-*exo*,5-*exo*-difluoronorbornane (**1**) and its analogous 2-*endo*,5-*exo* isomer (**2**) resulted.[3] This provided a distinct contrast to previously reported halogen and interhalogen additions to norbornene that selectively produce the *anti*- and *syn*-2,7-dihalonorbornane isomers through an ionic mechanism or the 2-*exo*,3-*exo*- and 2-*endo*,3-*exo*-dihalonorbornanes from a radical pathway.[4-10] Two past norbornene fluorinations produced three major products common to each reaction. Fluorination with lead tetraacetate/hydrogen fluoride in a Freon 112/dichloromethane solvent[9] and a more recent fluorination using difluoroiodobenzenes with a dichloromethane/hydrogen fluoride solvent[10] both afforded the ionically rearranged 2-*exo*,7-*anti*-difluoronorbornane **3** and 2-*exo*,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 nortricyclyl fluoride **11** as its major product. The 2,7-, 2,5-, and 2,3-difluoronorbornane isomer sets comprised the six additional isolated products.[11]

The boron trifluoride etherate catalyzed fluorination of norbornene with xenon difluoride represents the first

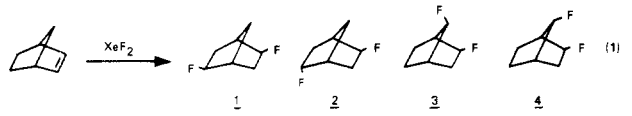
Table I. Difluoronorbornane Isomer Product Distribution from Boron Trifluoride Etherate Catalysis in CH_2Cl_2 Solvent

run	conditions[a]	1	2[g]	3	4	5	6	7	11
1	A	98.5		1.5	0	0	0	D	0
3	A	45	17	38	0	0	0	D	0
4	A	66.5	30	3	0	0	0	D	0
5	A	64	29	7	0	0	0	D	0
6	A (dark)	65	31	4	0	0	0	D	0
7	B[b]	58	26	3	0	0	0	13	0
	C[c]	24.5	26	43	7	0	0	0	0
8	B[d]	62	26	3	0	0	0	9	0
	C[e]	40	17	31	12	0	0	0	0
9	C[f]	22	26	42	9	0	0	0	0
10	A (no catalyst)	19	28	37	5	0	4	0	8
	(HF catalyst)[11]	11	20	19.5	6	2	3.5	0	38

[a] A, −78 °C to room temperature, 20-22 h; B, −46 °C to room temperature, 20-22 h; C, −46 to −39 °C, 1 h; D, not determined. [b] Product percentages change to 66% for **1**, 30% for **2**, and 4% for **3** when unknown **7** is not considered. [c] −43 to −39 °C during XeF_2 consumption. [d] Product percentages change to 68% for **1**, 28% for **2** and 4% for **3** when unknown **7** is not considered. [e] −46 °C during XeF_2 consumption. [f] −41 °C during XeF_2 consumption. [g] Combined.

(1) Currently a USAF/AFSC Exchange Scientist and presently located at DFVLR/Institut für Chemische Antriebe und Verfahrenstechnik, D-7101 Hardthausen am Kocher, Federal Republic of Germany.
(2) S. A. Shackelford, R. R. McGuire, and J. L. Pflug, *Tetrahedron Lett.*, 363 (1977).
(3) S. A. Shackelford, *Tetrahedron Lett.*, 4265 (1977).
(4) H. Kwart and L. Kaplan, *J. Am. Chem. Soc.*, **76**, 4072 (1954).
(5) M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 4293 (1965).
(6) F. H. Dean, D. R. Marshall, E. W. Warnhoff, and F. L. M. Pattison, *Can. J. Chem.*, **45**, 2279 (1967).
(7) D. D. Tanner and G. C. Gidley, *J. Org. Chem.*, **33**, 38 (1968).
(8) D. R. Marshall, P. R. Warnhoff, E. W. Warnhoff, and J. R. Robinson, *Can. J. Chem.*, **49**, 885 (1971).
(9) D. D. Tanner and P. Van Bostelen, *J. Am. Chem. Soc.*, **94**, 3187 (1972).
(10) A. Gregorcic and M. Zupan, *Bull. Chem. Soc. Jpn.*, **50**, 517 (1977).
(11) M. Zupan, A. Gregorcic, and A. Pollak, *J. Org. Chem.*, **42**, 1562 (1977).

selective high-yield synthesis of 2-*exo*,5-*exo*-difluoronorbornane (**1**) and 2-*endo*,5-*exo*-difluoronorbornane (**2**).[3] When this reaction is conducted over a 20–22-h period, the two combined 2,5 isomers represent 93% or more of the difluoride products and 87–91% of the total reaction products (Table I). 2-*exo*,7-*anti*-Difluoronorbornane (**3**) is the only other difluoride detected as a minor product.[12] Quenching a portion of this same reaction after only 1.25 h produces four initial difluoride products (eq 1). The



2,5-difluoronorbornane isomers **1** and **2** comprise slightly more than half of the fluorinated reaction products. The 2,7-difluoronorbornanes **3** and **4**, commonly the major products in nearly all other norbornene fluorinations, halogenations, and interhalogenations, represent the remaining two products.[13] The disappearance of the 2,7-difluoronorbornane isomers **3** and **4** during the extended reaction time results from a stereospecific isomerization that produces additional 2,5-difluoronorbornane products **1** and **2**. This paper outlines an unambiguous deuterium isotope assisted identification of the unique 2,5-difluoronorbornane isomers **1** and **2** that are available as the exclusive products in boron trifluoride etherate initiated XeF_2 fluorination of norbornene.[11,14] Deuterium labeling is employed further to elucidate the initial fluorination mechanism plus the subsequent Lewis acid isomerization pathway. These two reactions are jointly responsible for selective production of the 2,5-difluoronorbornanes. Finally, catalyst/solvent variation effects are outlined that demonstrate surprising major isomer reversals that could prove significant in correlating reaction conditions with fluorinated product control.

Results and Discussion

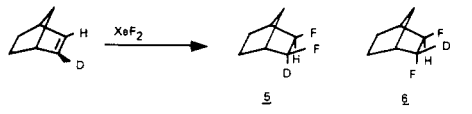
Deuterium Labeling Study. Depending upon the reaction conditions imposed, direct xenon difluoride fluorination of norbornene by boron trifluoride etherate initiation in a dichloromethane suspension produced either three or four difluoronorbornane compounds (**1**–**4**) (runs 7 and 8, Table I). The identities of **3** and **4** proved to be the previously reported 2-*exo*,7-*anti*- and 2-*exo*,7-*syn*-difluorobornane isomers, respectively;[9] however, compounds **1** and **2** represented an unreported isomeric pair.[14] The symmetrical pattern displayed by the ^1H and ^{19}F 2-*exo*,3-*exo*- spectra of **1** suggested this new difluoride to be either 2-*exo*,5-*exo*-difluoronorbornane or the analogous 2-*exo*,3-*exo* isomer.[15] Compound **2** was presumed to be a corresponding endo–exo isomer. Its somewhat similar *gem*-HF ^1H NMR splitting pattern to the geminal HBr pattern of a minor 2-*endo*,5-*exo*-dibromonorbornane product previously isolated[16] further supported this assignment. A dehydrofluorination of **1** yielded a fluoronorbornene which by itself failed to conclusively differentiate between 2-*exo*,5-*exo*- and 2-*exo*,3-*exo*-difluoronorbornane. Spectral characterization to identify **1** and **2** was also inadequate because a comparison of all four potential isomers was not possible from this selective reaction system. Therefore, deuterium-labeled norbornene was used to verify the isomeric identity of **1** and **2**.

Table II. Predicted and Actual Initial Product ^1H NMR Signals from 2-Deuterionorbornene/XeF_2 Fluorination

product	*gem*-HF	bridgehead	bridge[a]	norbornyl skeleton
6 pred	1.0	2.0		6.0
5 pred	1.0	2.0		6.0
4 pred	1.5	1.5		6.0
actual[b]	1.5	1.5		6.0
3 pred	1.0	1.5	0.5	6.0
actual[b]	1.0	1.5	0.5	6.1 (6.06)
2 pred	1.5	2.0		5.5
actual[b]	1.5	2.0		5.5
1 pred	1.5	2.0		5.5
actual[b]	1.4	2.0		5.6

[a] Only the 2-*exo*,7-*anti*-difluoronorbornane isomer **3** possesses a chemical shift which allows separate evaluation of the bridge proton(s). [b] Reaction conditions: −43 to −39 °C, 1.25 h all XeF_2 consumed.

Fluorination of 2-deuterionorbornene was conducted under the same reaction conditions used with unlabeled norbornene. A portion of this reaction mixture quenched after 1.25 h; then, the initial reaction products were isolated and analyzed (run 7C). The absence of a nuclear magnetic resonance 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 (eq 2).[5] These compounds would reveal a



gem-HF ^1H NMR signal of half the integrated value (one proton) of their analogous unlabeled compounds (Table II). Clearly the ^1H NMR results outlined in Table II reveal that the 2-*exo*,3-*exo*- and 2-*endo*,3-*exo*-difluoronorbornanes are not produced. Instead, fractional *gem*-HF ^1H NMR values appear for both the **1** and **2** isomers. Such fractional values must result from a norbornene structural rearrangement that is characteristic of an ionic reaction mechanism. Thus, **1** and **2** represent the rearranged 2-*exo*,5-*exo*-difluoronorbornane and 2-*endo*,5-*exo*-difluoronorbornane isomers, respectively. The simultaneous early formation of both ionically generated 2,7-difluoronorbornane isomers **3** and **4** with **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] strongly support an exclusive ionic fluorination mechanism.

Additional ^1H NMR analysis from the 2-deuterionorbornene/xenon difluoride fluorination permitted a mechanistic elucidation of both the reaction mechanism's selectivity and its subsequent preferential isomerization pathway. Scheme I represents an ionic mechanism consistent with the rearranged deuterium atom of all four initially formed products (**1**–**4**). The amount of deuterium

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

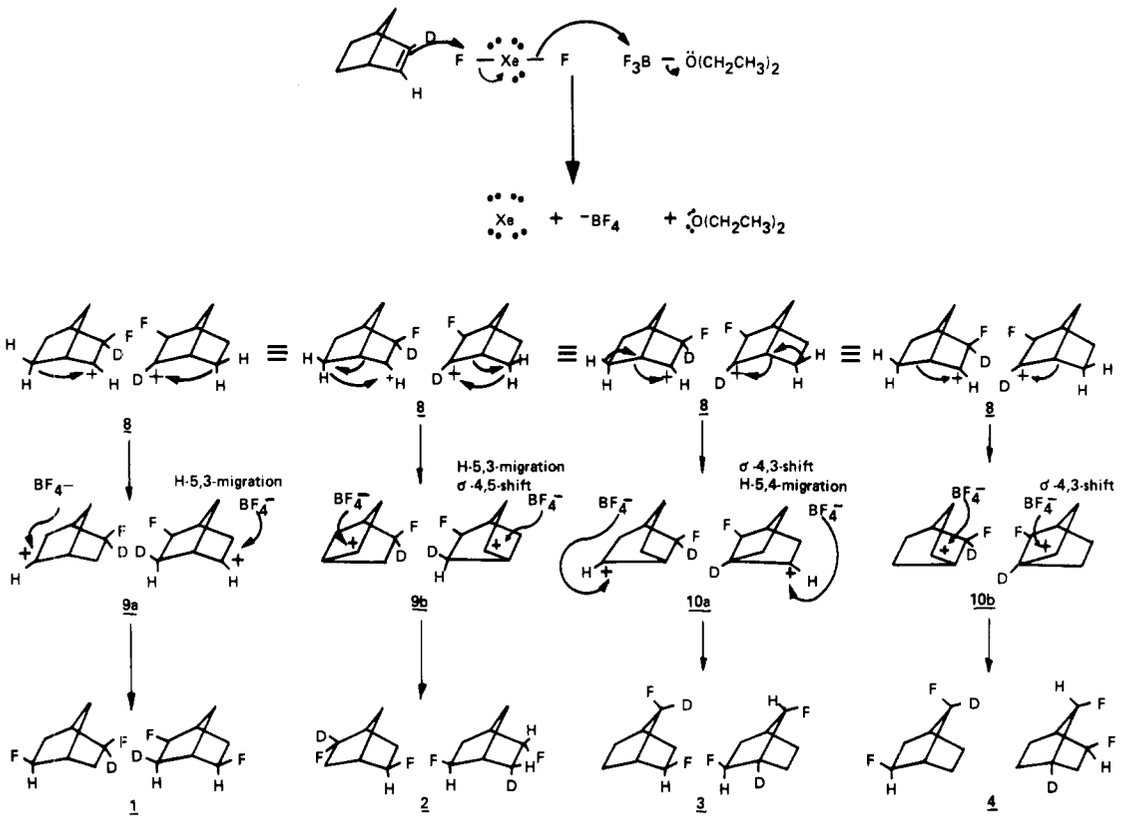
(13) Additional investigation after ref 3 revealed that 2-*exo*-7-*syn*-difluoronorbornane (**4**) initially forms a minor product (7–12%) but disappears under the extended 20–22-h reaction conditions.

(14) Subsequent to completing the deuterium labeling study described herein and in ref 3, Zupan, Gregorcic, and Pollak reported the spectroscopic characterization of both 2,5-difluoronorbornane isomers **1** and **2**. Both the spectroscopic characterization (ref 11) and this complementary deuterium labeling study agree.

(15) A pictorial ^1H NMR spectrum of **1** is presented in ref 3.

(16) Pictorial ^1H NMR spectra of **2** and 2-*endo*,5-*exo*-dibromonorbornane are presented in ref 3 and 8, respectively.

Scheme I



rearrangement predicted by Scheme I is recorded in Table II, and excellent agreement is obtained between that which is predicted and that which is found from ^1H NMR analysis. The slightly low *gem*-HF and high norbornyl skeleton ^1H NMR integration for **1** possibly results from a larger degree of initial fluorination at the deuterium-labeled vinyl carbon. After the initial fluorination that produces a concomitant generation of species **8** and the tetrafluoroborate anion, species **8** rapidly rearranges by one of two competing pathways. A 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 a σ-bond 4,3 shift. These competing rearrangements of species **8** result from the energetically unfavorable situation encountered in electrophilic additions when a positive charge resides adjacent to a fluorine-bonded carbon atom.[17]

Scheme I also reveals three possible contributing factors 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 by rearrangement of the initially formed **8** species. The fluorinated carbonium ions **9a** and **9b**, which produce the 2,5-difluoronorbornane isomers **1** and **2**, respectively, possess positive charge density which resides the farthest possible distance from the fluorine-bonded carbon atom. In this case, the positive charge density is situated three carbon centers away. The **10**-type fluorinated carbonium ion, which yields both 2,7-difluoronorbornanes, possesses its positive charge closer to the fluorine-bearing carbon atom only two centers away. The extremely high electron-withdrawing properties of the bonded fluorine atom in **8** must be sufficiently long range in the norbornyl structure to require the additional stabilization provided by the **9**-type species over the other rearranged **10**-type carbonium ions.[18]

Apparently, such additional stabilization is not required when norbornene additions are conducted with the other less electronegative halogens. A second factor contributing to the high degree of **1** and **2** isomer 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**–**3** constitute 90% 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 and fluorinations have often produced the analogous syn-2,7 isomer as the major dihalide product.[4,5,8–10] The third factor involves the role of the boron trifluoride etherate catalyst. The initial concomitant tetrafluoroborate anion formation could also promote the selective rearrangement of **8** to the most stable **9** species. This stable counteranion could provide a temporary site upon which the second fluorine atom from XeF_2 resides during the time required for rearrangement. Naturally, the attacking fluoride ion upon species **9** and **10** can be one of the fluorine atoms comprising the tetrafluoroborate anion and is not necessarily the same fluorine originally bonded in the xenon difluoride reactant. Evidence for the tetrafluoroborate anion formation and its participation is discussed and verified in the catalyst/solvent variation study outlined herein.

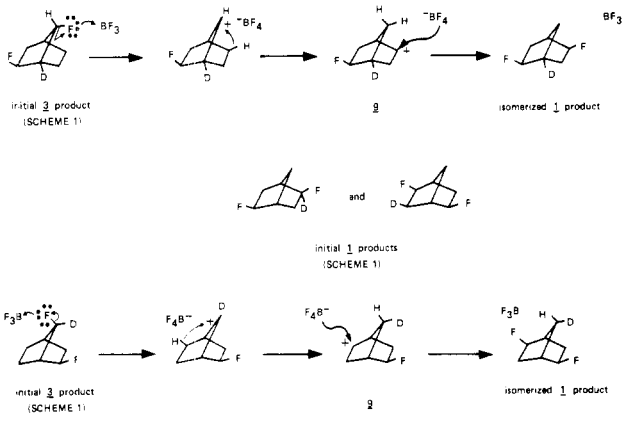
(17) R. D. Chambers, "Fluorine in Organic Chemistry", Wiley, New York, N.Y., 1973, p 171.

(18) An example of another long-range influence involving this fluorine atom, which covers more than two atomic centers, can be seen in the ^1H NMR spectrum of 5-*exo*-fluoronorborn-2-ene where the two vinyl protons differ in chemical shift by 24 Hz.

Table III. Proton Magnetic Resonance Analysis of Deuterium Atom Changes in Isomer 1 by $BF_3 \cdot O(CH_2CH_3)_2$-Assisted Isomerization

reacn cond	*gem*-HF	bridge-head H	norbornyl skeletal H
A, 1.25 h (−43 to −39 °C)	1.4	2.0	5.6
B, 21.25 h (−43 to room temp)	1.5	1.9	5.6
predicted change (A to B) by Scheme II	increase	decrease	no change

Scheme II



The tetrafluoroborate anion also participates in the selective isomerization of the *anti*-2,7-difluoronorbornane **3** mostly to 2-*exo*,5-*exo*-difluoronorbornane (**1**) and partly to 2-*endo*,5-*exo*-difluoronorbornane (**2**). A review of Table I illustrates that runs 1–6, 7B, and 8B are very consistent in the percentage of products **1**–**3** initially produced; however, run 3 provided an exception. Since neither varying the concentration of the boron trifluoride etherate catalyst (runs 1, 4, and 5)[19] 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 half of the reaction solution was removed and quenched 1.25 h after the addition and disappearance of the XeF_2 reagent (runs 7C and 8C). The remainder of the reaction solutions was allowed to proceed for a total of 20–22 h (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 3–4% of **3** isomerized mostly to **1** and partly 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 by GLPC revealed unisomerized **3** (4%), **1** (65%), **2** (29%), and the unidentified isomer **7** with a high GLPC retention time.[12] Additionally, ^1H NMR analysis of the 2-deuteronorbornene/XeF_2 fluorination reaction was used to trace the progress of this stereospecific isomerization of **3** to **1**. Reaction condition A in Table III represents the ^1H NMR integration of the initially formed **1** isomer listed in Table II and predicted in Scheme I. Reaction condition B displays the change in ^1H NMR integration of **1** after isomerization. Isomer **1** was chosen for this comparison because it is the predominant isomer produced during this selective isomerization of species **3**. Comparing both **1** isomers initially produced in Scheme I with the two **1** isomers predicted by the Scheme II pathway reveals that the selective isomerization of **3** to **1** should decrease the ^1H NMR at the bridgehead position where no deuterium atom initially existed. Additionally, the *gem*-HF ^1H NMR signal should increase by producing two new **1** isomers with no deuterium atom incorporated at this position, and no change should occur in the ^1H NMR signal in the remaining 2-*exo*,5-*exo*-difluoronorbornane structural skeleton. These changes outlined by Scheme II agree with those actually found. Nonselective isomerization of difluoronorbornane isomers in the presence of the Lewis acid hydrogen fluoride has been reported[11] and was attributed to an analogous process effected through an ionic hydrogen fluoride catalyzed hydrolysis of benzyl fluoride.[20] Just as the hydrogen fluoride Lewis acid 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 molecule could be expected to behave similarly. Formation of the stable tetrafluoroborate anion provides a stable species to transport the fluoride ion during isomerization and, once again, allows formation of the same stable **9** monofluoronorbornyl cation (Scheme I) that places the positive charge density three carbon atoms from the fluorine-bonded carbon. Continual overnight room temperature isomerization through species **9** (Scheme II) promotes the selective ionic isomerization which 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 pathway.

Table IV. XeF_2/Norbornene Fluorination Product Percentages: Catalyst and Solvent Variation Data[a]

catalyst	solvent	1	2	3	4	5	6	11	12[b]
blank	CH_2Cl_2	19	28	37	5	0	4	8	0
blank	diethyl ether	9	11	48	16	0	3	12	3
$LiBF_4$	diethyl ether	27	15	18	7	0	0	17	15[c]
$BF_3 \cdot O(CH_2CH_3)_2$	diethyl ether[e]	14	12	44	21	0	0	7	0[d]
$BF_3 \cdot O(CH_2CH_3)_2$	diethyl ether[f]	16	13	43	19	0	0	6	3

[a] Differences 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.[29] [d] Less than 1% (0.3%). [e] −44 °C to room temperature, 11 h. [f] −44 °C to room temperature, 24 h.

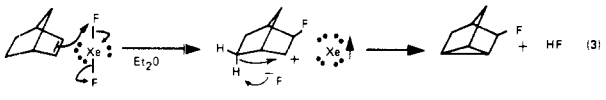
Catalysis/Solvent Studies. Comparison of the boron trifluoride etherate catalyzed reactions 1–9 (Table I) with a blank XeF_2/norbornene fluorination (reaction 10) shows that the greatest amount of isomer **1** is afforded by the selective boron trifluoride etherate assisted isomerization. However, the boron trifluoride etherate catalyzed reactions 7C, 8C, and 9C display some increased selectivity of **1** over that exhibited by the noncatalyzed reaction 10. Scheme I 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, we catalyzed a xenon difluoride fluorination of norbornene 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

(19) In runs 3, 5, and 6 (Table I) 0.20 g (1.41 mmol) of $BF_3 \cdot OEt_2$ was employed. Runs 1 and 4 contained 0.10 g (0.71 mmol) of $BF_3 \cdot OEt_2$.

(20) C. G. Swain and R. E. T. Spalding, *J. Am. Chem. Soc.*, **82**, 6104 (1960).

of this inorganic catalyst. Table IV reveals that the presence of the tetrafluoroborate anion significantly effects production of 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-difluoronorbornanes 3 and 4. However, an absence of the tetrafluoroborate anion in diethyl ether solvent gave product 1 as the minor difluoride, and both 2,7-difluoronorbornanes 3 and 4 significantly predominated over the 2,5-difluoronorbornanes 1 and 2. This comparative result strongly supports tetrafluoroborate anion formation as being one significant factor in the selective synthesis of 2-*exo*,5-*exo*-difluoronorbornane (1). It follows that the tetrafluoroborate anion from the catalytic lithium salt introduces the second fluorine atom into both types of monofluoronorbornyl cation species 9 and 10 in a manner analogous to that illustrated in Scheme I. The tetrafluoroborate anion continually is replenished by the xenon difluoride reagent as the XeF_2 molecule simultaneously introduces the first fluorine atom into the norbornene molecule to generate species 8–10.

Significant to the diethyl ether solvolyzed xenon difluoride fluorination of norbornene is the drastic product reversal that resulted when the catalytic species were varied or omitted entirely (Table IV). While reaction with the lithium tetrafluoroborate favored production of the 2,5-difluorides 1 and 2, the uncatalyzed fluorination effected a large selectivity for the 2,7-difluoride products 3 and 4. Such isomeric control and reversal in this fluorination is surprising and could be a consequence of at least two considerations. A greater solvating power of diethyl ether solvent over dichloromethane toward intermediate 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 significant amount of nortricyclyl fluoride 11 as a fluorination product in the blank diethyl ether solvent (Table IV) also supports this effect. The additional ionic stabilization provided by diethyl ether toward species 8 enhances the emergence of a competing fluorination–elimination pathway. Equation



8 11

3 illustrates a plausible fluorination–elimination pathway that incorporates very well into the common mechanistic process outlined in Scheme I. The second fluoride species from XeF_2 may fluorinate the rearranged cationic 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 nortricyclyl fluoride 11. Analogous eliminations previously have been reported with xenon difluoride/alkene fluorinations that produce monofluoroalkenes[2] or other halogenated alkenes.[21] Secondly, the role of tetrafluoroborate anion is greatly diminished in the diethyl ether solvent unless the tetrafluoroborate anion is directly introduced. Use of boron trifluoride etherate effects little change in the 3 and 4 product predominance when compared to the uncatalyzed fluorination in diethyl ether (Table IV). 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 II. Finally, it should be noted that the lack of tetrafluoroborate counterion formation also can enhance product 11 formation. When no boron trifluoride etherate is present or when any possible boron trifluoride etherate molecules can be complexed with diethyl ether solvent to prevent BF_4^- formation with the second fluoride species of XeF_2, the fluoride ion is free for direct participation in the elimination reaction that produces 11 (eq 3).

(21) M. Zupan and A. Pollak, *J. Fluorine Chem.*, 8, 275 (1976).

Conclusion

The boron trifluoride etherate initiated reaction between alkenes and the easily handled XeF_2 reagent afford a safe and direct open-system fluorination method. This convenient bench-top fluorination proceeds through an ionic reaction mechanism and can provide a high degree of product selectivity or flexibility. Scheme I outlines this ionic mechanism which was directly elucidated from the XeF_2 fluorination of 2-deuterionorbornene. Initially, four difluoronorbornane products form when this XeF_2 fluorination is conducted in a CH_2Cl_2 solvent suspension. The novel 2,5-difluoronorbornanes 2-*exo*,5-*exo*-difluoronorbornane (1) and 2-*endo*,5-*exo*-difluoronorbornane (2) collectively predominate over the 2-*exo*,7-*anti*-difluoronorbornane (3) and 2-*exo*,7-*syn*-difluoronorbornane (4) isomers. After initial fluorination to form species 8 (Scheme I), competitive rearrangements proceed by either a 5,3-hydride migration or a σ-bond 4,3 shift to produce intermediate species 9 and 10, respectively. Secondary fluorination of the 9 intermediates provides both 2,5-difluoronorbornanes, while the 10 intermediates yield the two 2,7-difluoronorbornanes.

The preferential formation of species 9 over 10 is without precedence in other fluorination, interhalogenation, and halogenation additions to norbornene. Species 9 results from the extremely high electron-withdrawing property of the 2-exo-bonded fluorine atom which destabilizes the adjacent positively charged carbon atom in the monofluoronorbornyl carbonium ion 8. Species 8 rapidly rearranges to both 9 and 10 and minimizes this destabilizing effect by shifting the positive charge a further distance from the fluorine-bearing carbon atom. However, in the monofluoronorbornyl structure this destabilizing electron-withdrawing effect is sufficiently long range to require the additional stabilization that 9 provides over 10 when the positive charge resides three carbon centers from the 2-*exo*-fluoro position instead of two carbon centers away. The simultaneous formation of the stable tetrafluoroborate counterion also contributes to the unprecedented high yield of the novel 2,5-difluoronorbornanes. The BF_4^- anion provides the second fluorine atom from XeF_2 a stable place to reside during the time required for species 8 rearrangement to 9. A favorable steric attack that minimizes repulsive interactions between the high electron density of the bonded fluorine atom in 9 and the attacking fluoride ion from BF_4^- further aids in 1 and 2 formation. Extended reaction times in CH_2Cl_2 solvent result in a Lewis acid catalyzed isomerization that converts the initially formed 2,7-difluoronorbornanes 3 and 4 into the 2,5-difluoronorbornane isomers 1 and 2. A nearly exclusive distribution (93% plus) of 1 and 2 results through the ionic isomerization pathway illustrated by Scheme II. This isomerization pathway owes its stereospecificity to the generation of the highly stabilized species 9 intermediate formed during boron trifluoride etherate's conversion to the stable tetrafluoroborate anion.

The initial formation of the 2,7-difluoronorbornanes **3** and **4** by a structural rearrangement, associated only with an ionic mechanism in other norbornene halogenations, verifies this boron trifluoride etherate initiated XeF_2 fluorination reaction as an ionic process. This was established further from a separate photochemically induced XeF_2 fluorination of norbornene which was conducted under reaction conditions designed to proceed through a radical pathway.[22] Photochemical initiation produced only the complementary, radically generated 2-*exo*,3-*exo*-difluoronorbornane (**5**) and 2-*endo*,3-*exo*-difluoronorbornane (**6**) isomers as pure difluoronorbornane addition products.

A surprising product reversal is effected by diethyl ether solvent, and the stereospecific Lewis acid isomerization nearly disappears. The 2,7-difluoronorbornanes **3** and **4** collectively constitute more than twice the amount of 2,5-difluoronorbornanes **1** and **2**. This results from the greater solvating power that diethyl ether possesses toward the intermediate monofluoronorbornyl carbonium ion **10**. The enhanced solvation stabilizes species **10** sufficiently that the additional stabilization gained from species **9** is largely compensated, and a much lower concentration of **9** results. The infinitely high concentration of the diethyl ether solvent molecules also causes a continual complexation of the boron trifluoride molecules and inhibits BF_4^- formation. This constant complexation eliminates the effective contribution of BF_4^- formation to the selective production of 2,5-difluoronorbornane isomers as outlined in either the initial fluorination mechanism (Scheme I) or the selective isomerization pathway (Scheme II).

The mechanistic elucidation of this boron trifluoride etherate initiated fluorination, plus its susceptibility to isomerization, catalyst, and solvent influences, outline key chemical considerations for planning future alkene reactions with xenon difluoride. By extending these considerations, one can readily explain the different major products previously obtained with 1,2-dibromoethene and 1-decene.[2] Careful evaluation of the ionic mechanisms encountered during initial fluorination and the subsequent boron trifluoride assisted product isomerization, plus an awareness of possible solvent/catalyst variation effects, will provide necessary insights to attain reaction selectivity and to maximize product yields in future syntheses of novel and important fluoroorganic compounds.

Experimental Section

General Procedures. In all cases the detailed reaction procedures described under method A were followed when storing, weighing, and transferring the solid XeF_2 and when introducing the norbornene, catalyst, and solvent into the reaction system.

Burdick & Jackson Distilled-in-Glass acetone was used as received to rinse and dry all items. 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 4A molecular seives in a Fisher Scientific Co. Isolator/Lab drybox. The drybox provided a dry N_2 atmosphere under which the solid $XeFe_2$ reagent was stored in a Teflon screw-top bottle. The diethyl ether solvent was Mallinckrodt 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.[23] The $LiBF_4$ (PCR, Inc.) was used as received, but the norbornene (Aldrich Chemical Co.) was fractionally distilled to a waxy colorless solid. The XeF_2 displayed 100% purity by mass spectral analysis with an instrument possessing a 99.9% detection limit. *Care must be taken to use only pure $XeFe_2$ in the procedure described. Samples of XeF_2 that are contaminated with trace amounts of XeF_4 will be explosive if the XeF_4 contaminant air hydrolyzes to XeO_3.*[2]

All glassware, capillary pipets, Teflon-coated magnetic stir bars, and Teflon-coated spatulas[24] were cleaned by a method proved to be successful for aqueous XeO_3 reactions.[25] A 7-L stainless steel beaker was 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 twice in succession with distilled H_2O and acetone. After air-drying, a 35-mL single-necked round-bottomed flask, a Teflon-coated magnetic stir bar, a 14/20 ground-glass stopper, a spatula, and a graduated cylinder were all placed into the Fisher Isolator/Lab drybox to stand overnight. All other glassware and equipment remained outside the drybox 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 and 5992A GC/MS terminal system or on a du Pont 21-491 dual-beam mass spectrometer. With the latter instrument, product volatility required direct injection, using methanol (M^+ at m/e 32) solvent. Nuclear magnetic resonance (^1H and ^{19}F) analyses were accomplished with a Varian T-60 spectrometer in $DCCl_3$ solvent. The ^1H NMR spectra were always referenced to Me_4Si. 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 Chromosorb W column. A variable column temperature range from 95 to 195 °C was used. All products were isolated from this GLPC column in small glass traps submerged in liquid N_2. 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 percents of all isolated products contained in Tables I and IV represent 86–94% of the total fluorinated products in the boron trifluoride etherate catalyzed, CH_2Cl_2 solvated reactions (95% uncatalyzed), 87–92% in the boron trifluoride etherate catalyzed, diethyl ether solvated reaction (63% uncatalyzed), and 83% in the $LiBF_4$ catalyzed, diethyl ether solvolyzed fluorination. All elemental analyses were accomplished by Gailbraith Laboratories.

Direct Fluorination of Norbornene with Xenon Difluoride in CH_2Cl_2 Solvent. Method A. Under a dry N_2 atmosphere, a 35-mL 14/20 single-necked round-bottomed order. was charged with a Teflon-coated magnetic stir bar and 0.35 g (2.07 mmol) of XeF_2. A small 14/20 jointed powder funnel and spatula were used to help transfer the XeF_2 into the 35-mL reaction flask. The 35-mL flask was then immediately stoppered with a 14/20 ground-glass stopper. Neither the flask nor the stopper was treated with any silicone vacuum grease. The spatula and funnel, used to transfer the XeF_2, were rinsed with CH_2Cl_2 to destroy any residual XeF_2.[26] Seven milliliters of the treated CH_2Cl_2 solvent was poured into a 50-mL graduated cylinder, and the drybox was then purged three successive times with fresh N_2. The spent N_2 was pumped directly into a fume hood exhaust. The stoppered 35-mL reaction flask and the CH_2Cl_2-containing graduated cylinder were removed from the drybox and hand-carried to a bench-top fume hood. The 35-mL reaction flask was submerged into a dry ice/acetone cooling bath (ca. −78 °C) to reduce the vapor pressure of the XeF_2 prior to the ground-glass stopper removal. Within 15 s the stopper was removed and immediately replaced with a 15-mL pressure-equalized addition funnel fitted with a Drierite-containing drying tube. All joints in this addition funnel/drying tube assembly had been greased with silicone vacuum grease prior to the XeF_2 weighing. The entire assembly was placed into the 35-mL reaction flask as one unit.

(22) R. A. Hildreth, M. L. Druelinger, and S. A. Shackelford, Fourth Winter Fluorine Conference, Daytona Beach, Fla., Jan 28–Feb 2, 1979.
(23) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, N.Y., 1967, p 1210.
(24) Initially only Teflon-coated stainless steel spatulas were used to handle, transfer, and weight out the XeF_2 reagnet. Later it was found that ordinary clean, dry stainless steel spatulas were satisfactory.
(25) S. A. Shackelford and G. U. Yuen, *J. Org. Chem.*, **40**, 1869 (1975).
(26) At room temperature a 0.35-g sample of XeF_2 reacted with pure CH_2Cl_2 within 5 min and was totally consumed within 10 min: S. A. Shackelford, unpublished results.

Next, 0.18 g (2.14 mmol) of norbornene was weighed into 2 mL of CH_2Cl_2; then, the solution was transferred by capillary pipet into the 15-mL addition funnel. The drying tube was removed from the addition funnel during this transfer but was then replaced. The norbornene solution was added dropwise to the solid XeF_2 over a 5–10-min period, and the resulting heterogenous suspension was stirred as soon as mechanically possible. A small amount of CH_2Cl_2 (ca. 0.5 mL) was used to rinse the inside of the addition funnel and was also added to the reaction suspension at the same rate. Subsequently 0.10 g (0.17 mmol) of boron trifluoride etherate[19] was weighed into 2 mL of CH_2Cl_2; then, this solution was transferred into the 15-mL addition funnel. Within 5–10 min after the norbornene solution addition, the $BF_3{\cdot}OEt_2$ solution was added dropwise to the stirred norbornene/XeF_2 suspension. Again a small amount (ca. 0.5 mL) of CH_2Cl_2 was used to rinse the inner walls of the addition funnel and was added to the reaction suspension. The reaction was stirred at −78 °C for 5.5–6.5 h; the reaction was extremely slow. The dry ice/acetone cooling bath then was packed once more and insulated with towels. Over the following 15–16 h, the bath gradually warmed to room temperature, and all of the solid XeF_2 disappeared leaving a dark brown solution. A 30-mL separatory funnel was charged with 10 mL of distilled H_2O and 0.25 g of NaF to take up any possible HF formed. The reaction solution was added to the separatory funnel. The 35-mL reaction flask was rinsed with 2 mL of CH_2Cl_2, and this rinse was added to the separatory funnel. The CH_2Cl_2 solution was washed and separated. The aqueous wash was then extracted with 2 mL of CH_2Cl_2, and this was combined with the first CH_2Cl_2 portion. The combined CH_2Cl_2 portions were dried over anhydrous $MgSO_4$ and filtered. In several cases, in vacuo solvent removal was accomplished and afforded 0.10–0.18 g of a dark brown waxy solid. Usually, 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. mp 109–111 °C); ^1H NMR ($DCCl_3$) δ 5.12 (doublet of broadened singlets, J_d = 58 Hz, 1 H), 4.58 (doublet of multiplets, J_d = 58 Hz, 1 H), 2.46 (doublet of multiplets, J_d = 12 Hz, 2 H), 2.20–0.90 (multiplets, 6 H); ^{19}F NMR ($DCCl_3$) +50.8 ppm from C_6F_6 or +163.6 ppm from $CFCl_3$ (doublet of multiplets, J_d = 58.7 Hz); mass spectrum M^+ at m/e 132 (base peak at m/e 81). Anal. Calcd for $C_7H_{10}F_2$: C, 63.6; H, 7.64; F, 28.7. Found: C, 63.8; H, 7.44; F, 28.8.

2-*endo*,5-*exo*-Difluoronorbornane (**2**): volatile white solid, mp 105.0–107.0 °C; ^1H NMR[16] ($DCCl_3$) δ 4.94 (doublet of multiplets, J_d = 56 Hz, 1H), 4.80 (doublet of broadened doublets, J_d = 56 Hz, 1 H), 2.62 (multiplet, 2 H), 2.30–0.60 (multiplets, 6 H); ^{19}F NMR ($DCCl_3$) +30.6 ppm from C_6F_6 (doublet of multiplets, J = 58.6 Hz); mass spectrum M^+ at m/e 132 (base peak at either m/e 85 or 86). Anal. Calcd for $C_7H_{10}F_2$: C, 63.6; H, 7.64. Found: C, 61.8; H, 7.32.

2-*exo*,5-*exo*-Difluoronorbornane (**1**): volatile white solid, mp 106.0–107.2 °C; ^1H NMR[15] ($DCCl_3$) δ 4.48 (doublet of multiplets, J = 56 Hz, 2 H) 2.46 (multiplet, 2 H) 2.20–1.10 (multiplets, 6 H); ^{19}F NMR ($DCCl_3$) +3.0 ppm from C_6F_6 (multiplet resembling a quintet); mass spectrum M^+ at m/e 132 (base peak at either m/e 85 or 86). Anal. Calcd for $C_7H_{10}F_2$: C, 63.6; H, 7.64; F, 28.7. Found: C, 63.3; H, 7.45; F, 29.1; product **7**.[12]

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, a reaction aliquot was removed early, quenched, and analyzed. The remainder of the reaction solution was allowed to proceed as in method A. The temperature in the chlorobenzene/dry ice bath varied from −46 to −41 °C. In one case (Table I), a reaction at −43 °C gradually warmed to −39 °C during the 15–20 min of XeF_2 consumption; two other reactions remained at −41 and −46 °C during XeF_2 consumption. One hour and fifteen minutes after the addition of the $BF_3{\cdot}OEt_2$ solution, approximately half of the reaction solution (ca. 3 mL) was removed and placed into 10 mL of an aqueous NaF solution. After workup, this aliquot provided four products by GLPC analysis on the Carbowax 20M column in the following order: **3**, **2**, **1**, **4**. 2-*exo*,7-*syn*-Difluoronorbornane (**4**): volatile white solid; ^1H NMR ($DCCl_3$) δ 4.80 (doublet of broadened singlets with shoulders, J_d = 56 Hz, 2 H), 2.46 (doublet of multiplets, J_d = 12 Hz, 2 H), 2.12–0.66 (multiplets, 6 H); mass spectrum M^+ at m/e 132 (base peak at m/e 81). Note: Method B was used in the XeF_2 fluorination of the 2-deuterionorbornene sample.

No $BF_3{\cdot}OEt_2$ Catalysis. All procedures outlined in method A were followed identically with one exception. No boron trifluoride etherate catalyst was added. Instead a 2-mL CH_2Cl_2 solvent blank was added to the stirred norbornene/XeF_2 reaction suspension. Analysis with the Carbowax 20M GLPC column afforded six products in the order **11**, **6**, **3**, **2**, **1**, and **4**. 2-Nortricyclyl fluoride (**11**): very volatile white solid; ^1H NMR ($DDCl_3$) δ 4.68 (doublet of broadened singlets, J_d = 60 Hz, 1 H), 1.98 (doublet of broadened singlets, J_d = 12 Hz, 2 H), 1.28 (broadened singlet, 7 H); mass spectrum M^+ at m/e 112 (base peak at m/e 97).

2-*endo*,3-*exo*-Difluoronorbornane (**6**): volatile white solid; mass spectrum M^+ at m/e 132 (base peak at m/e 67 with m/e 68 as 82%); GLPC retention time on Carbowax 20M column identical with that of the major product of a photochemical initiated XeF_2/norbornene fluorination,[22] identified as 2-*endo*,3-*exo*-difluoronorbornane by ^1H NMR and mass spectral analysis.

Direct Fluorination or Norbornene with Xenon Difluoride in Diethyl Ether Solvent. Initial preparations and procedures were conducted identically with those outlined for method A in the CH_2Cl_2-solvolyzed reactions except that diethyl ether solvent was used in place of CH_2Cl_2.

Boron Trifluoride Etherate Catalysis. A 35-mL single-necked round-bottomed flask, containing a Teflon-coated magnetic stir bar and 0.35 g (2.07 mmol) of XeF_2, was submerged into a chlorobenzene/dry ice cooling bath (−44 °C). Next, 0.23 g (2.44 mmol) of norbornene in 2 mL of Et_2O was added dropwise to the XeF_2-containing reaction flask. Stirring was begun as soon as mechanically possible. Next, 0.1 g of $BF_3{\cdot}OEt_2$ in 2 mL of Et_2O was added to the stirred reaction suspension. A reaction aliquot at 2.33 h, analyzed by GLPC/MS, showed no difluoride products. A CCl_4/dry ice bath was substituted, and a homogeneous solution resulted. Some fluorinated products resulted at 4.75-h reaction time. After 10.5 h the cold bath had warmed to −5 °C, and the bath was removed. At 11.0 h half the reaction was removed for workup and analysis. The CCl_4/dry ice cold bath was again placed around the reaction flask and was then repacked with dry ice and insulated with towels. The aliquoted solution was washed with 10 mL of distilled H_2O containing 0.22 g of NaF, 0.20 g of KI, and 2 capillary pipet drops of 2 N H_2SO_4.[27] The ethereal layer was washed, and 1.5 mL of fresh Et_2O was used to extract the separated aqueous solution. The combined ethereal portions were dried over anhydrous $MgSO_4$ and filtered. Analysis by GLPC gave products that eluted from the Carbowax 20M column in the following order: **11**, **3**, **2**, **1**, and **4**. The remainder of the reaction was worked up after 24 h.

No Boron Trifluoride Etherate Catalysis. All reaction preparations and procedures were similar to the analogous $BF_3{\cdot}OEt_2$-catalyzed reaction; however, this uncatalyzed reaction proceeded much more slowly. Initially the 35-mL reaction flask and contents were cooled in an acetone/dry ice bath. After 4.75 h, the acetone/dry ice bath was repacked, insulated with towels, and warmed to room temperature over the next 16 h. At 28.5 h the colorless reaction solution began to turn yellow. At 46.5 h, the dark brown reaction solution was worked up and GLPC analyzed as described. 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 ($DCCl_3$) δ 4.62 (doublet of sharp multiplets, J_d = 57 Hz, 1 H), 2.44 (doublet of multiplets, J_d = 11 Hz, 2 H), 2.06–0.80 (multiplet, 8 H);[28] mass spectrum M^+ at m/e 114 (base peak at m/e 68).

Lithium Tetrafluoroborate Catalysis. The 35-mL reaction flask containing a Teflon-coated magnetic stir bar was charged

(27) The acidified KI was employed as a protective measure should any XeO_3 form from an undetected contaminant in XeF_2. Acidic KI converts XeO_3 immediately to Xe and O_2.

(28) This ^1H NMR spectrum was identical with a previously published ^1H NMR spectrum of 2-fluoronorbornane: P. v. R. Schleyer, W. E. Watts, M. B. Comisarow, R. C. Ford, Jr., and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5679 (1964).

with 0.35 g (2.07 mmol) of XeF_2 and placed into a chlorobenzene/dry ice (−44 °C) cooling bath. Next, 0.20 g (2.13 mmol) of norbornene was weighed into 4 mL of Et_2O and added dropwise to the XeF_2. Stirring was begun as soon as mechanically possible. Within 4.5 min after addition of the norbornene solution, 0.20 g of $LiBF_4$ solid was added directly to the stirred suspension with the aid of a 30-mL 14/20 jointed powder funnel. After 7.5 h solid XeF_2 was still present in the reaction suspension. The chlorobenzene/dry ice cold bath was repacked and insulated. After 23 h, the dark brown reaction solution was poured into 10 mL of distilled H_2O that contained 0.4 g of NaF. The etheral layer was washed and separated. An additional 5 mL of H_2O was added to the aqueous wash before extraction with 2 mL of Et_2O. The combined Et_2O portions were dried over anhydrous $MgSO_4$ and filtered. Seven products were isolated from the Carbowax 20 M GLPC column in the following order: **12**, **11**, unknown,[29] **3**, **2**, **1**, and **4**.

Dehydrofluorination of 2-*exo*,5-*exo*-Difluoronorbornane. A previously reported dehydrofluorination procedure that provided 7-*anti*-fluoronorbornene from **3** and 7-*syn*-fluoronorbornene from **4**, respectively,[9] was used to synthesize 5-*exo*-fluoronorbornene from 2-*exo*,5-*exo*-difluoronorbornane (**1**). Beginning with 0.103 g (0.777 mmol) of **1**, a 42% conversion to 5-*exo*-fluoronorborn-2-ene resulted. The 5-*exo*-fluoronorborn-2-ene was isolated by continuous CH_2Cl_2 extraction of the Me_2SO solvent and preparative GLPC with the Carbowax 20M column. This compound is a volatile white solid: ^1H NMR ($DCCl_3$) δ 6.32 (multiplet, 1 H), 5.88 (multiplet, 1 H), 4.72 (doublet of multiplets, J_d = 58 Hz, 1 H), 2.96 (unsymmetrical multiplet, 2 H), 1.94–1.02 (multiplets, 4 H); mass spectrum M^+ at m/e 112 (37%) with m/e 97 (53), 86 (66), 84 (100), 73 (84), and 66 (82).

Synthesis of 2-Deuterionorbornene.[30] A 100-mL three-necked round-bottomed flask was charged with 22.1 g (0.384 mol) of a 1-μm 40% Na dispersion (Gray Chemical, Inc.) in petroleum ether and mineral oil. The flask was fitted with an N_2 stopcocked inlet and identical outlet, plus an overhead mounted mechanical stirrer apparatus. Next, 20 mL of Distilled-in-Glass hexane treated with neutral alumina (pH 6.3) was added to the reaction flask. The flask was submerged into a CCl_4/dry ice cooling bath (−23 °C).

This cooled suspension was stirred at high speed while 12.0 g (0.130 mol) of *n*-chlorobutane was dried over 4A molecular seives and passed through neutral alumina (pH 6.3) prior to its combination with the hexane solvent. After all of the *n*-butyl chloride was added dropwise, the CCl_4/dry ice bath was replaced with an ice bath for 35 min. Next, the CCl_4/dry bath was again placed around the reaction flask, and 8 min later 12.0 g (0.128 mol) of norbornene in 15 mL of hexane was added dropwise to the stirred reaction suspension. The reaction solution was then stirred at ambient temperature for 22.5 h. Again, the CCl_4/dry ice bath was placed around the reaction flask for 10 min, and the system was opened to the atmosphere. Next 8.9 g of 98% D_2O *was very cautiously added dropwise* to the rapidly stirring suspension. *The reaction exothermed slightly after the first few drops of D_2O were added, but all material was contained in the reaction flask.* After D_2O addition, the cooling bath was removed, and the reaction was stirred at ambient temperature for 4.5 h. The reaction solution was transferred into a separatory funnel; then, 75 mL of H_2O and 10 mL of hexane were added to the funnel. A distinct organic layer separated; 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, dried over anhydrous $MgSO_4$, and filtered. The solvent was removed by fractional distillation. The undistilled liquid portion was then distilled through a microware short-path apparatus, and only the material that condensed in the water-cooled condenser was retained. Further deuteration of this 1.9-g sample met with failure; however, the 2-deuterionorbornene sample (0.7 g) was recovered and afforded the following analysis: ^1H NMR ($DCCl_3$) δ 6.04 (sharp multiplet, 1 H), 2.86 (sharp multiplet, 2 H), 1.86–0.66 (multiplets 6 H); mass spectrum M + 1 at m/e 96 (5.6), M^+ at m/e 95 (12.7), M − 1 at m/e 94 (7.5) with m/e 68 (43.0), 67 (100), and 66 (56.5).

Acknowledgment. Dr. R. A. Hildreth provided valuable discussion and assistance. Constructive discussions and support were received from Dr. B. A. Loving, Dr. M. L. Druelinger, Dr. J. E. Franz, and Dr. L. A. King. Mr. J. L. Pflug provided literature assistance and performed all NMR and mass spectral analyses. Mrs. B. Plonsky (USAFA) and Fr. E. von Bissingen (DFVLR) typed the manuscript. Mr. F. C. Kibler provided extensive technical assistance and necessary glass-blowing support.

Registry No. 1, 61091-30-3; **2**, 61026-29-7; **3**, 36914-49-5; **4**, 36914-50-8; **5**, 71042-31-4; **6**, 71075-21-3; **11**, 695-03-4; **12**, 765-92-4; 5-*exo*-fluoronorborn-2-ene, 71042-32-5; 2-deuterionorbornene, 694-94-0; XeF_2, 13709-36-9; norbornene, 498-66-8; boron trifluoride etherate, 109-63-7.

(29) This unknown trace product afforded a mass spectrum with M^+ at m/e 112 (base peak at m/e 84). This mass spectrum is similar to that obtained for 5-fluoronorborn-2-ene.

(30) J. E. Franz, C. Osuch, and M. W. Dietrich, *J. Org. Chem.*, **29**, 2922 (1964); A. A. Morton, M. L. Brown, M. E. T. Holden, R. L. Letsinger, and M. E. Maget, *J. Am. Chem. Soc.*, **67**, 2224 (1945); R. E. Finnegan and R. McNees, *J. Org. Chem.*, **29**, 3234 (1964). The sodium metalation reaction required to synthesize the 2-deuterionorbornene proved to be hazardous and quite unpredictable. In one case, the reaction was cooled too much (−78 °C) while the *n*-butyl chloride was added dropwise to the stirred sodium metal suspension. At this cold temperature an immediate conversion to *n*-butylsodium apparently did not occur causing a buildup 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.

The Alkoxycarbonyl Moiety as a Blocking Group. A Generally Useful Variation of the Malonic Ester Synthesis

Henry C. Padgett, Ivan G. Csendes,[1] and Henry Rapoport*

Department of Chemistry, University of California, Berkeley, California 94720

Received April 23, 1979

A new, generally useful malonic ester synthesis has been developed on the basis of the alkoxycarbonyl moiety as a blocking group. Thus trialkyl methanetricarboxylates, symmetrical or unsymmetrical, were converted to their stable, nonhygroscopic sodio salts which were readily alkylated with multifunctional halides. Further elaboration could be carried out on the side chain, and reversion to the malonate was effected by monodecarbalkoxylation. The deblocking step occurs easily on exposure to alkoxide, diisopropylamide, or boron trichloride. When one of the esters is *tert*-butyl, anhydrous formic or trifluoroacetic acid also effects deblocking.

The alkylation of malonic esters is one of the oldest and most widely applicable of synthetic reactions.[2] It suffers from only limited side reactions, yet in some instances these side reactions, such as dialkylation, elimination, and

0022-3263/79/1944-3492$01.00/0