Regioselective Chemistry of Methoxyxenon Fluoride

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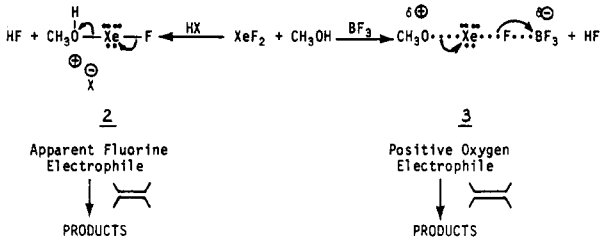
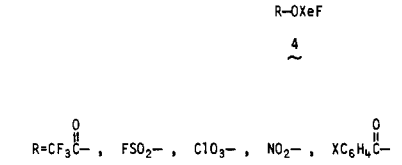
Xenon difluoride (XeF_2) reacts with methanol to form an unstable reactive species CH_3OXeF (1). Formaldehyde is produced quantitatively by disproportionation in the absence of unsaturated hydrocarbons or with unreactive alkenes. Hydrogen fluoride generated in situ complexes with 1 to form 2 which reacts with unsaturated hydrocarbons of intermediate reactivity such as *cis*- or *trans*-1-phenylpropene (**5c**, **5t**), indene (**6**), 2,3-dimethyl-1,3-butadiene (**7**), and norbornene (**8**) as an apparent fluorine electrophile and Markovnikov fluoromethoxy products are found. Reaction of XeF_2 with methanol in the presence of boron trifluoride as catalyst forms the complex **3** which disproportionates to formaldehyde. Intermediate **3** reacts with unsaturated hydrocarbons of intermediate reactivity (**5c**, **5t**, **6**, **7**, and **8**) as a positive oxygen electrophile to give anti-Markovnikov fluoromethoxy products. However, very reactive (electron rich) alkenes such as dihydropyran (**9**) react rapidly with XeF_2 to give a carbocation species before the intermediate 1 (or its complex **2** or **3**) can be formed.

Recently[1a] we reported on the methanolysis of xenon difluoride (XeF_2) to form an unstable electrophilic species CH_3OXeF (1).[2] Intermediate 1 functions as an apparent fluorine electrophile (2) with proton catalysts. On the other hand, boron trifluoride as catalyst induces 1 to react as a positive oxygen electrophile (3).[3] We rationalized this change in electrophilic character on the basis of hard–soft acid–base theory.[1]



Intermediate 1 is the first oxygen xenon fluoride species that contains an alkyl (electron-donating) substituent. Its formation, even as a transitory specie, is consistent with similar compounds reported when electron-withdrawing substituents are bonded to the oxygen as indicated by **4**.[4] In this paper we discuss the reactions of 1 with several unsaturated hydrocarbons and investigate the mechanism which produces an intriguing Markovnikov/anti-Markovnikov regioselective reversal with certain alkenes and catalysts.



Results

Reaction of XeF_2 in methanol with *cis*- and *trans*-phenylpropene (**5c**,**5t**), indene (**6**), 2,3-dimethyl-1,3-butadiene (**7**), norbornene (**8**), and dihydropyran (**9**) with protic acid (HF generated in situ)[1b] and boron trifluoride (etherate or methanol complex) are indicated in Scheme I. Intermediate 1 reacts with **5c**, **5t**, and **6** in the presence of HF catalyst to give Markovnikov products while anti-Markovnikov products predominate with boron trifluoride (BF_3) as catalyst. The products of the phenyl-substituted alkenes were isolated by column chromatography. Spectral data for the difluoro products from **5c**, **5t**, and **6** were identical with those reported in the literature (see Experimental Section). The regio- and stereochemistry of the fluoro methoxy products were determined by NMR and/or mass spectrometry except for compounds **16c** and **16t**. Product **16c** was independently synthesized from pure **10t**[5] by a nucleophilic substitution reaction because **16c**

(1) (a) Shellhamer, D. F.; Curtis, C. M.; Hollingsworth, D. R.; Ragains, M. L.; Richardson, R. E.; Heasley, V. L.; Heasley, G. E. *Tetrahedron Lett.* **1982**, *23*, 2157. Presented in part at the 183rd National Meeting of the American Chemical Society, Las Vegas, NV, April 2, 1982. (b) Addition of 0.02 equiv of H_2SO_4 to the reaction mixture induced a rapid reaction with alkenes **5c** or **6** and products **11** and **12** or **14c**, **14t**, and **15c** were formed. Products **13** or **16c** and **16t** are not produced in this reaction.

(2) In ref 1 we suggested that the intermediate may be either CH_3OF or CH_3OXeF. However, very strong oxidizers (F_2) are required to form hypofluorites. In our opinion, xenon difluoride could not oxidize methanol to methyl hypofluorite (CH_3OF). Professor R. Filler (Illinois Institute of Technology) has shown that phenyl substituted amino acids undergo electrophilic aromatic substitution with XeF_2 and the amino group is not oxidized in that reaction. Thus we suggest the electrophilic intermediate in our reaction is CH_3OXeF formed by a substitution reaction with CH_3OH and XeF_2. We want to thank professors R. Filler and D. Des Marteau for helpful discussions on this point.

(3) Oxygen was reported as the electrophile for addition of hypofluorous acid to alkenes and aromatics. See: Migliorese, K. G.; Appleman, E. H.; Tsangaris, M. N. *J. Org. Chem.* **1979**, *44*, 1711. Migliorese, K. G.; Appleman, E. H.; Bonnett, R.; Mateen, B. *Tetrahedron* **1977**, *33*, 2119. A positive oxygen electrophile was also reported for reaction of *p*-nitrobenzenesulfonyl peroxide to dihydropyran. See: Hoffman, R. V.; Buntain, G. A. *J. Org. Chem.* **1983**, *48*, 3308.

(4) Eisenberg, M.; Des Marteau, D. D. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 29. Gregoric, A.; Zupan, M. *J. Org. Chem.* **1979**, *44*, 4120. Bartlett, N.; Wechsberg, M.; Jones, G. R.; Burbank, R. D. *Inorg. Chem.* **1972**, *11*, 1124. Wechsberg, M.; Bulliner, P. A.; Sladky, F. O.; Mews, R.; Bartlett, N. *Ibid.* **1972**, *11*, 3063. Shustov, L. D.; Lywnovskaya-Gurova, L. B.; Fomin, O. P.; Nikolenko, L. N. *Zh. Obshch. Khim.* **1976**, *49*, 918 and references therein.

(5) Heasley, G. E.; Bower, T. R.; Dougharty, K. W.; Easdon, J. C.; Heasley, V. L.; Arnold, S.; Carter, T. L.; Yeager, D. B.; Gipe, B. T.; Shellhamer, D. F. *J. Org. Chem.* **1980**, *45*, 5150.

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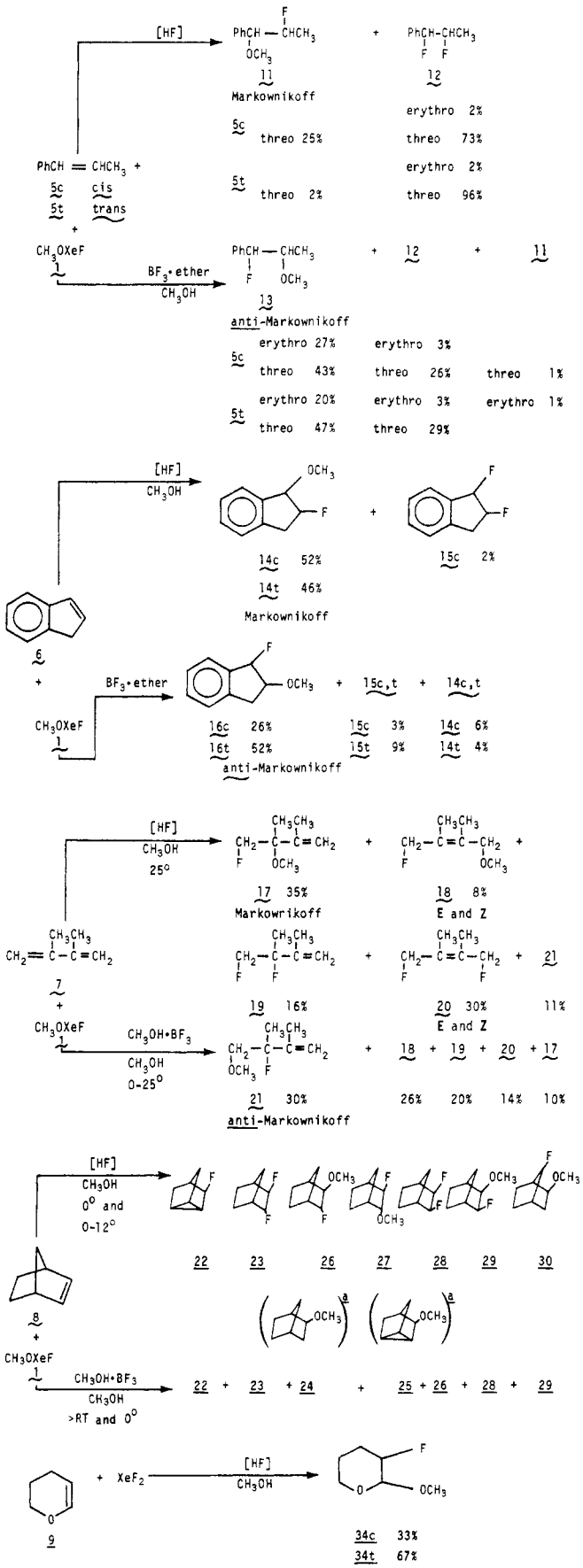
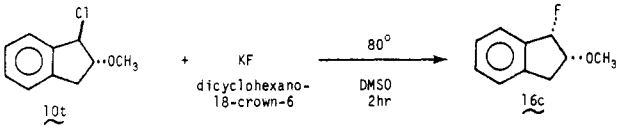
Scheme I



[a] See ref 33.

and **16t** gave identical vicinal proton–proton and proton–fluorine coupling.



Products from diene **7**, norbornene **8**, and dihydropyran **9**, were isolated by preparative gas-phase chromatography. Our best support for the fluoromethoxy products from diene **7** is mass spectral data. The anti-Markovnikov product **21** gave a base peak at m/e 45 which corresponds to $CH_2{=}O^+CH_3$ while the base peak for the Markovnikov adduct **17** was at m/e 99 (P – CH_2F) with no peak at m/e 45. GC mass spectral analysis of the 1,4-fluoromethoxy product (**18**) gave two peaks of equal intensity in the GC trace at 36 and 39 min. The two peaks gave almost identical mass spectral fragments and are the *E* and *Z* isomers of **18**. The important mass spectral peaks were m/e (relative intensity) $C_3H_5^+$ 41 (100), $CH_2{=}O^+CH_3$ 45 (71), and P – HF 112 (20). Chemical ionization mass spectrometry gave base peaks m/e 113 for **17**, **18**, and **21** via the following pathway:

$$M + CH_5^+ \rightarrow MH^+ + CH_4$$

$$MH^+ \rightarrow A^+ + HF$$

$$A^+ \equiv m/e\ 113$$

$$M = 17, 18, \text{ or } 21$$

Norbornene (**8**) reacts with **1** to give difluoro-, fluoromethoxy-, and nortricyclane products. When catalyzed by BF_3, norbornene reacted with XeF_2 in methanol at 0 °C to yield five products (Scheme I). Both fluoromethoxynorbornane products **26** and **29** are formed by an electrophilic methoxy group adding first; however, product **26** is the definite discriminator since **29** could also form from the fluorine substituent attacking first. Catalysis with hydrogen fluoride produces the same five products, but two new products appear, **27** and **30**, which can only be attributed to the fluorine atom adding first as the electrophilic substituent (Table I). When the five products common to both reactions are normalized to 100% in the HF catalyzed reactions, ratios of **26** and **29** remain the same within experimental precision. Therefore, product **29** results mainly from the anti-Markovnikov pathway where the electrophilic methoxy group adds first.

Products **22**, **23**, and **28** were readily identified by ^1H NMR and mass spectral comparison to known compounds.[6] Structural assignments for the other reaction products in Table I presented a more challenging problem although the yield of unrearranged 2,3-difluoronorbornane strongly suggested other 2,3-disubstituted products would be the prominant product adducts. Proton magnetic resonance and mass spectral comparisons to similar isomeric products were studied in detail; this included specific ^1H NMR chemical shifts and splitting patterns, plus major mass spectral fragmentation pathways. Products **26** and **29** initially were identified by ^1H NMR analogies to their corresponding 2-*endo*-fluoro-3-*exo*-acetamidonorbornane and 2-*exo*-acetamido-3-*exo*-fluoronorborane compounds, respectively, the latter of which was stereochemically verified by X-ray diffraction analysis.[6,7] Special attention

(6) Hildreth, R. A.; Druelinger, M. L.; Shackelford, S. A. *Tetrahedron Lett.* **1982**, *23*, 1059. Product VI is incorrectly displayed; it should be the *endo*-fluoro-3-*exo*-acetamidonorbornane product.
(7) Ely, N. FJSRL-TR-81-0006 (June, 1981).

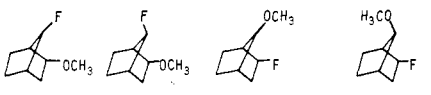
Table I. Product Distribution and Conditions of Norbornene Methoxyfluorination Reaction

			product, %								
run	temp, °C[a]	catalyst	22	23	24	25	26	27	28	29	30
1	−78–room temp[b]	BF_3	3	16	37	2	18	0	5	19	0
2	−78–0[c]	BF_3	7	27	0	0	31	0	8	27	0
5	−78–0[d]	BF_3	10	24	0	0	29	0	7	30	0
8	−78–0[e]	HF	10	17	0	0	22	9	4	20	18
4	−78–8[f]	HF	12	18	0	0	18	10	4	19	19
3	−78–8[g]	HF	10	20	0	0	22	12	5	19	12
7	−78–8[h]	HF	9	20	0	0	27	4	7	25	8
6	−78–8[i]	DF	7	16	0	0	30	5	6	29	8

[a] Acetone cooling bath (ca. −78 °C) used to mix all reactants. [b] Initial acetone bath removed; reaction left at ambient temperature and mildly exothermal during reaction. [c] Acetone bath changed to ice bath for $2^3/_4$ h. [d] Acetone bath changed to ice bath for $^1/_2$ h. [e] Acetone bath changed to ice bath for 5 h. [f] Acetone bath changed to ice 0 °C for $1^3/_4$ h, then to cyclohexane 6 °C for $1^1/_4$ h, and finally to *p*-dioxine 8–9 °C for 16 h. [g] Acetone bath changed to ice bath 0 °C for $1^3/_4$ h, then to *p*-dioxane 8 °C for 1 h. [h] Acetone bath changed to *p*-dioxane (8 °C); reaction split and analyzed after 1 h and 22 h; GLPC analysis showed no product isomerization at 8–12 °C (22 h). [i] Acetone bath changed to *p*-dioxane at 8 °C for 2 h.

was given to the proton chemical shifts and splitting patterns located at the geminal fluoro, geminal methoxy, and bridgehead positions. Synthesis of the α,α,α-trideuteriomethoxy compounds of **26** and **29** eliminated the large interfering singlet methoxy signal and confirmed the presence of an expected broadened doublet (J = 23 Hz) for the endo proton at the geminal methoxy position (C_3) in product **26** resulting from a planar vicinal endo–endo ^1H–^{19}F coupling. A sharp triplet-like (overlapping doublet of doublets) pattern resulted for the analogous endo proton (C_3) in product **29** which was very similar to the pattern seen in product **30**. Both compounds **29** and **30** have an endo proton at the geminal methoxy position, a planar endo proton at the adjacent position, and an *anti*-proton at the 7-position (W effect); a similar splitting pattern would therefore be expected. Both compounds **26** and **29** produced a 144 molecular ion by mass spectral analysis; and as with other individual 2,3-, 2,5-, and 2,7-disubstituted norbornane isomeric pairs,[6,8-10] their mass spectral fragmentation patterns were essentially identical. The major mass spectral fragmentation pathways of **26** and **29** represented similar analogues with those followed by both cited 2-acetamido-3-fluoronorborane isomers, both 2,3-difluoronorbornanes **23** and **28**, and 2-*exo*-(cyanomethyl)-3-*exo*-fluoronorbornane.[6] Products **27** and **30** also afforded 144 molecular ions but their totally different fragmentation patterns from one another reveal they are not an isomeric pair. The nearly similar but slightly longer GLPC retention time of **27** compared to compound **26** suggests **27** to be the converse isomer of **26** expected from the fluorine substituent adding first in the HF catalyzed reaction. Its endo proton at the geminal fluorine position (C_3) produced a doublet of very sharp multiplets since little vicinal ^1H–^1H coupling results with the only vicinal proton residing on the bridgehead position at a near 90° angle to the geminal fluorine's endo proton. The chemical shift of the geminal fluorine endo proton (C_3) of **27** appears unusually far downfield (δ 4.98) compared to the same endo proton of **29** (δ 4.55) and corresponding exo proton of product **26** (δ 4.68). This 0.43-ppm downfield shift of the endo C_3 proton is most likely caused by its position near the deshielding field of the *endo*-methoxy group's oxygen atom bonded to the adjacent C_2 position.[11a] The steric crowding of the remaining norbornyl endo protons would force the bulky methoxy group into a hindered rotation about the C_2-methoxy oxygen bond causing the geminal fluorine's endo methine proton at C_3 to remain in this deshielding spatial area. Numerous examples of "steric or local diagmetic deshielding" of protons in sterically congested and rigid norbornane systems have been reported.[11-14] The magnitude of such methoxy group deshielding falls between the hydroxyl and the acetyl group and is a direct relationship to the order of electron density on the O atom.[11b] In neutral molecules with appropriate stereochemistry and substituent orientation, shielding and deshielding effects will usually be in the +0.5- to −0.5-ppm range, respectively.[11a,14] The appearance of a third proton in the ^1H NMR signal in a region associated with the two bridgehead protons likely indicates that the endo C_6 proton is also being affected by this endo–endo steric deshielding phenomenon[14] in a manner analogous to the hydroxyl group ^{13}C deshielding of the methyl carbon atom observed in 2-*endo*-hydroxy-6-*endo*-methylnorbornane.[11b] The geminal methoxy exo proton (C_2) in **27** reveals itself as a complex multiplet in its α,α,α-trideuteriomethoxy compound where the strong methoxy singlet cannot interfere. This is consistent with the exo C_2 proton being vicinally split by two nonequivalent protons (the geminal fluoro endo C_3 proton and the adjacent C_1 bridgehead proton) and with a further ^1H–^{19}F vicinal splitting to provide a broadened complex multiplet. A similar complex multiplet is seen for the exo C_2 proton in the analogous difluoronorborane **23**[6] and the 2-*endo*,5-*exo*-difluoronorbornane.[9] The mass spectra of **27** produced a 144 molecular ion which readily lost the sterically crowded methoxy group as methanol for its primary fragmentation pathway. Its other major fragmentations, however, followed those found in the two other 2-fluoro-3-methoxynorbornane isomers **26** and **29**.

Compound **30** provided a ^1H NMR spectrum and mass spectrum totally consistent with a 2,7-fluoromethoxynorbornane isomer. Of the four possible isomers, **30**, **31**, **32**, and **33**, the product was identified as 2-*exo*-methoxy-7-



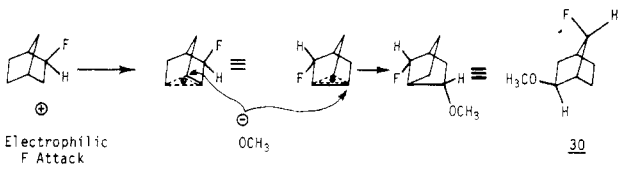
30 31 32 33

syn-fluoronorbornane (**30**). The ^1H NMR spectra afforded

(8) Zupan, M.; Gregorcic, A.; Pollak, A. *J. Org. Chem.* **1977**, *42*, 1562.
(9) Shackelford, S. A. *Tetrahedron Lett.* **1977**, 4265.
(10) Shackelford, S. A. *J. Org. Chem.* **1979**, *44*, 3485.

(11) (a) "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Jackson, L. M., Sternhell, S., Eds.; Pergamon Press: Oxford, 1969; pp 67–68, 80–81, and references cited therein. (b) Marchand, A. P. "Stereochemical Application of NMR Studies in Rigid Bicyclic Systems"; Verlag Chemie International: Deerfield, FL, 1982; Vol. 1, p 16.
(12) Carr, J. B.; Huitric, A. C. *J. Org. Chem.* **1964**, *29*, 2506.
(13) Zuercher, R. F. "Nuclear Magnetic Resonance in Chemistry"; Pesce, B., Ed.; Academic Press: New York, 1965; p 45.
(14) Winstein, S.; Carter, P.; Anet, F. A. L.; Bourn, A. J. R. *J. Am. Chem. Soc.* **1965**, *87*, 5247.

Scheme II[a]



[a] The nonclassical representation is used for brevity only; we do not intend to favor one specific viewpoint.

a C_7 geminal fluoro anti proton (doublet of sharp multiplets), centered at δ 4.78; this shift is almost identical with the same C_7 proton shift (δ 4.81) found in 2,7-*syn*-difluoronorbornane. Its major mass spectral fragmentation pathway proceeds by 144 molecular ion loss of the 2-*exo*-methoxy group as a methanol specie which is also the primary route followed by 2-*exo*-methoxynorbornane (**24**). Its fragmentation of the $FCHOCH_3$ radical follows those characteristic solely of the 2,7-difluoronorbornanes rather than the 2,3- or 2,5-difluoronorbornane isomeric pairs. One fragmentation pathway discriminates between the 2,7-*syn*- and 2,7-*anti*-difluoronorbornane isomers. The 2,7-*syn*-difluoronorbornane (*m/e* 132) readily loses a fluorine radical followed by a CH_2=CHF fragment to produce a *m/e* 67 specie (47%); however, the 2,7-*anti*-difluoronorbornane fragmentation pattern, which behaves like its corresponding syn isomer in all other respects, produces very little *m/e* 67 (18%). Compound **30** follows a major fragmentation pathway analogous to the syn configuration. Its 144 molecular ion losses a F radical and a CH_2=CH-OCH_3 specie to yield *m/e* 67 (93%) which verifies compound **30** to be in the syn configuration formed by the rearrangement illustrated in Scheme II. Finally, the ^1H NMR absorption signals of nongeminally substituted and nonbridgehead proton between δ 0.8 and 2.0 produce a sort of norbornyl "spectral pattern" which is characteristic to individual disubstituted norbornanes. This "spectral pattern" for compound **30** is identical with that produced by its analogous 2,7-*syn*-difluoronorbornane compound, but is very different from that produced by the 2,7-*anti*-difluoronorbornane. A comparison of the 2,3-fluoromethoxynorbornane products **26** and **27** ^1H NMR "spectral pattern" to that of 2-*endo*,3-*exo*-difluoronorbornane **23** was similar; but it was quite unlike that of the difluoronorbornane isomer **28** and both 2,5- and 2,7-difluoronorbornane isomers. Compound **29** afforded a spectral pattern similar to that provided by **28** between δ 2.00 and 0.80. Compound **24** was verified by ^1H NMR and mass spectral comparison to the spectra of 2-*exo*-methoxynorbornane synthesized independently by an ethereal coupling reaction between the sodium salt of 2-*exo*-norborneol and methyl iodide. Compound **25**, found as a trace amount in only one reaction, was identified by ^1H NMR and mass spectral comparison to the spectra of its analogous *exo*-fluoronortricyclane (**22**).

Dihydropyran (**9**), however, reacts with XeF_2 in methanol to give only the Markovnikov products **34c** and **34t**. These products were identified by their expected ^1H NMR and ^{19}F NMR spectral data.

Discussion

Scheme III outlines the reactions of XeF_2 with alkenes (indene **6**) in methanol as solvent. In the absence of alkene XeF_2 reacts with methanol at 25 °C by a pseudo-first-order process (path 1a) and formaldehyde is formed quantitatively.[1] The reaction was shown to be zero order in alkene with equimolar XeF_2, indene, and BF_3, and the anti-Markovnikov products (**16c**, **16t**) and formaldehyde predominate.[1] Therefore, XeF_2 is not reacting directly with alkenes (path 2, Scheme III) to form addition products. The alkene is intercepted in a subsequent fast step and both addition products (path 1b) and formaldehyde (path 1a) are produced. At a higher alkene concentration, and with BF_3 catalyst, the reaction did not remain zero order in alkene and the amount of Markovnikov addition products increased. This led us to speculate that XeF_2 was beginning to react directly with alkene fluorinations[10,15] when more than 2 equiv of alkene (**6**) are used. (Figure 1 shows the change in products when the initial indene: XeF_2 ratio is increased from 1 to 5 equiv). Anti-Markovnikov products **16c** and **16t** predominate when the alkene, XeF_2, and CH_3OH-BF_3 concentrations are equi-

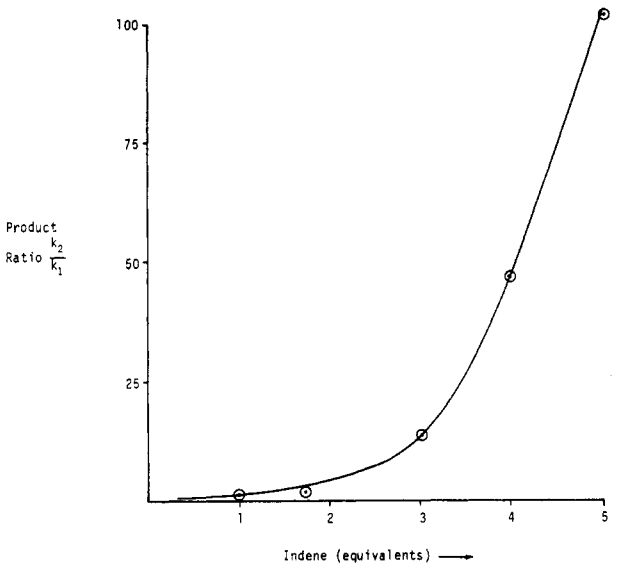
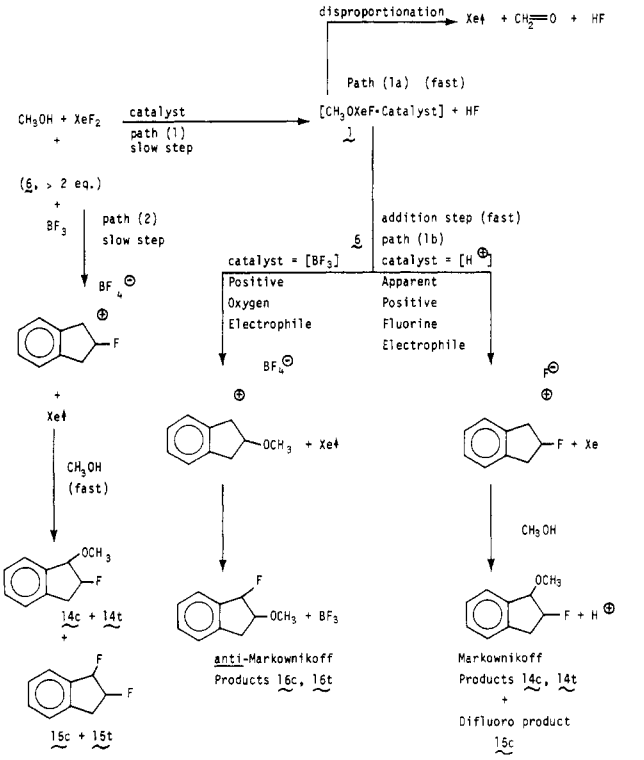


Figure 1. Plot of product ratio k_2/k_1 vs. equiv of indene. Reaction temperature 22 °C, $[XeF_2] = [BF_3 \cdot CH_3OH] = 0.236$ M.

Scheme III



(15) Gregorcic, A.; Zupan, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1085.

Figure 2.

molar (0.236 M). Above 2 equiv of indene:XeF_2 path 2 becomes competitive with path 1 (Scheme III) and the amount of Markovnikov products (**14c** and **14t**) and difluoro products (**15c** and **15t**) are increased (Figure 1). All of the products (**14c, 14t, 15c,** and **15t**) are formed via path 2 when 5 equiv of alkene are added to the reaction mixture. These data are consistent with the competing pathways indicated in Scheme III.

The Markovnikov and anti-Markovnikov products from the phenylpropenes (**5c, 5t**) and the diene (**7**) are also consistent with **1** functioning as both a positive oxygen and apparent fluorine electrophile (Scheme III, path 1b).[16] We ruled out a radical pathway and explained this unusual behavior of **1** on the basis of hard–soft acid–base theory.[1] The 1-fluoro-4-methoxy product (**18**) from diene **7**, however, can be formed by addition of either species (**2** or **3**). Product **18** does not represent the major component from either reaction.

The Markovnikov and anti-Markovnikov regioselectivity reversal observed with the XeF_2 methoxyfluorination of 1-phenylpropene,[17] indene,[17] and the 1,3-diene was investigated with norbornane. This bicyclic compound permitted another type of stereochemical verification of our proposed mechanistic duality wherein the methoxy group can add first through an apparent positive oxygen electrophile with Lewis acid BF_3 catalysis, or alternatively, an electrophilic fluorine atom can add first with HF catalysis. The first substituent adding to norbornene in an electrophilic reaction attacks the 2-exo position. Boron trifluoride catalysis of the norbornene methoxyfluorination with XeF_2 would produce products with the methoxy group at the initial 2-exo position; conversely, hydrogen fluoride catalysis would place the fluorine atom in the 2-exo position (Figure 2). The two products (Scheme I) designated as 2-*endo*-fluoro-3-*exo*-methoxynorbornene (**26**) and 2-*exo*-fluoro-3-*exo*-methoxynorbornane (**29**) would be expected from BF_3 catalysis in the case where no ionic norbornyl rearrangement occurs. Product **29** could result also from HF catalysis, but the 2-*endo*-methoxy-3-*exo*-fluoronorbornane (**27**) represents the compound from the fluorine atom adding first. A similar product analogy holds for the three corresponding 2-fluoro-5-methoxynorbornane isomers should extended product rearrangement occur;[10] however, potential product rearrangement into the four possible 2-fluoro-7-methoxynorbornane isomers requires the substituent adding first to reside in the 7-bridge position in either a syn or anti configuration.[10]

This norbornene reaction displays several intriguing features. First, no rearrangement of products in the BF_3 catalysis occurred, and only a minor amount resulted in the HF catalysis as evidenced by product **30**. In view of previous norbornene fluorination reactions with XeF_2, this result may appear surprising.[6,8-10,15] The lack of rearrangement comes from the highly polar methanol solvent stabilizing the initial unrearranged carbonium ion and negates its need to achieve a more stable intermediate species via rearrangement. Similar stabilization was observed with the less polar diethyl ether solvent whose oxygen atom is also far more effective at stabilizing this ionic system than is methylene chloride solvent where substantial rearrangement occurs.[10] Even when a small amount of rearrangement results during the HF catalyzed reactions, only one 2-fluoro-7-methyoxynorbornane isomer results. No rearrangement into the most stable 2,5-intermediate is required,[10] and the resultant 2,7-product **30** (Scheme II) is the syn isomer normally found as the major rearranged product in norbornene halogenations;[18-24] fluorinations conducted with XeF_2 in methylene chloride solvent are the one exception.[8-10,15] Secondly, the product distribution varies depending upon the reaction temperature (Table I). In the one ambient temperature reaction, no bath was used after removing the original −78 °C cooling bath (Run 1), and the major product was 2-*exo*-methoxynorbornane (**24**). Interestingly, this product then gradually disappeared from the reaction product solution over a period of several weeks. When the BF_3 reaction was conducted at 0 °C in an ice bath, this product was absent and the five products shown in Table I formed. Temperature variance within the range displayed in Table I had little or no effect upon the difluoronorbornane to fluoromethoxynorbornane product ratios. However, the product distribution obtained in the HF catalyzed reaction does display a temperature dependence (Table I). A comparison of the BF_3 and HF catalyzed reactions at 0 °C (runs 2, 5, and 8) plus the HF reactions at a lower temperature gradient (Runs 4 and 3) in Table I show substantial formation of the two fluorine electrophilic products **27** and **30** with the rearranged 2,7-syn isomer **30** predominating. The higher temperature bath reactions (runs 7 and 6) show a noticeable decrease in both products. The more rapid higher temperature reaction apparently does not permit sufficient time for the 2,7-syn rearrangement to proceed as far. Thirdly, both Markovnikov and anti-Markovnikov products associated with the positive oxygen and positive fluorine electrophiles result with the bicyclic norbornene. Apparently three addition pathways consistent with Scheme III are involved in the HF catalyzed reaction of the highly reactive norbornene. Boron trifluoride catalysis produces difluoronorbornane products **23** and **28** by an analogous mechanism to the reported electrophilic BF_3 etherate catalyzed norbornene fluorination[10] prior to substantial formation of **1** or **3**. Once intermediate **3** forms, it reacts as an electrophilic methoxy species to form the anti-Markovnikov methoxyfluoronorbornanes **26** and **29**. Apparently this same type of electrophilic mechanism operates in the absence of BF_3[10] until a threshold concentration of HF is generated. In the HF catalyzed reaction, a substantial portion of the reactive norbornene intially forms products **22, 23, 26, 28,** and **29** by reaction with XeF_2 and intermediate **1**. The protonated methoxy xenon fluoride intermediate **2** occurs once suf-

(16) A reviewer asked why no dimethoxy adducts were formed from the postulated ionic intermediate (Scheme III and Figure 2) of the boron trifluoride catalyzed reaction. We independently synthesized the dimethoxy products of 1-phenylpropene [Norman, R. O. C.; Parr, W. J. E.; Thomas, B. *J. Chem. Soc., Perkin Trans 1* **1976**, 811]. Coinjection of the authentic products with the boron trifluoride catalyzed reaction of XeF_2 and 1-phenylpropene suggests the dimethoxy products are present in ca. 1–3%. Why is so little of the dimethoxy product formed? Perhaps the BF_4^- ion (see the intermediate in Scheme III and in Figure 2) reacts with the cation as an intimate ion pair and does not give the solvent sufficient time to incorporate.

(17) The high syn stereoselective addition is characteristic of reagents which react as apparent fluorine electrophiles. See: Rozen, S.; Lerman, O. *J. Org. Chem.* **1980**, *45*, 672 and references therein.

(18) Kwart, H.; Kaplan, L. *J. Am. Chem. Soc.* **1954**, *76*, 4072.
(19) Poutsma, M. L. *J. Am. Chem. Soc.* **1965**, *87*, 4293.
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(21) Tanner, D. D.; Gidley, G. C. *J. Org. Chem.* **1968**, *33*, 38.
(22) Marshall, D. R.; Warnhoff, P. R.; Warnhoff, E. W.; Robinson, J. R. *Can. J. Chem.* **1971**, *49*, 885.
(23) Tanner, D. D.; Van Bostelen, P. *J. Am. Chem. Soc.* **1972**, *94*, 3187.
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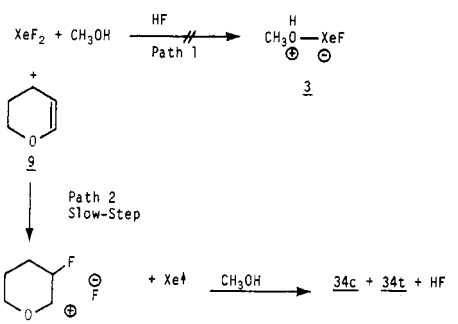
Scheme IV



ficient HF is generated in situ to provide the Markovnikov products **27**, **30**, and possibly a trace of **29**. Finally, the BF_3 catalyzed reaction proceeds about sixty times faster than when HF catalyzed. Run 5 was completed in 5 min and likely was reacting even below 0 °C. The HF catalyzed reaction at 0 °C proceeded far more slowly and required 5 h to consume all the XeF_2 solid.

Dihydropyran **9** reacts with XeF_2 in methanol to give products **34c** and **34t**. Alkene **9** is quite nucleophilic (electron rich) and reacts rapidly without BF_3 catalyst with XeF_2 as indicated in Scheme IV. Thus reaction of XeF_2 with methanol (path 1, Scheme IV) is not competitive when reactive alkenes such as **9** are utilized.

In conclusion, we have shown that XeF_2 reacts with methanol to form an unstable electrophilic species **1** (or its complex **2** or **3**) which is sensitive to the catalyst used in the reaction. Intermediate **1** is unstable and disproportionates rapidly to formaldehyde (Scheme III, path 1a). Unreactive alkenes such as 1-hexene, butadiene, or methyl crotonate do not intercept **1** and formaldehyde is produced quantitatively.[1a] Unsaturated hydrocarbons of intermediate reactivity such as **5c**, **5t**, **6**, **7**, and **8** are required to trap **1**. Very reactive alkenes like **9** react directly with XeF_2 and formation of **1** (or the protonated species **2**) is not competitive.

Experimental Section

General Procedures. All chemicals were used as received from the suppliers. The XeF_2 was purchased from PCR Research Chemicals, Inc., and was stored in a nitrogen purged Braun-Knecht-Heilmann Co. laboratory dry box where XeF_2 weighing operations were conducted. In some cases, the XeF_2 was weighed indirectly in an ordinary fume hood. The methanol solvent was Burdick & Jackson distilled-in-glass purity which was stored in the N_2 dry box or J.T. Baker Chem. Co. HPLC purity which was outside the dry box and stored over 4Å molecular sieves. The unsaturated hydrocarbons were obtained from the Aldrich Chemical Co., Inc.; methanol with 10–14% boron trifluoride (Eastman Kodak Co.) was used in the BF_3 catalyzed reactions. The hydrogen fluoride used in the HF catalyzed reactions was generated in situ as the reaction proceeded. The 99.5% isotopically pure methanol-d_4 used in the experimental run 6 (Table I) was obtained from Wilmad Glass Co., Inc., in individual 1-mL glass vials. Standard taper glassware was used as described earlier.[25a] Glassware items and transfer pipets for the norbornene reaction were cleaned as described in previous XeF_2 fluorination[9,10,25a] and aqueous XeO_3 investigations.[25b] A 7-L stainless steel beaker was filled with deionized water and ca. 8 mL of Micro Liquid Laboratory Cleaner (International Products Corp.). After air drying, a 35 mL single-necked round-bottomed flask, a Teflon coated magnetic stir bar, two 14/20 ground glass stoppers, a spatula, and a 14/20 jointed 10-mL graduated cylinder were placed into the dry box prior to weighing the XeF_2. All other glassware and hardware remained outside the dry box until needed.

Proton and ^{19}F NMR spectra were obtained on a Nicolet Magnetics Corp. NT-200WB, JOEL FX90Q, or a Varian T60A spectrometer. Several spectra were also obtained on 270- and 360-MHz instruments located at the Oklahoma Medical Research Foundation and the National Science Foundation Regional Center located at Fort Collins, CO, respectively. Spectra are referenced relative to Me_4Si or $CFCl_3$. Mass spectral analyses were obtained at 20 and 70 eV on a Finnigan Automated Gas Chromatograph/EI-C1 Mass Spectrometer or at 70 eV on a Hewlett-Packard 5790A GC interfaced with a HP5970A Mass Selective Detector. A Shimadzu GC-9A GLPC and a Hewlett-Packard 5750 GC were each interfaced to a Hewlett-Packard 3380A Integrator Recorder. All norborane products were analyzed with a 10 ft by $^1/_4$ in. 10% Carbowax 20M on 80/100 mesh Chromasorb W column at 50 mL/min He flow and with the following temperature programming profile: 80 °C/6 min; 20 °C/min rise; 95 °C/6 min; 10 °C/min rise; 165 °C/2 min; 20 °C rise; 180, 190, or 195 °C/6 min; all three latter temperatures were used at various times. Because of the small product concentrations and high background GLPC scans, product percentages from norbornene were hand calculated by multiplying the peak width measured at half peak height by the peak height itself; these products were isolated in small custom made glass traps submerged in liquid N_2. Gas chromatography columns and data for the remaining reactants are described below.

The product ratios did change when some of the crude reaction mixtures were at room temperature overnight. However, isolated products were stable to the reaction conditions and VPC analysis except for the 1,4-product (**20**) from the diene **7** which decomposes. The stability and indirect characterization of **20** was described in an earlier paper.[26]

***cis*- or *trans*-1-Phenylpropene (5c or 5t) Methoxyfluorination with XeF_2.** To 58.0 mg (0.343 mmol) of XeF_2 in a dry 5-mL round-bottom flask fitted with a drying tube and stirring bar at 0 °C was added 0.600 mL of anhydrous methanol. 3-Phenyl-2-propene (**5c** or **5t**), 0.195 mL (1.50 mmol), and 0.340 mmol boron trifluoride ether were added via separate syringes. The stirred mixture was allowed to warm to room temperature and the reaction was complete in ca. 15 min (reactions without BF_3 ether were stirred overnight at room temperature). The mixture was poured into an aqueous sodium bicarbonate solution, extracted three times with ether, dried over anhydrous magnesium sulfate, and analyzed by VPC on a 17 ft × $^1/_8$ in. ss column of 2.5% FFAP on Chromosorb W. The products had the following retention times (min) at 85 °C: *erythro*-**12** (11), *threo*-**12** (12.5), *erythro*-**11** (13.5), *threo*-**11** (15), *erythro*-**13** (18), *threo*-**13** (20). Yields (60–70%) were determined by NMR with toluene as internal standard. The products were isolated by column chromatography on silica gel with petroleum ether (35–60 °C) and petroleum ether/ether as the elutant. Products **11** and **12** gave identical spectral data with that reported in the literature.[27] Product **13** gave the following spectral data: *erythro*-**13** NMR 270 MHz ($CDCl_3$) δ 1.18 (dd, J = 6.2 and J = 1.4 Hz, 3 H), 3.47 (s, 3 H), 3.60–3.70 (m, 1 H), 5.27 (dd, J = 47 and J = 6.0 Hz, 1 H), 7.25–7.45 (m, 5 H); *threo*-**13** NMR 270 MHz ($CDCl_3$) δ 1.00 (d, J = 7.0 Hz, 3 H), 3.35 (s, 3 H), 3.52–3.68 (m, 1 H), 5.44 (dd, J = 46 and J = 4.0 Hz, 1 H), 7.25–7.43 (m, 5 H).

Indene (6) Methoxyfluorination with XeF_2. The reaction was accomplished and the products isolated as described above for **5c** and **5t**. VPC analysis on the FFAP column described above (110 °C for 15 min, then programmed to 130 °C at 60 °C/min) gave the product distributions listed in Scheme I with the following retention times (min): **15t** (11), **15c** (12), **14t** (33), **16t** (35), **14c** (62), **16c** (66). The yields were ca. 70% as determined by NMR with cyclohexane as internal standard. Compounds **15c** and **15t** gave spectral data identical with that reported in the literature.[28] The following data were obtained for the remaining products: **14t** NMR 270 MHz ($CDCl_3$) δ 2.90–3.65 (m, 2 H), 3.51 (s, 3 H), 4.82 (dd, J = 20.5 and J = 4.2 Hz, 1 H), 5.24 (dm, J = 63 Hz, 1 H), 7.20–7.50 (m, 4 H); **14c** δ 2.95–3.40 (m, 2 H), 3.52 (s, 3 H), 4.64 (dd, J = 17.4 and J = 5.1 Hz, 1 H), 5.38 (dm, J = 64 Hz, 1 H), 7.10–7.50 (m, 4 H); **16t** δ 2.78–2.90 (m, 2 H), 3.47 (s, 3 H), 4.20–4.36

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(m, 1 H), 5.92 (dd, J = 58 and J = 4.0 Hz, 1 H), 7.20–7.44 (m, 4 H); **16t** ^{19}F NMR ($CDCl_3$) ϕ 177 (dd, J = 58 and J = 4.0 Hz); **16c** NMR 270 MHz ($CDCl_3$) δ 3.10–3.20 (m, 2 H), 3.58 (s, 3 H), 3.98–4.15 (m, 1 H), 5.78 (dd, J = 58 and J = 4.0 Hz, 1 H), 7.20–7.58 (m, 4 H); **16c** ^{19}F NMR ($CDCl_3$) ϕ 188 (dd, J = 58 and J = 4.0 Hz).

Independent Synthesis of 16c. *trans*-1-Chloro-2-methoxyindan (**10t**) was prepared as a cis–trans mixture[5] and **10t** was isolated pure by column chromatography on silica gel with petroleum ether (35–60 °C) and increasing amounts of ether as the elutant. To 140.6 mg (0.770 mmol) of **10t**, 0.500 g of anhydrous potassium fluoride (8.60 mmol), and 126.8 mg of dicyclohexano-18-crown-6 (0.340 mmol) was added 10 mL of dimethyl sulfoxide. The stirred mixture was heated to 80 °C for 2 h. The product was isolated by column chromatography as described above and was found to have identical properties with those reported for **16c** above.

2,3-Dimethyl-1,3-butadiene (7) Methoxyfluorination with XeF_2. The reaction was accomplished as described above for **5c** and **5t** except that boron trifluoride methanol (12%) was used (similar results were obtained with 90% boron trifluoride ether complex). Analysis on the $^1/_8$ in. FFAP column above (25 °C for 20 min then heated to 45 °C) gave the products listed in Scheme I with the following retention times (min): **19** (8), **20** (10), **21** (16), **17** (18), **18** (*E*) and (*Z*) isomers (36 and 39). The yields determined by VPC analysis corrected for flame response with toluene as internal standard were 39 and 51% for the CH_3OH-BF_3 and HF catalyzed reactions, respectively. The yields of formaldehyde[29] were also determined because the amount of addition products was low and it was 24 and 28%, bringing the total yield to 63 and 79% for the CH_3OH-BF_3 and HF catalyzed reactions. The products were isolated by preparative VPC on a $^1/_4$ in. column similar to the analytical column above. Products **19** and **20** were characterized in our earlier paper.[26] The fluoromethoxy products gave the following spectral data. **17**: IR (CCl_4) 3020 (m), 2940 (s), 2840 (w), and 1140 (s) cm^{-1}; NMR 60 MHz (CCl_4) δ 1.25 (s, 3 H), 1.83 (d, J = 0.8 Hz, 3 H), 3.40 (s, 3 H), 4.50 (d, J = 52 Hz, 2 H), 4.8–5.1 (m, 2 H); mass spectrum (70 eV), m/e (relative intensity) P – CH_3 117 (2), P – CH_2F 99 (100); chemical ionization (CH_4) gave a base m/e 113. **21**: IR (CCl_4) 3020 (m), 2940 (s), 2840 (w), and 1115 (s) cm^{-1}; NMR 60 MHz (CCl_4) δ 1.38 (d, J = 20.8 Hz, 3 H), 1.73 (brd s, 3 H), 3.27 (d, J = 9.5 Hz, 1 H), 3.37 (s, 3 H), 3.40 (d, J = 18.0 Hz, 1 H), 4.7–5.2 (m, 2 H); mass spectrum (70 eV), m/e (relative intensity) parent 132 (0.2), P – HF 112 (7), P – (CH_2=OCH_3) 87 (12), and CH_2=O^+CH_3 45 (100); chemical ionization (CH_4) gave a base m/e 113. Compound **18** was collected as a mixture of *E* and *Z* isomers: IR (CCl_4) 2980 (s), 2940 (s), 2840 (w), 1120 (s), and 1100 (s) cm^{-1}; NMR 60 MHz (CCl_4) δ 1.73 (brd s, 6 H), 3.12 (s, 3 H), 3.20–3.40 (m, 2 H) 4.29 (d, J = 47.0 Hz, 2 H). GC mass spectral data were obtained on the *E* and *Z* isomers individually. Isomer retention time 36 min (70 eV), m/e (relative intensity) P – HF 112 (19), CH_2=O^+CH_3 34 (71), 41 (100). Isomer retention time 39 min P – HF 112 (20), $CH_2O^+CH_3$ 45 (70), 41 (100). Both isomers gave a base peak at m/e 113 with chemical ionization using methane.

Norbornene (8) Methoxyfluorination with XeF_2. Both the BF_3 catalyzed and HF catalyzed reactions were conducted in an identical manner except a 1 mL methanol (10–14% BF_3) aliquot was added to the reaction solution to introduce the BF_3 species; in the HF reaction, a 1-mL methanol blank was added at the same point.[30] The different temperature regulating sequences and the cooling baths used are outlined (Table I). The following general procedure is described for reaction runs 2, 5, and 8. Under a dry N_2 atmosphere, a 35-mL 14/20 single-necked round-bottom flask was charged with a Teflon-coated magnetic stir bar and 0.250 g (1.48 mmol) XeF_2. A 30-mL 14/20 jointed glass funnel and teflon-coated spatula[31] were used to transfer the XeF_2. The 35-mL funnel was stoppered with a 14/20 solid ground glass stopper; no grease was used on this joint. The spatula and funnel were immediately washed with CH_2Cl_2 in a 250-mL beaker to destroy any residual XeF_2. Methanol (7–10 mL) was poured into a 10-mL graduated cylinder which was also stoppered with a 14/20 solid ground glass stopper. The dry box was purged sufficiently with fresh N_2 to remove residual XeF_2 vapors. The stoppered 35-mL reaction flask and methanol filled graduated cylinder were then removed from the dry box and placed by hand into a laboratory benchtop fume hood. The 35-mL reaction flask was submerged into a dry ice/acetone or liquid N_2/acetone bath (ca. –78 °C) to reduce the XeF_2 vapor pressure prior to stopper removal. The stopper was removed and immediately replaced with a pregreased (low-vacuum stopcock grease, Halocarbon Products Co.) 15-mL pressure-equalized addition funnel fitted with a Drierite-containing drying tube with greased joint. The entire assembly was placed onto the 35-mL flask as one unit. Next, 0.140 g (1.49 mmol) minimum of norbornene was weighed into 1 mL of methanol in a 25-mL single-necked pear-shaped flask; this solution was transferred via capillary pipet into the 15-mL additional funnel. The 25-mL pear shaped flask was rinsed with two successive 0.5-mL portions of methanol, and these were added to the 15-mL additional funnel. (Note. The drying tube was removed from the addition funnel whenever solvent and substrate were transferred into the addition funnel.) The 2 mL of methanol/norbornene solution was added dropwise to the stirred XeF_2 solid over a 9–25-min period to provide a stirred heterogeneous suspension. One milliliter of methanol (10–14% boron trifluoride complex) was placed into the addition funnel for the BF_3 catalyzed reactions; for the HF catalyzed reactions, 1 mL of pure methanol was used.[30] This was added dropwise to the suspension over a 4–13-min period. At this point the acetone (–78 °C) cooling bath was removed and immediately replaced with an ice bath (0 °C) in experimental runs 2, 5, and 8. No cooling bath was used in run 1 after the acetone bath removal; other cooling baths were used as described in Table I for runs 3, 4, 6, and 7. The BF_3 catalyzed reactions at 0 °C were over in a few (ca. 5) minutes, but the HF catalyzed reaction required 5 h. Following reaction completion, 0.622 g of NaF was added to the reaction to scavenge any HF present; the cooling bath was removed and the reaction was stirred at ambient temperature at least 15 min. The reaction solution was then transferred via capillary pipet into another capillary pipet packed with a glass wool plug, $1^1/_2$–2 cm of neutral A_2O_3 (or 40/140 mesh SiO_2), and $^1/_2$–1 cm of anhydrous $MgSO_4$ (or anhydrous Na_2SO_4). Upon occasion some N_2 pressure was required to push the solution through the capillary pipet filter column. A minimum amount (ca. $^1/_2$–1 mL) was used to wash the filtration column and this was combined with the reaction solution. The solution was introduced to the GLPC Carbowax 20M column which provided the reaction products in the following order: (BF_3 catalyzed) **22**, **23**, **24**, **25**, **26**, **28**, and **29**.[32] (HF catalyzed) **22**, **23**, **26**, **27**, **28**, **29**, and **30**. Minute amounts of H_2O in these dilute FT NMR samples often caused integration values to be high in the δ 2.00–0.80 region; integrations are then based upon the one proton geminal to the F atom.

2-*endo*-Fluoro-3-*exo*-methoxynorbornane (26): ^{1}H FT NMR 200 and 90 MHz ($DCCl_3$) δ 4.68 (doublet of sharp double multiplet, J_d = 54 Hz), 3.34 (singlet, 3 H), 3.10 (doublet of sharp multiplets, J_d = 19 Hz, 1 H), 2.99 (sharp multiplet, 1 H), 2.48 (sharp multiplet, 1 H), 1.90–1.00 (fingerprint multiplets, norbornyl skeleton); mass spectrum (70 eV) M+ 144 (9), m/e (%) 124 (100), 116 (8), 97 (51), 92 (67), 85 (40), 84 (17), 81 (22), 79 (52), 76 (69), 71 (98), 67 (71), 66 (78), 59 (32), and 58 (18).

2-*endo*-Methoxy-3-*exo*-fluoronorbornane (27): ^{1}H FT NMR 90 MHz ($DCCl_3$) δ 4.98 (doublet of sharp singlet-like multiplets, J = 57 Hz, 1 H), 3.25 (singlet) and 3.22 (complex broad multiplet) both overlap to provide 4 H, 2.29 (doublet multiplet, 3 H), 2.00–1.05 (fingerprint multiplets, norbornyl skeleton); mass spectrum (70 eV) M+ 144 (16), m/e (%) 116 (0), 112 (97), 97 (100), 85 (24), 84 (48), 81 (10), 79 (29), 76 (0), 71 (30), 67 (23), 66 (19), 59 (30), and 58 (38).

2-*exo*-Fluoro-3-*exo*-methoxynorbornane (29): ^{1}H FT NMR 200 and 90 MHz ($DCCl_3$) δ 4.56 (doublet of sharp multiplets, J_d = 54 Hz, 1 H), 3.41 (singlet) and 3.30 (triplet-like doublet of overlapping doublets) both overlap to provide 4 H, 2.36 (unsymetrical doublet, 2 H), 2.00–0.80 (fingerprint multiplets, norbornyl

(29) The percent formaldehyde was determined by a colorimetric procedure with rosaniline hydrochloride. See: Walker, F. J. "Formaldehyde", 3rd ed.; Reinhold Publishing Corp.: New York, 1964; p 468.

(30) This 1-mL addition was omitted in experimental run 4 (Table I).

(31) References 10 and 6. Clean stainless steel spatulas appear suitable for handling XeF_2 in dry box weighing operations.

(32) Products **24** and **25** appeared only in the exothermic reaction conducted in an ambient temperature environment (run 1, Table I).

skeleton); mass spectrum (70 eV) M+ 144 (9), *m/e* (%) 124 (100), 116 (11), 97 (64), 92 (72), 85 (42), 84 (15), 81 (24), 79 (49), 76 (61), 71 (94), 67 (67), 66 (75), 59 (36), and 58 (17).

2-*exo*-Methoxy-7-*syn*-fluoronorbornane (30): ^{1}H FT NMR 90 MHz ($DCCl_3$) δ 4.77 (doublet of sharp multiplets, J = 58 Hz, 1 H), 3.47 (triplet-like multiplet, 1 H), 3.33 (singlet, 3 H), 2.35 (split multiplet, 2 H), 1.89 (split multiplet, 2 H), 1.70–0.90 (fingerprint multiplets, norbornyl skeleton); mass spectrum M+ 144 (1), *m/e* (%) 124 (25), 116 (1), 112 (81), 97 (49), 92 (12), 85 (11), 84 (5), 81 (13), 79 (100), 76 (12), 71 (11), 67 (93), 66 (83), 59 (27), and 58 (33).

Neither product isomerization nor the workup procedure altered the isolated product distribution. In run 7, half the reaction solution was worked up soon after XeF_2 depletion (1-h reaction). The remaining half of the reaction was stirred an additional 21 h (22-h reaction) at 8–12 °C. Both aliquots afforded the same GLPC product distribution, via GLPC; therefore, no isomerization occurs in the HF reaction solution as with difluoronorbornane isomers in CH_2Cl_2.[10] After completion of run 8 (5-h reaction), half the reaction mixture was analyzed by a direct GLPC aliquot. The remaining reaction solution was worked up as described. No difference in reaction product GLPC distribution resulted.

2-*exo*-Methoxynorbornane (24): ^{1}H FT NMR 200 and 90 MHz ($DCCl_3$) δ 3.26 (singlet) and 3.30–3.15 (broad multiplet) both overlap to provide 4 H, 2.31 (broad multiplet) and 2.23 (broad multiplet) partially overlap to give 2 H, 1.70–0.90 (complex multiplets, norbornyl skeleton); this FT NMR was identical to one obtained for **3** by the independent synthesis described below; mass spectrum M+ 126 (2), *m/e* (%) 111 (7), 97 (21), 95 (15), 94 (100), 79 (88), 71 (27), 67 (52), 66 (88), and 58 (39).

2-Methoxynortricyclane (25): ^{1}H FT NMR 200 and 90 MHz ($DCCl_3$) δ 3.37 (singlet) and 3.38–3.26 (multiplet) overlapping, 2.06 (sharp multiplet), 1.96–1.88 (complex multiplet), 1.70–1.10 (two broad multiplets). Sample too dilute for acceptable integration but its bridgehead protons, and norbornyl skeleton protons were similar in pattern and value to those of 2-fluoronortricyclane (**22**), plus its OCH_3 and endo ^{1}H geminal to the OCH_3 group was the same pattern as that seen in **24**; mass spectrum (20 eV) M+ 124 (55), *m/e* (%), fragment loss 109 (78) – CH_3, 92 (100) – CH_3OH, 79 (58) – CH_2OCH_3, 66 (61) – CH_2CHOCH_3. This fragmentation pattern was very similar to an analogous pattern followed by **22** at 70 eV M+ 112 (21), *m/e* (%) fragment loss 97 (100) – CH_3, 91 (15) – H_2F, 79 (63) – CH_2F, and 66 (60) – CH_2CHF.

Independent Synthesis of 24. The well-known sodium alkoxide and alkyl halide ether coupling reaction was used. 2-Norborneol (97%, Aldrich) was chosen as the sodium alkoxide precursor to negate any possible norbornyl product rearrangement. Diethyl ether (Mallinckrodt AR anhydrous) was dried over CaH_2 and distilled immediately prior to use. THF (Burdick & Jackson UV purity) with 0.008% H_2O was used directly; the CH_3I was distilled (bp 40 °C) prior to use.

A 14/20 100-mL three-necked round-bottom flask was charged with a Teflon-coated magnetic stir bar, 75 mL of diethyl ether, and 0.500 g (4.46 mmol) of 2-norborneol; not all the norborneol dissolved. The reaction flask was fitted with a Liebig water-jacketed condensor topped with a Dreirite-containing drying tube, and a 25-mL pressure equalized addition funnel. Through the third neck, 0.102 g (4.43 mmol) of sodium metal cut into small pieces was carefully added to the stirred reaction solution; no exothermic reaction resulted. The third neck was fitted with an N_2 stopcocked 14/20 glass inlet and the reaction was flushed once with N_2 gas. Reaction was very slow at room temperature; therefore, it was refluxed 20 h. Reaction still proceeded slowly, it was then cooled, 10 mL of THF was added, and another dry N_2 flush followed. After an additional 25 h of reflux ca. 90% of the Na metal was consumed. The reaction was refluxed another 133 h to give a fine light yellowish colored suspension. At room temperature, 0.565 g (3.98 mmol) of CH_3I in 10 mL of diethyl ether was added dropwise to the stirred sodium norbornoxide suspension over a 29-min period. The reaction stirred at room temperature 3 h, was then refluxed 5 h, and finally was stirred at room temperature for 16 h. Gravity filtration followed; the filtrate was then added dropwise into 10 mL of H_2O and washed. Eight 25-mL H_2O washings of the organic layer followed; the ethereal/THF layer was then dried over anhydrous Na_2SO_4, filtered, and concentrated by distillation. The concentrate was subjected to GLPC isolation for FT NMR and mass spectral analyses; not all the product was isolated so no yield was determined. Product GLPC retention time suggested it was the same compound as **24**; the ^{1}H FT NMR and mass spectrum were the same as compound **24** (2-*exo*-methoxynorbornane).

Dihydropyran (9) Methoxyfluorination with XeF_2. The reaction was accomplished as above for **5c** and **5t**. Only the 3-fluoro-2-methoxy products were formed with boron trifluoride or hydrogen fluoride generated in situ. The yields were ca. 60% and determined by NMR with toluene as internal standard. Analysis by VPC on a 10 ft × $^1/_8$ in. ss column of 5% SE30 on 80/100 Chromosorb W at 50 °C gave products **34t** and **34c** with retention times of 5 and 6 min, respectively. The products were obtained pure by preparative VPC on a $^1/_4$ in. column and gave the following data: **34t** NMR 90 MHz ($CDCl_3$) δ 1.28–2.10 (m, 4 H), 3.45–3.80 (m, 2 H), 3.44 (s, 3 H), 4.33 (dm, J = 48.5 Hz, 1 H), 4.53 (dd, J = 8.4 and J = 2.6 Hz, 1 H);[33] ^{19}F NMR ($CDCl_3$) ϕ −191, mult. **34c**: δ 1.58–2.07 (m, 4 H), 3.50–3.82 (m, 2 H), 3.46 (s, 3 H), 4.48 (dm, J = 47 Hz, 1 H), 4.59 (dd, J = 2.1 and 2.0 Hz, 1 H);[33] ^{19}F NMR ϕ −188 (dm, J = 47 Hz).

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Registry No. 1, 96728-69-7; *cis*-**5**, 766-90-5; *trans*-**5**, 873-66-5; **6**, 95-13-6; **7**, 513-81-5; **8**, 498-66-8; **9**, 110-87-2; *erythro*-**11**, 86894-38-4; *threo*-**11**, 82936-94-5; *erythro*-**12**, 14251-60-6; *threo*-**12**, 14251-61-7; *erythro*-**13**, 79186-46-2; *threo*-**13**, 79186-45-1; *cis*-**14**, 82936-90-1; *trans*-**14**, 82936-91-2; *cis*-**15**, 61550-23-0; *cis*-**16**, 82936-92-3; *trans*-**16**, 82936-93-4; **17**, 96728-70-0; (*E*)-**18**, 96728-71-1; (*Z*)-**18**, 96728-72-2; **19**, 92901-63-8; (*E*)-**20**, 96728-73-3; (*Z*)-**20**, 96728-74-4; **21**, 96728-75-5; **22**, 695-03-4; **23**, 61026-28-6; **24**, 10395-53-6; **25**, 21516-65-4; **26**, 96728-76-6; **27**, 96789-75-2; **28**, 61091-31-4; **29**, 96789-76-3; **30**, 96728-77-7; *cis*-**34**, 96728-78-8; *trans*-**34**, 96728-79-9; XeF_2, 13709-36-9; MeOH, 67-56-1; HF, 7664-39-3; boron trifluoride etherate, 109-63-7; boron trifluoride methanol, 373-57-9.

(33) The vicinal cis coupling is generally smaller than the trans for 2,3-disubstituted pyrans. See: Hoffman, R. V.; Buntain, G. A. *J. Org. Chem.* **1983**, *48*, 3308.