Addition reactions of alkenes with electronegatively substituted alcohols in the presence of xenon difluoride

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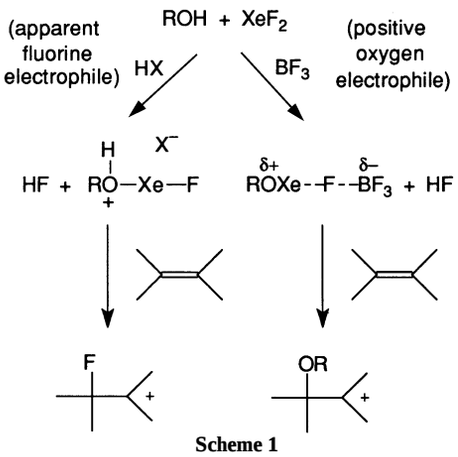
The electrophilic reactivity of proposed alkoxyxenon fluoride (ROXeF) intermediates based on electronegatively substituted (polyfluorinated and polynitroaliphatic) alcohols has been characterized with model alkenes norbornene, 2-methylpent-1-ene and hex-1-ene. The alkoxyxenon fluorides can react as positive oxygen electrophiles—initially incorporating alkoxy substituents—or as apparent fluorine electrophiles—resulting in initial fluorine incorporation—depending on conditions. Efficient simple addition of poorly nucleophilic alcohols to norbornene was observed in certain systems. Selectivity between the various reaction paths (simple fluorination, alkoxyfluorination or alcohol addition) was observed to be a sensitive function of various reaction conditions, especially solvent, temperature and catalyst.

In previous reports, we have described mechanistic aspects of the regioselectivity observed in additions of certain alkoxyxenon fluoride intermediates to alkenes, including reactions of methoxyxenon fluoride with norbornene as a model alkene[1] as well as those of alkoxyxenon fluorides formed from a variety of alcohols, using indene as a model alkene.[2] The products of electrophilic addition of alkoxyxenon fluorides to alkenes may include the corresponding alkoxyfluoroalkanes as well as difluoro-substituted products. In our later study,[2] the nature of the alcohols used for alkoxyfluorination reactions was extended particularly to electronegatively substituted alcohols. Alcohols in this class may also produce electronegatively substituted fluorinated ethers. Fluoroalkyl polynitroalkyl ethers or acetals have been of interest as rocket propellant ingredients,[3,4] while polyfluoroalkyl ethers find potential application as pharmaceutical ingredients.[5,6] Such products are formed here in a single step. Regiochemical data from these model reactions may serve as a test for the mechanism and synthetic utility of this transformation.

In our previous study of the regiochemistry of methoxyxenon fluoride,[1] mechanisms of methoxyfluorination of norbornene were elucidated. Although alkoxyxenon fluoride was not directly observed as a discrete intermediate then or in our later study,[2] the kinetic studies reported therein (*e.g.* alkoxyfluorinations that were zero-order in alkene) strongly supported the proposed mechanisms. Those results also showed that methoxyxenon fluoride could selectively add to alkenes, such as norbornene, either as a positive oxygen electrophile (OE), which adds a methoxy substituent first, or as an apparent fluorine electrophile (FE), which adds fluorine first. Whether the OE or FE reaction pathway predominated depended on reaction conditions, particularly the catalyst used. Indene was used as a model alkene in our study of a series of alkoxyxenon fluorides of varying electronegativity. Less electronegative alkoxyxenon fluorides (methoxy, 2-propoxy, *tert*-butoxy) reacted as positive oxygen electrophiles when boron trifluoride–diethyl ether was used as a catalyst, but as apparent fluorine electrophiles with proton catalyst, in the form of adventitious HF (Scheme 1).



Scheme 1

With more electronegatively substituted alcohols (*e.g.* 2-fluoroethanol, 2,2,2-trifluoroethanol, perfluoro-*tert*-butyl alcohol) as solvents, the alkoxyxenon fluoride intermediates tended to react as oxygen electrophiles regardless of the catalyst. An interesting but unfortunate complication was the discovery that the most acidic (least nucleophilic) alcohols (*e.g.* perfluoro-*tert*-butyl alcohol, 2-fluoro-2,2-dinitroethanol and 2,2,2-trinitroethanol) failed to inhibit an apparent Lewis acid-catalysed polymerization of indene (by BF_3 or XeF_2) in dichloromethane or acetonitrile. This prevented the mechanistic characterization of alkoxyfluorination reactions using the most electronegatively substituted alcohols.

In the present study of electronegatively substituted alkoxyxenon fluorides, norbornene, hex-1-ene and 2-methylpent-1-ene were used as model alkenes less susceptible to polymerization. The norbornene system in particular offered potential advantages for mechanistic elucidation through its rich regio- and stereo-chemistry, as observed in electrophilic addition reactions involving xenon difluoride.[7,8] The present study also emphasizes the alkoxyxenon fluoride intermediates (**2**) derived

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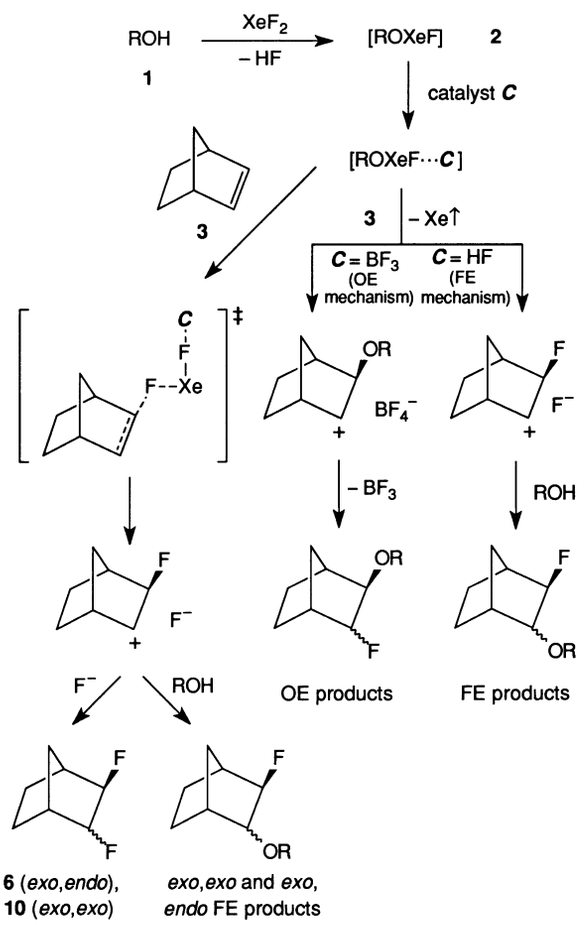
from a variety of electronegatively substituted alcohols (**1**) for comparison with the previously reported methoxyxenon fluoride (**2a**).

$$R{-}OH + XeF_2 \rightarrow [R{-}O{-}XeF]$$

1 **2**

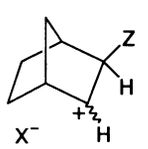
a	R = CH_3	Code: MeOH
b	R = $CF_3(CF_2)_7SO_2N(Et)CH_2CH_2$	FC-10
c	R = CF_3CH_2	TFE
d	R = $CH_3C(NO_2)_2CH_2$	DNP
e	R = $CF_3(CF_2)_6CH_2$	L-9185
f	R = $CF(NO_2)_2CH_2$	FDNE
g	R = $C(NO_2)_3CH_2$	TNE

The value of norbornene (**3**) as a model substrate for alkoxyfluorinations is indicated by its pathways for electrophilic addition shown in Scheme 2. It is well established[7,8] that addition



Scheme 2

of a generic electrophile, ZX, to norbornene will add *z* stereochemically as a 2-*exo* substituent, initially generating the carbocation intermediate (**4**). Depending on the nature of the catalyst



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involved in complexation with **2** (Scheme 2), an oxygen electrophile (OE) mechanism or apparent fluorine electrophile (FE) mechanism may prevail—either route being competitive with conventional difluorination of **3** by XeF_2.[1] The regio- and stereo-chemistry of the products of norbornene substitution thus offer insight into the mechanistic pathways occurring in such electrophilic additions.

Results

The variety of fluoro-, alkoxy- and alkoxyfluoro-substituted products of addition of alkoxyxenon fluorides (*via* Scheme 2) to norbornene (**3**), 2-methylpent-1-ene and hex-1-ene are indicated in Table 1. The products observed can be rationalized by the following mechanistic considerations. The nature of the electrophilic mechanism (FE or OE) leading to the alkoxy-substituted structures is indicated. The great variety of regio- and stereo-isomers of substituted norbornanes attests to the complexity of the norbornyl system in the course of electrophilic reactions involving norbornyl cations.[8] This complexity may include hydride migrations and σ-bond shifts starting with intermediate **4**, which lead to 2,5-disubstituted (**8**, **9**, **16**, **17**) and 2,7-disubstituted (**7**, **11**, **18**) norbornanes as well as nortricyclenes (**5**, **12**). Structure **13** is formed by direct addition of alcohol to **3**.

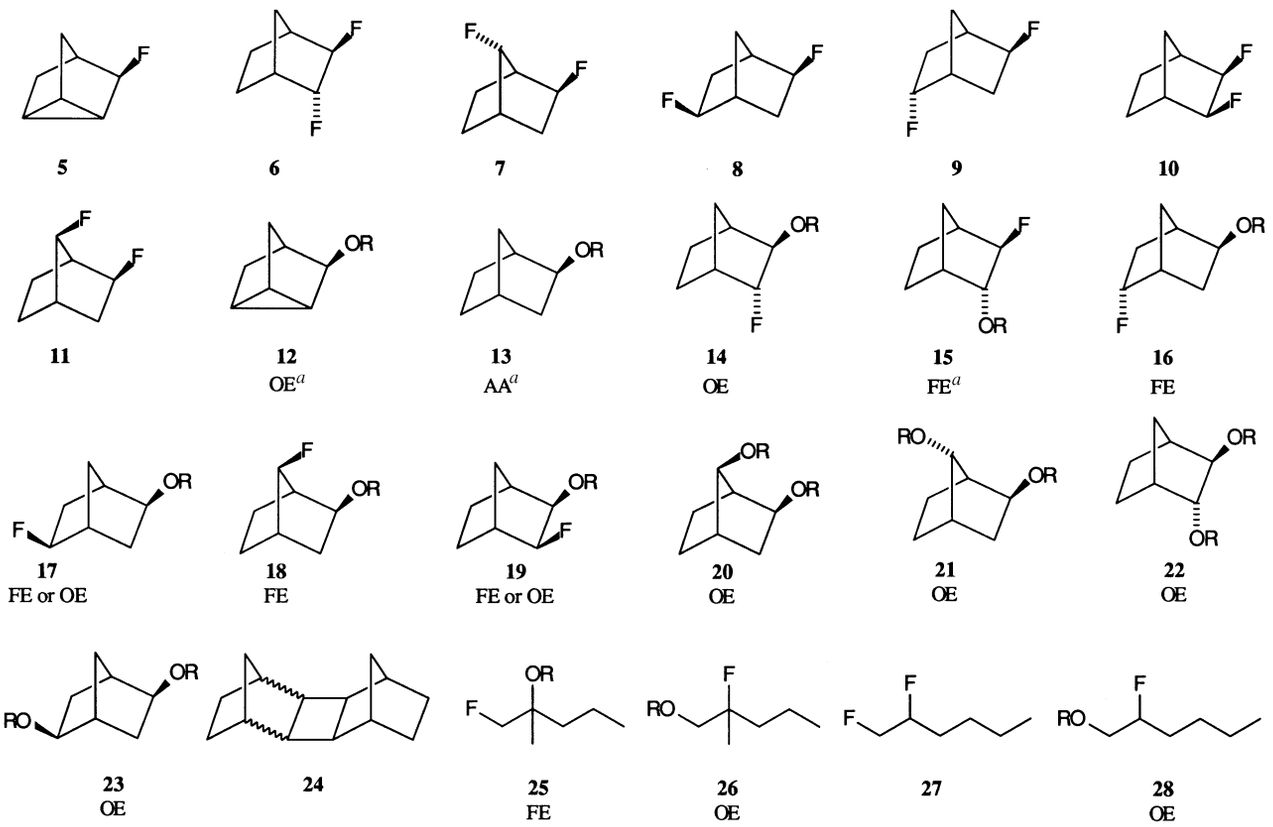
Product distributions for reactions of XeF_2 (*via* intermediate **2**) with norbornene, involving seven different alcohols and conducted under a variety of conditions, are listed in Table 2. Intermediates **2** are listed in order of increasing electron-withdrawing power of the alkoxy group, estimated as described in the Discussion section below. The conditions include: boron trifluoride–diethyl ether or adventitious hydrogen fluoride (from solvolysis of XeF_2 by **1**) as catalyst; either neat alcohol (when feasible) or its dichloromethane solution; varying reaction temperatures ranging from dry ice–solvent temperatures to room temperature. Among the electronegatively substituted alcohols (**1b**–**g**), only TFE (**1c**) is a liquid at 0 °C. The others required a solvent suitable for use in the range of −82 to 0 °C. Dichloromethane was found to be convenient for the reaction and subsequent work-up. FDNE (**1f**) (mp lit., 7 °C[9] or 12 °C[10]) in the presence of **3** and $BF_3{\cdot}OEt_2$ could be run as a liquid mixture at 0 °C.

The regio- and stereo-chemistry of the norbornane products (Table 1) from reactions with trifluoroethanol (**1c**) were determined by multinuclear NMR and mass spectrometry using analytical interpretations of spectral data previously described in detail for difluoronorbornanes[8] and fluoromethoxynorbornanes.[1] Products were also isolated from the reaction of XeF_2 with norbornene in CF_3CD_2OD solvent; deuterium-labelled trifluoroethanol simplified analytical interpretation of the NMR spectra of the norbornane products. For the other new norbornane products from alkoxyxenon fluorides (**2b**,**d**–**g**), product yields and regio- and stereo-chemical assignments were based mainly on gas chromatography–mass spectrometry (GC–MS) analyses and by comparison of these data with those for norbornane products from the thoroughly characterized reactions with **2a**[1] and **2c** and from pure fluorination reactions.[7,8] Analytical strategies for interpretation of mass spectral data of substituted norbornanes were used as previously described.[1,7,8]

In the case of 2,3-disubstituted product **15f** (from FDNE), initial ^1H NMR results after preparative GC isolation were consistent with product **15**; but a GC–MS analysis several days later produced three chromatographic peaks. It was found that, at room temperature, this compound is unstable and rearranges over several days to **16** (major) and **17** (minor).

The reaction of XeF_2 with 2-methylpent-1-ene in trifluoroethanol (**1c**) under adventitious HF catalysis gives two regioisomers: **25**, an FE product, and **26**, an OE product, in a ratio of 43:57, respectively. However, intermediate **2c** from trifluoroethanol was intercepted by hex-1-ene with HF catalysis to give

Table 1 Products formed from alkoxyxenon fluoride reactions with alkenes



[a] Nature of electrophile in alkoxyfluorination as a Markovnikov addition: AA = alcohol addition, OE = oxygen electrophile, FE = apparent fluorine electrophile.

1,2-difluorohexane (**27**) and the OE product **28** in a ratio of 49:51. These products were characterized by NMR and mass spectrometry.

Discussion

Table 2 shows significant changes in the distributions of products as the alcohols become progressively more electronegative and less nucleophilic. As a measure of nucleophilicity, relative electron-withdrawing power of the substituents on the 'substituted methanols' (**1**) was estimated from their Taft substituent constants, σ_I, calculated from standard treatments of this theory.[11,12] These are listed in Table 3 along with summaries of product distributions from the key mechanistic pathways in these electrophilic additions. Previously, we used absolute pK_a data for the alcohols as an indicator of the nucleophilicity of a series of substituted alcohols.[2] Although that is a valid approach to estimating electron-withdrawing power, acid dissociation constants (in the sense of a quantitative measure of alkoxide ion formation) are unavailable for polynitroaliphatic alcohols, which undergo stoichiometric deformylation rather than acid dissociation in the presence of bases strong enough to abstract a proton.[13,14]

A noteworthy indicator of a change in behaviour in the norbornyl system is that 2,3-isomers of fluoromethoxynorbornanes (**14**, **15**, **19**) are formed from **2a** while 2,5-isomers (**16**, **17**) are completely absent.[1] As the alcohols (**1b**–**g**) become progressively more electronegative and less nucleophilic, 2,5-isomers increasingly predominate over the 2,3-isomers. This is evidence of 5,3-hydride shifts occurring in the norbornyl cation intermediate (**4**) to form 2-*endo*,5-*exo*-substituted products and—in conjunction with a 4,5-σ-bond shift—2-*exo*,5-*exo*-substituted norbornanes.[8] These rearrangements of **4**, when Z is an electronegative substituent such as fluoro, result from the energetically unfavourable situation in electrophilic additions when a positive charge resides adjacent to a fluorine-substituted carbon. The 5,3-hydride shift plus accompanying 4,5-σ-bond shift produce a more stable cation with the positive charge on a carbon far removed from fluorine. In OE products from BF_3-catalysed addition of **2a** to **3**, norbornyl cation **4** (Z = OCH_3) showed no tendency to undergo rearrangements to form 2,5- or 2,7-disubstituted norbornanes.[1] In the case of an HF-catalysed FE mechanism competing in the absence of BF_3, some rearrangement to 7-fluoro-2-methoxynorbornane (**18**) occurred; but the absence of 2,5-isomers may be attributed to the high nucleophilicity of methanol and its use as a solvent in those systems. In contrast, less-nucleophilic alcohols (**2b**–**g**) will be poorer scavengers of 3-norbornyl cation (**4**) even in the event of an FE mechanism, so rearrangements of **4** to a 5-norbornyl cation become kinetically allowed and therefore more significant or even predominant.

Unrearranged 2,3-disubstituted products **14** and **15** readily identify an OE and an FE reaction pathway, respectively; the key is noting which substituent occupies the 2-*exo* position, where the first substituent adds to norbornene. Related product **19**, with *exo* substituents at both the 2- and 3-positions, could result from either the OE or FE pathway and affords no definitive indication of either pathway. Previous mechanistic studies of XeF_2 fluorination of 2-deuterionorbornane strongly suggest that 2,5-disubstituted product **16** and 2,7-disubstituted **18** result solely from an FE pathway.[8] Initial addition of a fluorine electrophile to the 2-*exo* position, forming **4** (Z = F), followed by a 3,5-hydride migration and a subsequent 2,5-σ-bond shift, would place the fluorine substituent in the 5-*endo* position.[8] After rearrangement and final attack by the alcohol at the newly created 2-*exo* position, product **16** would result. Likewise, initial fluorine attack at the 2-*exo* position, to give **4** (Z = F), followed by a 4,3-σ-bond shift, would place the fluorine atom in the 7-*syn* (bridge carbon) position[8] prior to bonding of the alkoxy group at the newly formed 2-*exo* position, giving

Table 2 Product distributions (%) from alkoxyfluorination reactions of norbornene determined by GC

Alkoxyxenon fluoride **2** (**1** code)	Catalyst[a] (solvent),[b] T/°C × t/h	Products **5**	**6**	**7**	[**8** + **9**]	**10**	**11**	**12** OE[c]	**13** AA[c]	**14** OE	**15** FE[c]	**16** FE	**17** FE or OE	**18** FE	**19** FE or OE
2a[d]	BF_3 (n), 0 × 0.5	10	24			7				29					30
(MeOH)	BF_3 (n), room temp.	3	16			5		2	37	18					19
	[HF] (n), 0 × 5.0	10	17			4				22	9			18	20
2b	BF_3 (d), room temp. × 0.5			4	7		3		83	[. . . . . 3[e] . . . . .]					
(FC-10)	[HF] (d), room temp. × 6.0	41	16	11	5		9		8	[. . . . . 7[e] . . . . .]					
2c	BF_3 (d),[f] 0 × 0.5			<1	[9 + 14]				42–43		<1	10	12–13	3	
(TFE)	BF_3 (n), 0 × 0.5								92–96						
	[HF] (n), 0 × 0.5	8–11	1–4	2–5	[~1 + ~1]	<1		⩽1	19–25	1–2	19	8–12	0–5	14–17	11
	[HF] (d), 0 × 6.0	50	1	15	[11 + 6]		3				5	1	5	2	
	[HF] (d), room temp. × 0.5	4	2	2	1	1			35		19	12	10	10	3
2d	BF_3 (d),[g] 0 × 0.5			17	24		7	6	27			11			
(DNP)	BF_3 (d), −82 × 2.0 + −8 × 2.0			3	14			8	29			22	23		
	[HF] (d), 0 × 0.5	36		29			8					26			
	[HF] (n), room temp. × 6.0			3	1		1		46			29	19		
2e	BF_3 (d), 0 × 0.5			22	17		11		16	4	13	5		11	
(L-9185)	BF_3 (d), room temp. × 0.5								92						
	[HF] (d), room temp. × 2.0			19	16		11		19	2	13	10		10	
2f	BF_3 (d), −5–0 × 0.5			9–15	8–15		5–9		56–76			3–5			
(FDNE)	BF_3 (n), 5 × 0.5			4					90			6			
	BF_3 (d), −82 × 2.5 + −8 × 2.5			1	12		4					83			
	[HF] (d), 0 × 0.5	28		12	24		4				13	7	12		
	[HF] (d), −80 × 3.0 + −17 × 2.0	21	1	16	18		4	1			16	9	13		
2g	BF_3 (d), 0 × 0.5			5	7		3		83			2			
(TNE)	BF_3 (d), −82 × 2.0 + −8 × 2.0			5	64				16			5	10		
	[HF] (d), 0 × 6.0	37		19	9		17		4			4	10		

[a] BF_3 as $BF_3{\cdot}OEt_2$; HF is adventitious. [b] Solvent: d = dichloromethane, n = neat (alcohol). [c] OE = oxygen electrophile product, FE = apparent fluorine electrophile product, AA = alcohol addition product. [d] Data for methoxyxenon fluoride from ref. 1. [e] Alkoxyfluoronorbornane isomers not resolved by this chromatography. [f] This run also produced the following products, not tabulated above: **20c** (OE), 2%; **21c** (OE), <1%; **22c** (OE), 5%; **23c** (OE), 2%. [g] This run also produced **24** (8%).

Table 3 Electrophilic addition product[a] distributions (%) from additions of alkoxyxenon fluorides to norbornene

Alkoxyxenon fluoride **2** (**1** code)	$\sigma_I(X)$[b]	BF_3 etherate catalyst				Adventitious HF catalyst			
		Solvent, *T*/°C × *t*/h	diF	AA	Alkoxyfluoro	Solvent, *T*/°C × *t*/h	diF	AA	Alkoxyfluoro
2a[c] (MeOH)	0.00	Neat, 0 × 0.5	41	0	59	Neat, 0 × 5.0	31	0	69
		Neat, room temp.	24	37	39				
2b (FC-10)	0.23	CH_2Cl_2, room temp. × 0.5	14	83	3	CH_2Cl_2, room temp. × 6.0	82	8	7
2c (TFE)	0.42	CH_2Cl_2, 0 × 0.5	23	~43	~26	Neat, 0 × 0.5	~16	~22	~60
		Neat, 0 × 0.5		~94		CH_2Cl_2, 0 × 6.0	86	0	14
						CH_2Cl_2, room temp. × 0.5	10	35	54
2d (DNP)	0.45	CH_2Cl_2, 0 × 0.5	48	27	11	CH_2Cl_2, 0 × 0.5	73	0	26
		CH_2Cl_2, −82 × 2.0 + −8 × 2.0	17	29	45	Neat, room temp. × 6.0	5	46	48
2e (L-9185)	0.56	CH_2Cl_2, 0 × 0.5	50	16	33	CH_2Cl_2, room temp. × 0.5	46	19	35
		CH_2Cl_2, room temp. × 5.0	0	92	0				
2f (FDNE)	0.64	CH_2Cl_2, −5–0 × 0.5	~30	~66	~4	CH_2Cl_2, 0 × 0.5	68	0	32
		CH_2Cl_2, −82 × 2.5 + −8 × 2.5	17	0	83	CH_2Cl_2, −80 × 3.0 + −17 × 2.0	60	0	38
		Neat, 0 × 0.5	4	90	6				
2g (TNE)	0.70	CH_2Cl_2, 0 × 0.5	15	83	2	CH_2Cl_2, 0 × 6.0	82	4	14
		CH_2Cl_2, −82 × 2.0 + −8 × 2.0	69	16	15				

[a] Nature of electrophile in alkoxyfluorination as a Markovnikov addition: diF = pure fluoride product (including fluoronortricyclene), AA = alcohol addition product, Alkoxyfluoro = alkoxyfluoronorbornane. [b] Estimated Taft equation substituent constant for group X in XCH_2OXeF (see text). [c] Data for methoxyxenon fluoride from ref. 1.

product **18**. Like the 2,3-disubstituted product **19**, the 2,5-disubstituted product **17** with both substituents in *exo* positions is not definitive for either the FE or OE pathway. Definitive 2,5- and 2,7-disubstituted products *via* the OE pathway would have the alkoxy group in the 5-*endo* and 7-*syn* positions, respectively, after the rearrangement of **4** (Z = OR). Each regioisomer would contain a fluorine substituent in the newly rearranged 2-*exo* position. Neither of such OE products appears with any of the alcohols investigated. This would suggest that despite the poorly nucleophilic nature of the electronegatively substituted alcohols, initial addition of the alkoxy group into the 2-*exo* position does not require additional carbocation stabilization by the rearrangement of **4** (Z = OR) to 2,5- or 2,7-disubstituted products.

The value of this study lies in the success of demonstrating the feasibility of alkoxyfluorination of alkenes with poorly nucleophilic alcohols. As with our study of the indene system,[2] there are clear indications that these alkoxyfluorinations tend toward the OE pathway as the alcohol reactant becomes increasingly electronegative (Table 2). This trend is reasonable since protonation of the alkoxy oxygen in the alkoxyxenon fluoride intermediates (Scheme 1), required for the FE pathway, would become increasingly difficult as the electron density of this oxygen decreases.

Another interesting result is apparent in the product distributions of Tables 2 and 3. The product (**13**) of simple alcohol addition to **3** becomes increasingly prevalent with increasing electronegativity of the alcohol, especially with catalysis by $BF_3{\cdot}OEt_2$. Although Lewis acid-catalysed addition of alcohols to alkenes has been known for a long time,[15] examples have usually required relatively nucleophilic alcohols. Addition of relatively non-nucleophilic alcohols, such as polynitroaliphatics, have required more-reactive alkenes and special conditions. For example, a variety of polynitroaliphatic alcohols (**1d**,**f**,**g**) could be added to 2-fluoro-2,2-dinitroethyl vinyl ether by catalysis with BF_3 etherate;[16] and FDNE (**1f**) could be added to a variety of vinyl ethers or activated alkenes by catalysis with mercury salts,[17] but norbornene (**3**) proved resistant to its addition under the typical conditions used for the other alkenes. (Conventional base-catalysed Michael additions of polynitroaliphatic alcohols to alkenes are unfeasible because of their alkaline deformylation cited above; they tend to give Michael adducts of the corresponding 1,1-dinitroalkanes.[18]) In contrast, Table 3 shows examples of additions of polynitroaliphatic alcohols with efficiencies >80%: FDNE (**1f**) 90% and TNE (**1g**) 83%.

Conditions that favour simple alcohol addition are not optimal for alkoxyfluorination, the primary objective of this work. The data in Table 3 show that several reaction conditions significantly affect the course of the electrophilic addition reactions involving alkoxyxenon fluorides, **2**. Clearly, the electronegativity of **2**, correlating to the Taft substituent constant σ_I, influences the distribution between alkoxyfluoronorbornanes and difluoronorbornanes or alkoxynorbornane as alternative products. While high yields of fluoromethoxynorbornanes are achievable under convenient, mild conditions, the electronegatively substituted alcohols tend toward difluorides and alcohol addition under similar conditions. The clearest way to alleviate the alcohol addition pathway is the use of low temperatures and of adventitious HF, rather than $BF_3{\cdot}OEt_2$, as catalyst. This is most evident with the most electronegatively substituted alcohols (**1f**,**g**): alcohol addition is predominant at *ca.* 0 °C, but good yields of fluoro(2-fluoro-2,2-dinitroethoxy)norbornanes can be obtained at dry ice temperatures. Without $BF_3{\cdot}OEt_2$, alcohol addition is minor or insignificant. With TNE (**1g**), even low temperatures allow only *ca.* 15% conversion to alkoxyfluoronorbornane products and difluoride formation predominates.

Solvent also significantly affects the course of the reaction. The use of neat alcohol and $BF_3{\cdot}OEt_2$ strongly favours alcohol addition, even for 'more nucleophilic' TFE (**1c**). At room temperature in neat alcohols, some alcohol addition can occur (though not predominantly) even without BF_3; of course, XeF_2 is initially present in all of these reactions. These were the conditions under which methanol addition to **3** also was seen.[1]

Previously, methoxyxenon fluoride (**2a**) could not be intercepted by alkenes less reactive than norbornene, indene, 1-phenylpropene or 2,3-dimethylbuta-1,3-diene.[1] With alkenes such as hex-1-ene, cyclohexene or methyl crotonate, only formaldehyde was formed. Electron-rich alkenes like dihydropyran reacted too rapidly with XeF_2 (generating the fluorinated pyranyl carbocation, which was intercepted by methanol solvent) to proceed *via* intermediates such as **2a**. Thus, the range of reactivity of alkenes that can intercept reactive alkoxyxenon fluorides is not extensive. However, electron-withdrawing substituents are known to stabilize xenon–oxygen bonds.[19] This stabilization apparently decreases disproportionation of intermediates **2** to corresponding aldehydes (as observed with **2a**) and allows alkoxyfluorination to become competitive even using less reactive alkenes such as 2-methylpent-1-ene and hex-

1-ene. Intermediate **2c** is intercepted by 2-methylpent-1-ene in good yield (76%) to give approximately equal amounts of regioisomers **25** and **26**. Reaction of **2c** with the less reactive hex-1-ene gives 1,2-difluorohexane (**27**) and 2-fluoro-1-(2,2,2-trifluoroethoxy)hexane (**28**). Difluoride **27** and apparent FE product **25** may also form *via* direct fluorination by XeF_2, followed by interception of the corresponding 2-alkyl cation with fluoride or alcohol nucleophile, without participation of an alkoxyxenon fluoride (**2c**). The finding of regiochemically clean 1,2-difluorination of hex-1-ene may be surprising since fluorination of aliphatic alkenes without a substituent that stabilizes the carbocation generally gives rearranged products.[20] The absence of difluoride products from 2-methylpent-1-ene suggests that the tertiary carbocation may be captured from a solvent-separated ion-pair while the secondary carbocation from hex-1-ene is intercepted by the fluoride ion in an intimate ion-pair.

Conclusions

The feasibility of performing alkoxyfluorinations on several model alkenes using electronegatively substituted (polyfluorinated and polynitro) alcohols has been successfully demonstrated. A broad survey of reaction conditions was conducted (summarized in Table 3 for norbornene), though conditions were not optimized for any particular alcohol system. For the most electronegatively substituted alcohol systems, low temperatures (dry ice–solvent) favour the desired alkoxyfluorinations over difluorinations. The norbornyl system exhibits rearrangement as the alcohols become more electronegative. This complicates interpretation of the specific mechanism (FE or OE) by which certain regioisomers are formed. A judiciously labelled alkene would be a more helpful model for clarifying the ambiguities inherent in the isomeric products of this system; 2-deuterionorbornene would be ideal in this regard,[8] but other alkene systems would be useful if they resist polymerization that was observed in the indene system.[2] In several systems, an interesting phenomenon of efficient addition of electronegatively substituted, poorly nucleophilic alcohols to alkenes was observed, a transformation which may have useful synthetic applications.

Experimental

Instrumentation

^1H and ^{19}F NMR spectra were acquired on a JEOL FX-90Q spectrometer (δ_H 90 MHz *vs.* Me_4Si, δ_F 84.7 MHz *vs.* $CFCl_3$) unless otherwise indicated; *J* values are given in Hz. Mass spectral analyses were obtained at 70 eV (electron impact) on a Hewlett-Packard 5890 GC [0.2 mm × 25 m H-P Ultra-2 (DB-5/SE-54 equivalent) capillary column] interfaced with an H-P 5970B mass-selective detector; the following temperature profile was usually used: 60 °C × 3 min, 8 °C min^{-1} to 225 °C, hold at 225 °C for 45 min. Mass spectral data interpretation was facilitated by the software MassSpec version 2.0 from Trinity Software (Campton, NH). Analytical GLC data (product distributions) for reactions in TFE (**1c**) were obtained with a Hewlett-Packard 5890 GC (f.i.d.), using the same type of column as above, interfaced to an H-P 3392A integrator. Preparative GLC was carried out on reactions involving TFE (**1c**) at San Diego, California with a Hewlett-Packard Model 700 GC (t.c. detector) on a $\frac{3}{8}$ in × 10 ft column of 5% Carbowax-20M on 80/100 Chromosorb W, and on reactions involving other electronegatively substituted alcohols **1** at Pueblo, Colorado with a Shimadzu Model GC-9A GC on a $\frac{1}{4}$ in × 6 ft column of either 3% QF-1 or 10% QF-1.

Materials

Xenon difluoride was purchased from PCR, Inc. (Gainesville, FL). Alcohols FC-10 (**1b**) and L-9185 (**1e**) were a gift of the 3M Co. (St. Paul, MN); DNP (**1d**) was a gift of GenCorp Aerojet (Sacramento, CA); FDNE (**1f**) was a commercial sample prepared by Fluorochem Inc. (Azusa, CA); TNE (**1g**) was a gift of the US Air Force Academy, Colorado. Other chemicals were reagent grade; Aldrich Chemical Co. was a typical source.

General procedures

Alcohol solvent. The following procedure for a reaction in TFE (**1c**) is typical of neat-alcohol-solvent reactions. To XeF_2 (58.0 mg, 0.343 mmol) in a dry 5 ml round-bottomed flask fitted with a drying tube and stirring bar at 0 °C was added 0.500 ml of TFE (**1c**). Solid norbornene (**3**) (65.5 mg, 0.686 mmol) was added. After stirring the mixture for a desired reaction time (Table 2), it was allowed to warm to room temp.; the mixture was poured into aqueous sodium hydrogen carbonate, extracted with diethyl ether (3×), dried over $MgSO_4$ and analysed by GLC. The following temperature profile was used: 30 °C × 5 min, 2 °C min^{-1} to 80 °C, hold at 80 °C. Retention times (min) of the products are as follows: **5**, 11.9; **6**, 12.5; **7**, 13.0; **8**, 13.3; **9**, 13.4; **10**, 15.8; **12**, 16.4; **13c**, 19.2; **14c**, 20.1; **19c**, 22.1; **15c**, 22.3–22.5; **16c**, 22.6; **17c**, 22.7; **18c**, 27.1. The product distributions are given in Table 2. The overall yield (82%) was determined by GLC with chlorobenzene as an internal standard corrected for flame response. Spectral data for **5**–**10** are identical to those reported in the literature.[8,21] Characterizations of the new products are given below.[22]

Dichloromethane solvent. The following procedure for a reaction with DNP (**1d**) is typical of alcohol reactions run in dichloromethane at *ca.* 0 °C. XeF_2 (66.4 mg, 0.392 mmol) was added to a dried 25 ml round-bottomed flask, followed by the addition of CH_2Cl_2 (2.0 ml). The stoppered flask was placed in an ice–water bath at 0 °C. DNP (95.2 mg, 0.634 mmol) was added, followed by the addition of norbornene (**3**) (77.2 mg, 0.820 mmol). Immediately after the addition of the norbornene, boron trifluoride–diethyl ether (42 μl, 0.341 mmol) was added using a glass syringe. After the reaction was complete (Table 2), diethyl ether and saturated aqueous sodium hydrogen carbonate were added. The two phases separated and a second extraction using diethyl ether and saturated aqueous $NaHCO_3$ was performed on the aqueous layer. The organic layer was dried over $MgSO_4$, placed into a sealed vial, and refrigerated at 4 °C immediately. Analyses by GC and GC–MS were then performed. Assignments of products from reactions based on FC-10 (**1b**) were deduced from GC retention times by analogy to those of products from reactions with all other alcohols (**1c**–**g**), which were characterized by GC–MS and/or NMR as well.

For analysis of the products from the reaction of TFE (**1c**), the following temperature profile was used: 30 °C × 3 min, 2 °C min^{-1} to 120 °C, hold at 120 °C. Retention times (min) of the products are as follows: **7**, 9.1; **8**, 11.3; **9**, 10.6; **13c**, 20.0; **15c** + **19c**, 21.2; **16c**, 23.2; **17c**, 23.5; **18c**, 28.1; **20c**, 32.4; **21c**, 33.7; **22c**, 34.6; **23c**, 35.1.

The following general procedure is typical of polynitroaliphatic alcohol reactions run in dichloromethane at dry ice–solvent temperatures. A 25 ml round-bottomed flask was purged with nitrogen for 5 min, equipped with a magnetic stirring bar, and stoppered. XeF_2 was added, and the flask was fitted with a pressure-equalizing addition funnel. The flask was placed in a −78 °C dry ice–acetone bath. Norbornene (**3**) was dissolved in dry CH_2Cl_2; this solution was added to the addition funnel and then to the flask containing the XeF_2. The addition funnel was rinsed again with CH_2Cl_2. A solution of boron trifluoride–diethyl ether in dry CH_2Cl_2 was added to the addition funnel and then added to the reaction flask over a period of 20 min. After the reaction was complete (Table 2), the dry ice–acetone bath was changed to an ice–water bath and the reaction was quenched using a 0.1 M aqueous solution of sodium fluoride to remove HF. Extraction of the aqueous layer was done using CH_2Cl_2, followed by drying of the extract over anhydrous $MgSO_4$. The sample was refrigerated at 4 °C immediately. Analyses by GC and GC–MS were then performed.

Reaction of 2-methylpent-1-ene

The reaction in TFE (**1c**) was carried out as described in the General Procedures section. GLC analysis was conducted at 90 °C on a $\frac{1}{8}$ in × 20 ft stainless-steel column of 2.5% FFAP on 80/100 Chromosorb G-HP, giving products **26** and **25** (ratio 57:43) with retention times of 7 and 13 min, respectively. Product yield (76%) was obtained by GLC analysis using chlorobenzene, corrected for flame response, as an internal standard. Products were isolated by preparative GLC as described in the Instrumentation section. 1-Fluoro-2-methyl-2-(2,2,2-trifluoroethoxy)pentane (**25**): $\delta_H(CDCl_3)$ 1.00 (3 H, t, *J* 6.4), 1.21 (3 H, d, *J* 1.8), 1.25–1.63 (4 H, m), 3.85 (2 H, q, *J* 8.6), 4.31 (2 H, d, *J* 47.8). $\delta_F(CDCl_3)$ −75.4 (3 F, t, *J* 8.6), −226.8 (1 F, t, *J* 48). *m*/*z* 187 (3%, M − CH_3), 169 (56, M − CH_2F), 159 (100, M − C_3H_7), 127 (85), 69 (60) and 43 (56). 2-Fluoro-2-methyl-1-(2,2,2-trifluoroethoxy)pentane (**26**): $\delta_H(CDCl_3)$ 1.04 (3 H, t, *J* 7.2), 1.20–1.80 (4 H, m), 1.39 (3 H, d, *J* 29), 3.90 (d, *J* 17), 3.94 (q, *J* 8.6), the latter two absorptions overlap to give 4 H; $\delta_F(CDCl_3)$ −74.6 (3 F, t, *J* 8.6, CF_3), −191.7 to −193.0 (1 F, m). *m*/*z* 187 (6%, M − CH_3), 141 (100), 113 (4), 69 (5), 61 (80) and 43 (51).

Reaction of hex-1-ene

The reaction in TFE (**1c**) was carried out as described in the General Procedures section. GLC analysis was conducted at 90 °C on a $\frac{1}{8}$ in × 20 ft stainless-steel column of 2.5% FFAP on 80/100 Chromosorb G-HP, giving products **27** and **28** (ratio 49:51) with retention times of 9 and 20 min, respectively. Product yield (32%) was obtained by GLC analysis using chlorobenzene, corrected for flame response, as an internal standard. Products were isolated by preparative GLC as described in the Instrumentation section. 1,2-Difluorohexane (**27**): $\delta_H(CDCl_3)$ 0.93 (3 H, t, *J* 5.7), 1.15–1.60 (4 H, m), 1.60–2.00 (2 H, m), 4.0–5.2 (1 H, m), 4.48 (2 H, ddd, *J* 5.0, 24.0 and 48.0). $\delta_F(CDCl_3)$ −189, −230. *m*/*z* 89 (0.2%), 69 (41), 59 (28), 57 (21), 56 (26), 55 (27), 43 (69), 42 (73) and 41 (100). 2-Fluoro-1-(2,2,2-trifluoroethoxy)hexane (**28**): $\delta_H(CDCl_3)$ 0.96 (3 H, t, *J* 5.8), 1.10–1.58 (4 H, m), 1.58–1.90 (2 H, m), 3.71 (2 H, dd, *J* 4.4 and 24.0), 3.89 (2 H, q, *J* 8.8), 4.60 (1 H, dm, *J* 45). $\delta_F(CDCl_3)$ −74.9 (t, *J* 8.8, CF_3), −186 (m). *m*/*z* 173 (0.8%), 113 (100, $CH_2OCH_2CF_3$), 69 (39), 61 (33), 56 (61), 55 (45), 43 (56) and 41 (90).

Spectral characteristics of norbornyl products

3-(2,2,2-Trifluoroethoxy)nortricyclene (**12c**): $\delta_H(CDCl_3)$ 0.90–1.40 (4 H, complex m, norbornyl skeleton), 1.40–2.60 (4 H, two br m), 3.55–4.00 (m, norbornyl 2-H), 3.76 (q, *J* 8.7), the latter two absorptions overlap to give 3 H; $\delta_F(CDCl_3)$ −75.1 (t, *J* 9). *m*/*z* 192 (M^+, 28%), 177 (50), 93 (52), 92 (33), 79 (100), 77 (46), 66 (50), 41 (33) and 39 (50).

2-*exo*-(2,2,2-Trifluoroethoxy)norbornane (13c). $\delta_H(CDCl_3)$ 0.95–1.80 (8 H, 2 × m, norbornyl skeleton), 2.17–2.50 (2 H, m, 1-H and 4-H), 3.40–3.65 (m, 2-H), 3.75 (q, *J* 8.8), the latter two absorptions overlap to give 3 H; $\delta_F(CDCl_3)$ −74.9 (t, *J* 9). *m*/*z* 194 (M^+, 0.9%), 95 (40), 94 (92), 79 (93), 68 (49), 67 (100), 66 (64), 41 (55) and 39 (50).

3-*endo*-Fluoro-2-*exo*-(2,2,2-trifluoroethoxy)norbornane (14c). $\delta_H(CDCl_3)$ 1.00–1.85 (6 H, m, norbornyl skeleton), 2.20–2.39 (1 H, m), 2.39–2.40 (1 H, m), 3.34 (1 H, d, *J* 18.3, 2-H), 3.82 (2 H, q, *J* 8.5), 4.69 (1 H, dd, *J* 4.7 and 52.6, 3-H); $\delta_F(CDCl_3)$ −74.9 (t, *J* 9), −195.2 (dd, *J* 18 and 53). *m*/*z* 212 (M^+, 3%), 192 (66), 139 (54), 113 (51), 97 (62), 79 (60), 67 (100), 59 (58), 41 (68) and 39 (70).

2-*exo*-Fluoro-3-*endo*-(2,2,2-trifluoroethoxy)norbornane (15c) (containing 19c contaminant from preparative GC). $\delta_H(CDCl_3)$ 0.95–2.10 (6 H, m, norbornyl skeleton), 2.15–2.50 (2 H, m, 1-H and 4-H), 3.30–4.00 (m, 3-H), 3.75 (q, *J* 8.7), the latter two absorptions overlap to give 3 H, 4.99 (1 H, d, *J* 57.4, 2-H); $\delta_F(CDCl_3)$ −74.9 (t, *J* 9, CF_3), −210.4 (dd, *J* 5 and 57, 2-F). *m*/*z* 212 (M^+, 0.2%), 112 (91), 97 (100), 84 (41), 79 (37), 59 (35), 41 (35) and 39 (47).

2-*endo*-Fluoro-5-*exo*-(2,2,2-trifluoroethoxy)norbornane (16c). $\delta_H(CDCl_3)$ 0.90–2.00 (6 H, m, norbornyl skeleton), 2.20–2.60 (2 H, m, 1-H and 4-H), 3.45–4.00 (m, 5-H), 3.78 (q, *J* 8.6), the latter two absorptions overlap to give 3 H, 4.95 (1 H, dm, *J* 57, 2-H); $\delta_F(CDCl_3)$ −75.0 (t, *J* 9, CF_3), −190 (ddd, *J* 15, 28 and 57, 2-F). *m*/*z* 212 (M^+, 0.8%), 192 (24), 113 (43), 112 (38), 97 (69), 83 (36), 79 (81), 67 (66), 66 (100), 59 (44), 41 (53) and 39 (65).

2-*exo*-Fluoro-5-*exo*-(2,2,2-trifluoroethoxy)norbornane (17c). $\delta_H(CDCl_3)$ 0.90–2.00 (6 H, m, norbornyl skeleton), 2.20–2.65 (2 H, m, 1-H and 4-H), 3.42 (1 H, m, 5-H), 3.75 (2 H, q, *J* 8.5), 4.49 (1 H, dm, *J* 55.0, 2-H); $\delta_F(CDCl_3)$ −74.9 (t, *J* 9, CF_3), −164 (m, 2-F). *m*/*z* 212 (M^+, 0.7%), 192 (17), 165 (15), 139 (16), 126 (52), 113 (41), 112 (14), 97 (34), 83 (28), 79 (100), 67 (37), 66 (94), 59 (35), 41 (42) and 39 (55).

7-*syn*-Fluoro-2-*exo*-(2,2,2-trifluoroethoxy)norbornane (18c). $\delta_H(CDCl_3)$ 0.90–1.20 (2 H, m, norbornyl skeleton), 1.40–1.75 (2 H, m, norboryl skeleton), 1.80–2.10 (2 H, m, norbornyl skeleton), 2.20–2.50 (2 H, m, 1-H and 4-H), 3.60–3.90 (m, 2-H), 3.82 (q, *J* 8.7), the latter two absorptions overlap to give 3 H, 4.78 (1 H, d, *J* 56.5, 7-H); $\delta_F(CDCl_3)$ −74.5 (t, *J* 9, CF_3), −202.5 (d, *J* 57, 7-F). *m*/*z* 212 (M^+, 0.3%), 192 (8), 113 (17), 112 (20), 83 (22), 79 (54), 67 (100), 66 (50), 59 (19), 53 (14), 41 (23) and 39 (30).

2-*exo*-Fluoro-3-*exo*-(2,2,2-trifluoroethoxy)norbornane (19c). *m*/*z* 212 (M^+, 7%), 192 (69), 139 (48), 113 (40), 97 (69), 79 (58), 68 (48), 67 (100), 59 (52), 41 (58) and 39 (61). Preparative GC produced **19c** in a fraction with **15c** as the major constituent.

2-*exo*,7-*syn*-Bis(2,2,2-trifluoroethoxy)norbornane (20c). $\delta_H(CDCl_3)$ 0.85–1.20 (2 H, m, norbornyl skeleton), 1.25–1.95 (4 H, m, norbornyl skeleton), 2.05–2.45 (2 H, m), 3.30–4.05 (6 H, 2 × m superimposed on 2 × q); $\delta_F(CDCl_3)$ −74.8 (t, *J* 9), −75.0 (d, *J* 9). *m*/*z* 263 (0.7%), 192 (23), 165 (12), 139 (29), 93 (38), 92 (63), 83 (42), 79 (100), 78 (45), 77 (18), 67 (58), 66 (29).

2-*exo*,7-*anti*-Bis(2,2,2-trifluoroethoxy)norbornane (21c). A very minor product not isolated for NMR: *m*/*z* 263 (1%), 192 (44), 165 (13), 139 (31), 93 (68), 92 (61), 83 (62), 79 (100), 78 (41), 77 (25), 67 (64), 66 (44).

2-*exo*,3-*endo*-Bis(2,2,2-trifluoroethoxy)norbornane (22c). δ_H(200 MHz; $CDCl_3$) 1.20–1.41 (2 H, m), 1.48–1.75 (4 H, m), 2.14–2.28 (2 H, m), 2.28–2.37 (1 H, m), 2.38–2.48 (1 H, m), 3.55–3.98 (4 H, m); δ_F(188 MHz; $CDCl_3$) −74.8 (t, *J* 9). *m*/*z* 292 (M^+, 1.5%), 263 (0.5), 192 (27), 165 (25), 139 (15), 93 (45), 92 (17), 83 (27), 79 (40), 78 (3), 77 (13), 67 (31), 66 (100).

2-*exo*,5-*exo*-Bis(2,2,2-trifluoroethoxy)norbornane (23c). δ_H(200 MHz, $CDCl_3$) 1.34–1.72 (6 H, m), 2.32–2.48 (2 H, m), 3.36–3.50 (2 H, m), 3.69–3.84 (4 H, m); δ_F(188 MHz; $CDCl_3$) −74.8 (t, *J* 8.7). *m*/*z* 292 (M^+, 2%), 263 (0.5), 192 (34), 165 (38), 139 (23), 93 (58), 92 (21), 83 (34), 79 (45), 78 (4), 77 (16), 67 (44), 66 (100).

3-(2,2-Dinitropropoxy)nortricyclene (12d). *m*/*z* 242 (M^+, <1%), 113 (45), 109 (100), 93 (26), 81 (68), 79 (43), 67 (75), 66 (22), 41 (43) and 39 (28).

2-*exo*-(2,2-Dinitropropoxy)norbornane (13d). *m*/*z* 244 (M^+, <1%), 95 (54), 93 (100), 79 (33), 68 (28), 67 (99), 66 (34), 41 (53) and 39 (31).

5-*exo*-(2,2-Dinitropropoxy)-2-*endo*-fluorononorbornane (16d). *m*/*z* 262 (M^+, <1%), 113 (100), 109 (61), 92 (63), 81 (95), 79 (100), 67 (84), 66 (83), 41 (93) and 39 (60).

5-*exo*-(2,2-Dinitropropoxy)-2-*exo*-fluorononorbornane (17d). *m*/*z* 262 (M^+, <1%), 113 (100), 111 (69), 109 (65), 93 (65), 81 (78), 79 (74), 67 (69), 41 (90) and 39 (62).

2-*exo*-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluorooctyloxy)-norbornane (13e). *m*/*z* 494 (M^+, <1%), 95 (67), 94 (100), 93 (26), 79 (87), 67 (70), 66 (58), 55 (20), 41 (37) and 39 (29).

3-*endo*-Fluoro-2-*exo*-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyloxy)norbornane (14e). *m*/*z* 512 (M^+, <1%), 439 (64), 131 (26), 113 (98), 112 (82), 97 (44), 79 (82), 69 (40), 67 (100) and 66 (73).

2-*exo*-Fluoro-3-*endo*-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyloxy)norbornane (15e). *m*/*z* 512 (M^+, <1%), 113 (84),

112 (100), 97 (80), 84 (27), 79 (29), 69 (32), 67 (59), 41 (26) and 39 (32).

2-*endo*-Fluoro-5-*exo*-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyloxy)norbornane (16e). *m*/*z* 512 (M^+, <1%), 97 (39), 92 (23), 81 (47), 79 (100), 78 (14), 69 (26) and 67 (41).

7-*syn*-Fluoro-2-*exo*-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyloxy)norbornane (18e). *m*/*z* 512 (M^+, <1%), 113 (55), 112 (55), 97 (41), 81 (23), 79 (76), 69 (34), 67 (100), 66 (62) and 41 (18).

3-(2-Fluoro-2,2-dinitroethoxy)nortricyclene (12f). *m*/*z* 246 (M^+, <1%), 113 (31), 109 (46), 81 (48), 80 (23), 79 (45), 67 (100), 66 (26), 59 (23) and 30 (34).

2-*exo*-(2-Fluoro-2,2-dinitroethoxy)norbornane (13f). δ_H(300 MHz; $CDCl_3$) 0.92–1.20 (3 H, m, norbornyl skeleton), 1.25–1.78 (5 H, m, norbornyl skeleton), 2.26 (1 H, m, 4-H), 2.30 (1 H, m, 1-H), 3.52 (1 H, d, *J* 6.8, 2-H), 4.45 and 4.52 (2 H total, AB q, *J* 18 and 12.2, OCH_2CF); δ_F(282 MHz; $CDCl_3$) −111.0 (m). *m*/*z* 248 (M^+, <1%), 93 (49), 79 (38), 68 (57), 67 (100), 66 (38), 55 (34), 41 (65), 39 (43) and 30 (59).

2-*exo*-Fluoro-3-*endo*-(2-fluoro-2,2-dinitroethoxy)norbornane (15f). *m*/*z* 266 (M^+, <1%), 112 (100), 111 (85), 97 (87), 85 (73), 79 (79), 67 (70), 59 (69), 41 (70) and 30 (100).

2-*endo*-Fluoro-5-*exo*-(2-fluoro-2,2-dinitroethoxy)norbornane (16f). δ_H(200 MHz; $CDCl_3$) 0.90–1.70 (6 H, m, norbornyl skeleton), 2.29 (2 H, m, 1-H and 4-H), 3.52 (m, 5-H), 4.52 (2 H, d, *J* 17.7, OCH_2CF), 4.94 (1 H, dm, *J* 57, 2-H); δ_F(188 MHz; $CDCl_3$) −111.1 (1 F, m, OCH_2CF), −189.4 (1 F, ddd, *J* 14, 27 and 57, 2-F). *m*/*z* 266 (M^+, <1%), 113 (49), 85 (59), 79 (100), 67 (43), 66 (45), 59 (41), 41 (39), 39 (37) and 30 (68).

2-*exo*-Fluoro-5-*exo*-(2-fluoro-2,2-dinitroethoxy)norbornane (17f). δ_H(60 MHz; $CDCl_3$) 0.80–2.00 (6 H, m, norbornyl skeleton), 2.18–2.40 (2 H, m, 1-H and 4-H), 3.70 (1 H, m, 5-H), 4.50 (2 H, d, *J* 17.9, OCH_2CF), 4.58 (1 H, dd, *J* 15.4 and 50, 2-H); δ_F(282 MHz; $CDCl_3$) −111.9 (1 F, m, OCH_2CF), −110.9 (1 F, m, 2-F). *m*/*z* 266 (M^+, <1%), 113 (43), 97 (39), 81 (50), 79 (100), 67 (71), 66 (87), 41 (48), 39 (41) and 30 (58).

2-*exo*-(2,2,2-Trinitroethoxy)norbornane (13g). *m*/*z* 275 (M^+, <1%), 93 (75), 79 (52), 68 (65), 67 (100), 66 (42), 55 (31), 41 (51), 39 (34) and 30 (43).

2-*endo*-Fluoro-5-*exo*-(2,2,2-trinitroethoxy)norbornane (16g). *m*/*z* 293 (M^+, <1%), 85 (65), 81 (49), 79 (100), 67 (52), 66 (60), 59 (49), 41 (58), 39 (60) and 30 (79).

2-*exo*-Fluoro-5-*exo*-(2,2,2-trinitroethoxy)norbornane (17g). *m*/*z* 293 (M^+, <1%), 97 (38), 85 (39), 81 (57), 79 (100), 67 (69), 66 (82), 41 (45), 39 (43) and 30 (66).

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21 R. A. Hildreth, M. L. Druelinger and S. A. Shackelford, *Tetrahedron Lett.*, 1982, 1059. In this paper, product **VI** is incorrectly displayed; it should be 3-*exo*-acetamido-2-*endo*-fluoronorbornane.
22 Reactions based on alcohols **1b** and **1d**–**g** were conducted at the University of Southern Colorado in a time period without access to a suitable spectrometer to provide detailed NMR characterizations of all products. Interpretations based on our reported GC–MS data for the products derived from these alcohols are completely consistent with the fully characterized reactions using **1a**[1] and **1c**, reported herein.

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