Regioselectivity in the Addition Reactions of Alkoxyxenon Fluorides with Indene[1]

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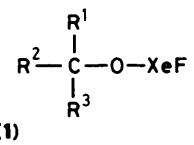
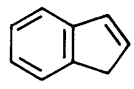
Xenon difluoride (XeF_2) reacts with alcohols to form unstable alkoxyxenon fluoride intermediates (ROXeF). The regio- and stereo-chemistry of products from reaction of ROXeF with indene were determined. Alkoxyxenon fluorides [R = CH_3, $(CH_3)_2CH$, and $(CH_3)_3C$] react as positive oxygen electrophiles (OE) when boron trifluoride–ether is used as catalyst. However, these alkoxyxenon fluorides react as apparent fluorine electrophiles (FE) with proton catalyst (hydrogen fluoride generated *in situ*). Reactions of XeF_2 and alcohols with electron-withdrawing substituents give alkoxyxenon fluorides which add to indene as an OE species even though boron trifluoride–ether was not used as catalyst. Reactions of XeF_2 with polynitroaliphatic alcohols and indene give rapid polymerization of indene rather than alkoxyfluorination.

Xenon difluoride (XeF_2) is an excellent fluorinating agent for unsaturated hydrocarbons.[2] Substitutions of XeF_2 with oxygen-containing organic[3] and inorganic acids[4] have been documented. Recently[5] we reported on the methanolysis of xenon difluoride to form an unstable electrophilic species, CH_3OXeF (**1a**). In that study we found that (**1a**) reacts with certain alkenes in methanol and proton catalyst as an apparent fluorine electrophile. However, (**1a**) adds to alkenes in methanol as a positive oxygen electrophile with boron trifluoride as catalyst as shown in Scheme 1.



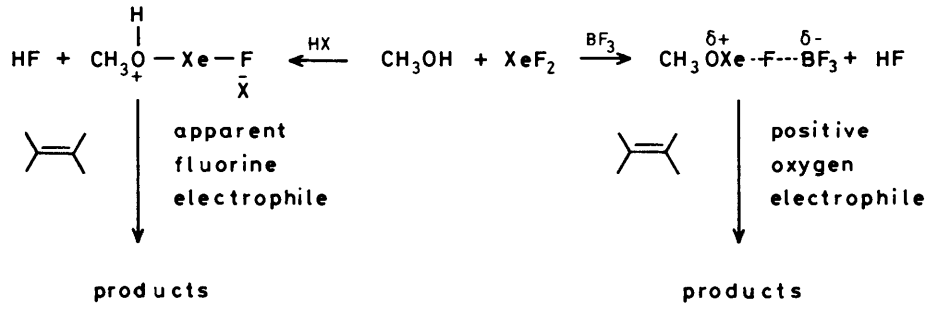
(**1**)

a: $R^1 = R^2 = R^3 = H$
b: $R^1 = R^2 = CH_3, R^3 = H$
c: $R^1 = R^2 = R^3 = CH_3$
d: $R^1 = ClCH_2, R^2 = R^3 = H$
e: $R^1 = FCH_2, R^2 = R^3 = H$
f: $R^1 = CF_3, R^2 = R^3 = H$
g: $R^1 = R^2 = R^3 = CF_3$
h: $R^1 = CF(NO_2)_2, R^2 = R^3 = H$
i: $R^1 = C(NO_2)_3, R^2 = R^3 = H$
j: $R^1 = CH_3C(NO_2)_2, R^2 = R^3 = H$



(**2**)

In this paper we extend this study to include other alcohols which contain electron-donating and -withdrawing substituents such as the isopropyl, t-butyl, 2-chloroethyl, 2-fluoroethyl, 2,2,2-trifluoroethyl, and perfluoro-t-butyl groups. Intermediates (**1a**–**g**) from these alcohols were intercepted with indene (**2**). Reactions were also investigated with the energetic alcohols 2-fluoro-2,2-dinitroethanol, 2,2,2-trinitroethanol, and 2,2-dinitropropanol. The energetic alcohols were also expected to react with XeF_2 to give intermediates (**1h**, **i**, and **j**), respectively. Data from these reactions are presented and serve as a test for the mechanism and utility of alkoxyfluorinations.

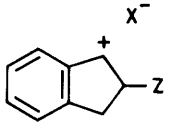


Scheme 1.

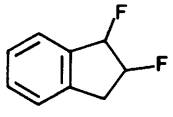
Table 1. Product distributions (%) from alkoxyfluorination reactions of indene determined by gas chromatography

Alkoxyxenon fluoride	Catalyst[a]	Products						Total isolated yield (%)[b]	pK_a (alcohol)
(1a)		(4)	(5)	(6)	(7)	(8)	(9)		
	BF_3	3	9	6	4	26	52	70	15.5[c,d]
	[HF]	2		52	46			70	
(1b)		(4)	(5)	(10)	(11)	(12)	(13)		
	BF_3	16	6		26	33	19	40—45	17.1[d]
	[HF]	14	8	30	40		8	40—45	
(1c)		(4)	(5)	(14)	(15)	(16)	(17)		
	BF_3	24	4	4	40	26	2	40—45	19.2[d]
	[HF]	3	7	38	52			40—45	
(1d)		(4)	(5)	(18)	(19)	(20)	(21)		
	[HF]		10	49	31	4	6	62	14.3[c,d]
(1e)		(4)	(5)	(22)	(23)	(24)	(25)		
	[HF]		13	40	26	5	16	49	(14.7)[e]
(1f)		(4)	(5)	(26)	(27)	(28)	(29)		
	[HF]	2	5	4		75	14	45	11.3[f]
(1g)		(4)	(5)	(30)	(31)	(32)	(33)		
	[HF]	20	16		7	12	45	10—15	5.2[g]

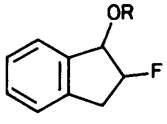
[a] BF_3 as BF_3–ether; hydrogen fluoride generated *in situ*. [b] Determined by n.m.r. with cyclohexane or toluene as internal standard. [c] pK_a from P. Ballinger and F. A. Long, *J. Am. Chem. Soc.*, 1960, **82**, 795. [d] E. P. Serjeant and B. Dempsey, 'Ionization Constants of Organic Acids in Aqueous Solutions,' Pergamon Press, Oxford, 1979. [e] Interpolated from data in notes *b* and *c*. [f] R. N. Haszeldine, *J. Chem. Soc.*, 1953, 1757. [g] R. Filler and R. M. Schure, *J. Org. Chem.*, 1967, **32**, 1217.

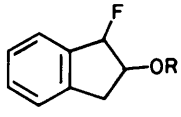


(3) X,Z as defined in Scheme 2



(4) *cis*
(5) *trans*





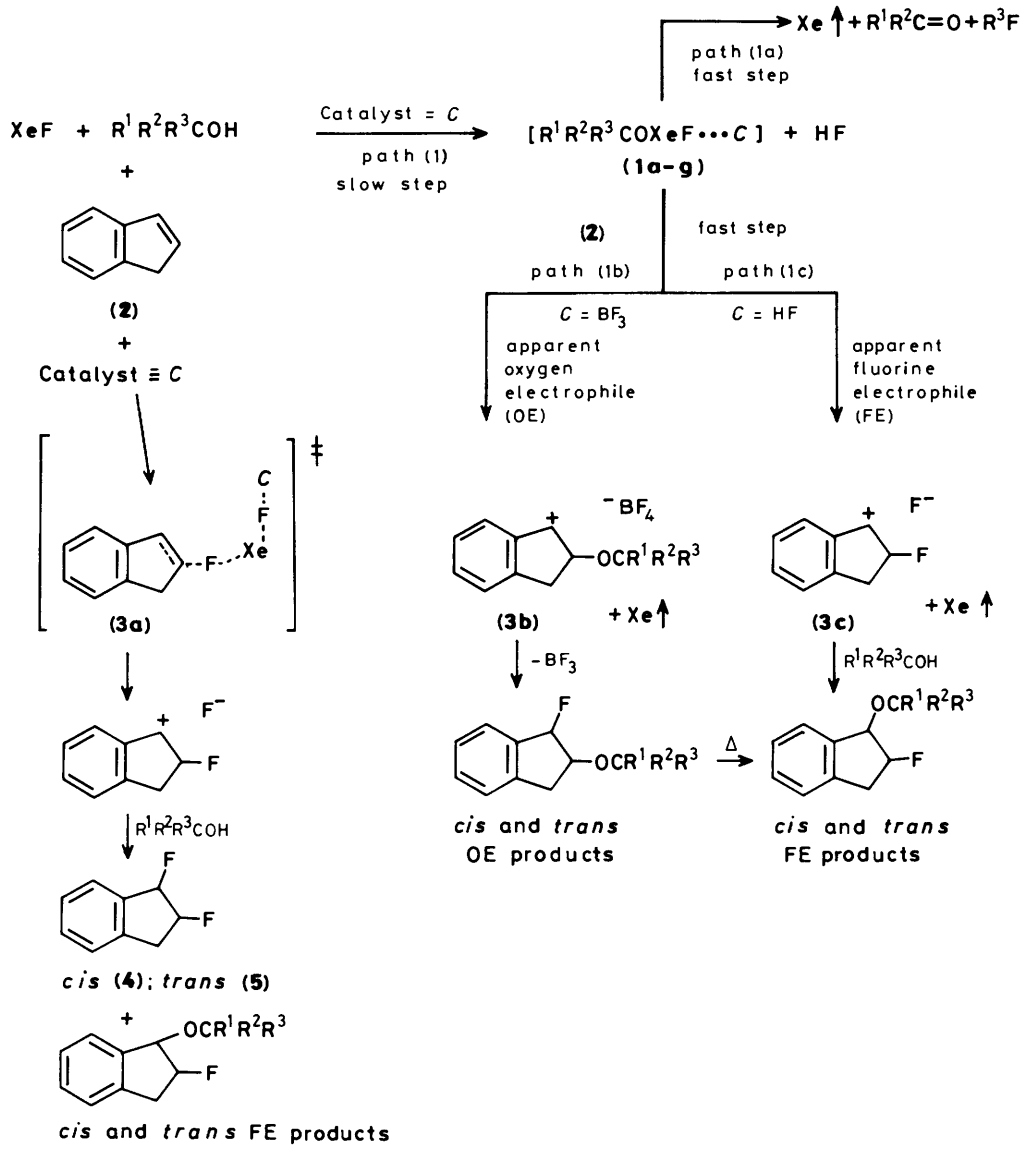
	cis	*trans*	*cis*	*trans*
R = CH_3	(6)	(7)	(8)	(9)
R = $(CH_3)_2CH$	(10)	(11)	(12)	(13)
R = $(CH_3)_3C$	(14)	(15)	(16)	(17)
R = $ClCH_2CH_2$	(18)	(19)	(20)	(21)
R = FCH_2CH_2	(22)	(23)	(24)	(25)
R = CF_3CH_2	(26)	(27)	(28)	(29)
R = $(CF_3)_3C$	(30)	(31)	(32)	(33)

Results

Product distributions for reactions of XeF_2 with indene [involving an intermediate (3)] in seven different alcohol solvents are given in Table 1, resulting in difluorindan products (4) and (5) and alkoxyfluoroindan products (6)—(33). The *cis*- and *trans*-1-alkoxy-2-fluoroindans are the major components (70—90%) with a proton catalyst (anhydrous hydrogen fluoride, generated *in situ*) in isopropyl or t-butyl alcohol as solvent. These data are similar to those reported [5] for methanol as solvent (Table 1). Reactions of XeF_2 with (2) and boron trifluoride–ether as catalyst give primarily *cis*- and *trans*-2-alkoxy-1-fluoroindan products along with significant amounts of the 1-alkoxy-2-fluoroindans. The 2-alkoxy-1-fluoroindans rearrange slowly under the reaction conditions with BF_3•ether to the thermodynamically more stable 1-alkoxy-2-fluoroindan isomers. Product distributions for reactions with BF_3•ether as catalyst were obtained after the reactions were quenched with aqueous sodium hydrogen carbonate solution. Rearrangement was slow (several days) in the absence of BF_3•ether. Data in Table 1 for the BF_3•ether reactions in methanol closely approximate to a kinetic product distribution since the 2-t-butoxy- and the 2-isopropoxy-indans rearrange faster than the 2-methoxyindans. Thus we were unable to obtain n.m.r. data for *trans*-2-t-butoxy-1-fluoroindan (**17**) because of rapid rearrangement to the *trans*-1-t-butoxy-2-fluoroindan (**15**). The data in Table 1 for reactions with HF catalyst (generated *in situ*) represent kinetic product distributions.

Reactions of XeF_2 and alcohols with electron-withdrawing substituents are faster due to the catalytic activity of the more acidic alcohols. The pK_a values of the alcohols range from 19.2 to 5.2 (Table 1). 2-Alkoxy-1-fluoroindan products (10—21%) are formed in 2-chloro- and 2-fluoro-ethanol even though no BF_3•ether catalyst was added. The predominant alkoxy products from 2,2,2-trifluoroethanol and perfluoro-t-butyl alcohol are the 2-alkoxy-1-fluoroindans even though the *trans*-2-perfluoro-t-butoxy-1-fluoroindan (**33**) has rearranged to the *trans*-1-perfluoro-t-butoxy-2-fluoroindan (**31**). The *cis*- and *trans*-1-alkoxy-2-fluoroindans (**26**), (**27**), and (**31**) were isolated from an equilibrated mixture of the 2-alkoxy-1-fluoroindans. Reaction with perfluoro-t-butyl alcohol gives a poor yield because the acidic nature of the alcohol (pK_a 5.2) does not inhibit polymerization of indene (see below).

The regio- and stereo-chemistry of the alkoxyfluoroindans were determined by n.mr. spectroscopy using chemical shifts,



Scheme 2.

multiplicities, and the vicinal couplings of the methine hydrogens. Table 2 contains the n.m.r. data.

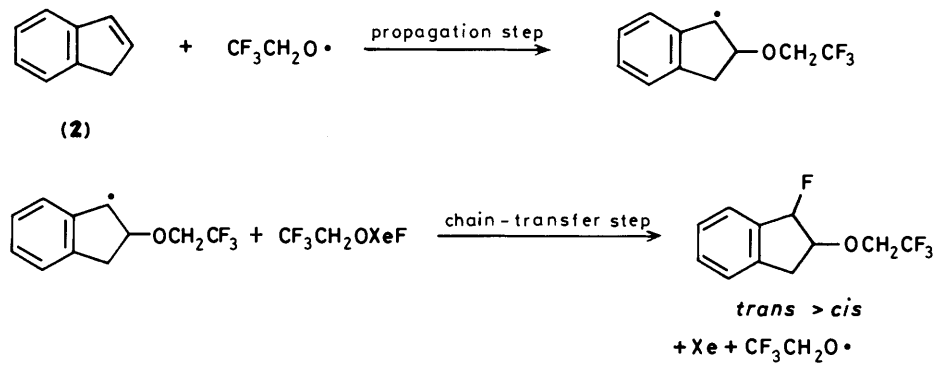
Mass spectral data (see Experimental section) for compounds (**10**)—(**33**) are similar to those we found for products (**6**)—(**9**) from methoxyfluorination of indene.[5] Characteristic fragments are the parent ions, *m/z* 151 (loss of the alkyl group from the ether linkage), 135 (loss of alkoxy group), and 123 (loss of a carbon plus alkoxy group to give a benzyl cation). Both regioisomers generally show a parent ion which is larger in the 2-alkoxy-1-fluoroindans than in the 1-alkoxy-2-fluoroindan isomers. The *m/z* 135 ion is a larger fragment in the 1-alkoxy-2-fluoroindans, while the *m/z* 123 ion is larger in the 2-alkoxy-1-fluoroindans.

Turning to the energetic (polynitroaliphatic) alcohols, we found it generally impractical, due to physical properties (m.p., solubility, *etc.*), to use the alcohols as both solvent and reactant. We elected to use methylene dichloride in the 0 °C to room temperature range. The most extensive studies involved 2-fluoro-2,2-dinitroethanol, although the same general results were obtained from 2,2,2-trinitroethanol and 2,2-dinitropropanol, where pK_a value is not known but is anticipated to have an acidity comparable to or greater than the polyfluoro alcohols described earlier.

Reactions were run both in the presence and absence of boron trifluoride and HF generated *in situ* with one equivalent of 2-fluoro-2,2-dinitroethanol. G.c. analysis revealed, in both cases, the complete disappearance of indene but *no* product formation, not even difluoroindan (**4**) or (**5**) (capillary g.c.–m.s. later revealed traces of these compounds). There was no evidence of the desired alkoxyfluorination adducts in methylene dichloride.

Discussion

Scheme 2 outlines the reactions of xenon difluoride with alcohols to give intermediates (**1a**—**g**). In the absence of alkene or with unreactive alkenes, oxidation of the alcohol occurs *via* path (1a).[5,6] Intermediates (**1a**—**g**) are intercepted with sufficiently reactive alkenes as shown with indene in Scheme 2. Reactions in t-butyl, isopropyl, and methyl alcohols give intermediates which react as positive oxygen electrophiles (OE) with BF_3-ether as catalyst[5] by path (1b). The various amounts



Scheme 3.

of 1-alkoxy-2-fluoroindan products are from rearrangement of the kinetically formed 1-fluoro isomers. Intermediates (**1a**, **b**, and **c**) function as apparent fluorine electrophiles [FE, path (1c)] with proton catalysts.[5] Product distributions are given in Table 1.

Addition of electron-withdrawing substituents to the alcohol induces the alkoxyxenon fluoride to react as an oxygen electrophile even without BF_3·ether. Thus, (**1d**) from 2-chloroethanol gives 10% of the OE products, and (**1e**) from 2-fluoroethanol gives *ca.* 20% of the OE products (Table 1). Reaction of XeF_2 in 2,2,2-trifluoroethanol or perfluoro-t-butyl alcohol gives (**1f** or **g**), respectively, which intercepts indene only as an OE even though BF_3·ether was not used as catalyst. Small amounts of 1-alkoxy-2-fluoroindans from 2,2,2-trifluoroethanol and perfluoro-t-butyl alcohol arise from rearrangement of the labile 2-alkoxy-1-fluoroindans.

The observation that electron-withdrawing substituents induce intermediates (**1d**—**g**) to give 2-alkoxy-1-fluoroindans in

Table 2. ^1H N.m.r. data (δ_H; reference Me_4Si) of indene alkoxyfluorination products

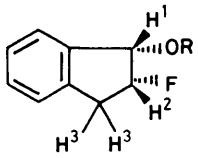
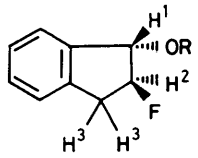
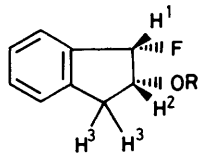
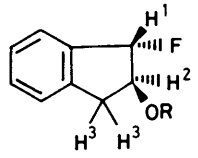
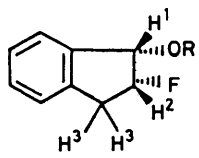
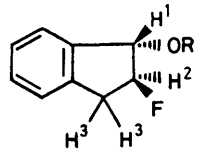
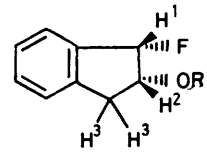
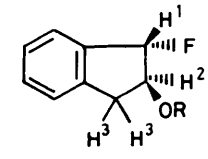
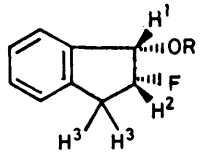
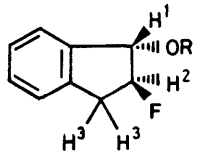
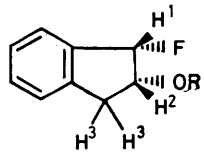
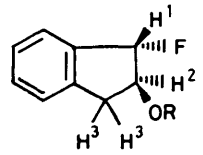
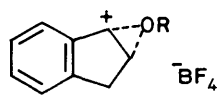
				
$(CH_3)_2CH$	**(10)**[a]	**(11)**[a]	**(12)**[a]	**(13)**[b]
	H^1: 4.90 (dd, $J_{1,2}$ 4.2, J_{HF} 11.2 Hz)	H^1: 5.10 (dd, $J_{1,2}$ 4.2, J_{HF} 16.8 Hz)	H^1: 5.43 (dd, $J_{1,2}$ 4.8, J_{HF} 44.8 Hz)	H^1: 5.94 (dd, $J_{1,2}$ 4.5, J_{HF} 57.0 Hz)
	H^2: 5.37 (dm, J_{HF} 50 Hz)	H^2: 5.30 (dm, J_{HF} 50 Hz)	H^2: 4.12—4.40 (m)	H^2: 4.13—4.25 (m)
	H^3: 2.80—3.70 (m)	H^3: 2.82—3.60 (m)	H^3: 2.80—3.10 (m)	H^3: 3.08—3.22 (m)
	CH_3: 1.20 (d, J 6.0 Hz)	CH_3: 1.17 (d, J 6.0 Hz)	CH_3: 1.23 (d, J 6.0 Hz)	CH_3: 1.23 (d, J 6.0 Hz)
	CH: 3.93 (sept, J 6.0 Hz)	CH: 4.00 (sept, J 6.0 Hz)	CH: 4.4 (m, superimposed on H^2)	CH: 4.4 (m, superimposed on H^2)
	Aromatic: 7.22—7.63 (m)	Aromatic: 7.27—7.62 (m)	Aromatic: 7.20—7.60 (m)	Aromatic: 7.27—7.62 (m)
$(CH_3)_3C$	**(14)**[b]	**(15)**[b]	**(16)**[c]	**(17)**[c]
	H^1: 4.96 (dd, $J_{1,2}$ 3.8, J_{HF} 21.0 Hz)	H^1: 5.12 (dd, $J_{1,2}$ 4.0, J_{HF} 18.0 Hz)		
	H^2: 5.25 (dm, J_{HF} 55 Hz)	H^2: 5.22 (dm, J_{HF} 57 Hz)		
	H^3: 2.95—3.60 (m)	H^3: 2.90—3.40 (m)		
	CH_3: 1.33 (s)	CH_3: 1.38 (s)		
	Aromatic: 7.30—7.55 (m)	Aromatic: 7.15—7.40 (m)		
				
$ClCH_2CH_2$	**(18)**[d]	**(19)**[d]	**(20)**[c]	**(21)**[c]
	H^1: 4.83 (dd, J_{12} 4.0, J_{HF} 14.5 Hz)	H^1: 5.00 (dd, J_{12} 3.4, J_{HF} 17.0 Hz)		
	H^2: 5.28 (dm, J_{HF} 50 Hz)	H^2: 5.30 (dm, J_{HF} 52 Hz)		
	H^3: 2.96—3.73 (m)	H^3: 2.70—3.90 (m)		
	$ClCH_2CH_2$: 3.60 (t, J 5.5 Hz)	$ClCH_2CH_2$: 3.91 (d, J 4.9 Hz)		
	$ClCH_2$: 3.97 (t, J 5.5 Hz)	$ClCH_2$: 4.10 (t, J 4.9 Hz)		
	Aromatic: 7.20—7.42 (m)	Aromatic: 7.20—7.40 (m)		

Table 2 (*continued*)

FCH_2CH_2	**(22)**[e]	**(23)**[e]	**(24)**[b,c,f]	**(25)**[b,c,f]
	H^1: 4.91 (dd, $J_{1,2}$ 4.4, J_{HF} 15.0 Hz) H^2: 5.33 (dm, J_{HF} 53 Hz) H^3: 2.90—3.56 (m) FCH_2CH_2: 3.84 (dm, J_{HF} 30 Hz) FCH_2: 4.60 (dm, J_{HF} 50 Hz) Aromatic: 7.20—7.30 (m)	H^1: 5.03 (dd, $J_{1,2}$ 3.5, J_{HF} 17.3 Hz) H^2: 5.31 (dm, J_{HF} 53 Hz) H^3: 2.90—3.57 (m) FCH_2CH_2: 3.84 (dm, J_{HF} 27 Hz) FCH_2: 4.60 (t, J_{HF} 48 Hz) Aromatic: 7.20—7.30 (m)	H^1: 5.73 (dd, $J_{1,2}$ 4.4, J_{HF} 57.0 Hz)	H^1: 5.94 (dd, $J_{1,2}$ 4.2, J_{HF} 56.0 Hz)
				
CF_3CH_2	**(26)**[b,g]	**(27)**[b,g]	**(28)**[h]	**(29)**[h]
	H^1: 5.02 (dd, $J_{1,2}$ 4.3, J_{HF} 11.7 Hz) H^2: 5.35 (dm, J_{HF} 52 Hz) H^3: 3.15 (1 H, ddd, J_{HF} 21.0, $J_{3,3'}$ 16.5, $J_{2,3}$ 5.6 Hz), 3.30 (1 H, ddd, J_{HF} 20.3, $J_{3,3'}$ 16.5, $J_{2,3'}$ 4.1 Hz) CF_3CH_2: 4.13 (q, J 8.6 Hz) Aromatic: 7.24—7.45 (m)	H^1: 5.14 (dd, $J_{1,2}$ 3.7, J_{HF} 16.0 Hz) H^2: 5.32 (dm, J_{HF} 53 Hz) H^3: 3.07 (1 H, ddd, J_{HF} 22.5, $J_{3,3'}$ 16.5, $J_{2,3}$ 5.6 Hz), 3.42 (1 H, ddd, J_{HF} 16.2, $J_{3,3'}$ 16.5, $J_{2,3'}$ 4.1 Hz) CF_3CH_2: 4.06 (q, J 8.5 Hz) Aromatic: 7.21—7.42 (m)	H^1: 5.67 (dd, $J_{1,2}$ 5.2, J_{HF} 41.2 Hz) H^2: 5.08—5.21 (m) H^3: 3.05—3.30 (1 H, m), 3.40—3.70 (1 H, m) CF_3CH_2: 4.30 (q, J 8.6 Hz) Aromatic: 7.50—7.80 (m)	H^1: 5.63 (dd, $J_{1,2}$ 4.0, J_{HF} 50.0 Hz) H^2: 5.00—5.40 (m) H^3: 2.70—3.40 (m) CF_3CH_2: 4.29 (q, J 8.6 Hz) Aromatic: 7.40—7.90 (m)
$(CF_3)_3C$	**(30)**[i]	**(31)**[b,g]	**(32)**[j]	**(33)**[c]
		H^1: 4.49 (dd, $J_{1,2}$ 4.8, J_{HF} 30.3 Hz) H^2: 5.78 (dm, J_{HF} 54 Hz) H^3: 3.10—3.50 (m) Aromatic: 7.17—7.54 (m)		

[a] 60 MHz (CCl_4). [b] 360 MHz ($CDCl_3$). [c] These compounds rearranged rapidly to the 1-alkoxy-2-fluoro products. [d] 90 MHz ($CDCl_3$). [e] 200 MHz ($CDCl_3$). [f] The n.m.r. spectra showed a mixture of all four isomers and only the chemical shift of H^1 was resolved. See Experimental section for other data on these compounds. [g] These products were not formed kinetically. They were isolated from an equilibrated reaction mixture. [h] 60 MHz ($CDCl_3$). [i] This compound was not observed in the reaction mixture. [j] This compound thermally degraded in transit before analysis at the Colorado State University Regional Center.



(34) R = CH_3, $(CH_3)_2CH$, $(CH_3)_3C$

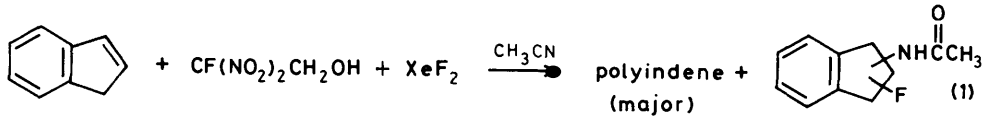
the absence of BF_3·ether catalyst might suggest a free-radical pathway as shown in Scheme 3. We favour the OE pathway [Scheme 2, path (1b)] over the free-radical pathway for the following reasons.

(1) We were unable to alter the reaction time or product distributions with free-radical inhibitors.

(2) The *trans* product is slightly favoured in a free-radical pathway, due to the steric requirements of the chain-transfer step,[7] as shown in Scheme 3. Open-ion ionic intermediates generally give more of the *cis* isomer from *syn* addition.[7,8] The *cis*:*trans* product ratios of the 2-alkoxy-1-fluoroindans of **(28)** > **(29)** and **(32)** > **(33)** (Table 1) from intermediates (**1f** and **g**) indicate an OE pathway. Our data do not rule out an ion–radical pathway.

Intermediate (**1a**) from methanol reacts by the OE pathway with BF_3 catalyst to give 1-fluoro-2-methoxyindans where the *trans* isomer predominates (52:26, Table 1). We suggest that the intermediate on the OE pathway is an open-ion species as indicated by (**3b**) [Scheme 2, path (1b)] when the alkoxy substituent contains electron-withdrawing moieties, such as the 2,2,2-trifluoroethyl- and perfluoro-t-butyl groups. Electron-donating substituents, as found in (**1a**—**c**), form weakly bridged intermediates (**34**) rather than the open ion (**3b**). Intermediate (**34**) reacts with the BF_4^- anion to give predominantly *trans*-2-alkoxy-1-fluoroindan products. The *trans*-2-alkoxy-1-fluoroindans from (**1b** and **c**) rearrange under the reaction conditions to give the *trans*-1-alkoxy-2-fluoroindans.

The absence of alkoxyfluorination adducts from XeF_2 and the energetic alcohols became explicable following a series of n.m.r. studies in acetonitrile, methylene dichloride, and methanol. In the initial experiment, the purity of XeF_2 was examined by xenon-129 n.m.r. in acetonitrile. The alcohol was added, with no resulting change. Addition of indene to the n.m.r. tube produced an immediate precipitate; no BF_3 had been added. This suggested polymerization of indene to polyindene.[9] We then confirmed, using carbon-13, fluorine-19, and ^1H n.m.r., that indene is rapidly polymerized by either XeF_2 or BF_3 alone in methylene dichloride or acetonitrile. Using capillary g.c.–m.s., trace amounts of indene and the 1,2-difluoroindanes were detected, showing that, while the polymerization is rapid and rather complete, it is not total. There was no indication,



however, by n.m.r. or g.l.c. of any energetic alkoxyfluorinated products. 2-Fluoro-2,2-dinitroethanol by itself did not polymerize indene.

The original experiments with XeF_2 and indene in methylene dichloride were repeated in the n.m.r. spectrometer. Polymerization was readily observed, and the polymer is soluble, which explains why the polymerization was not detected in earlier reports.[10] Our studies repeating literature experiments confirmed why those published reports indicated no awareness of this major problem.

Other revealing experiments in deuteriated methanol showed that polymerization does not occur in that solvent with either XeF_2 or BF_3. This is in sharp contrast to the results in acetonitrile and methylene dichloride. Apparently, methanol prevents polymerization. A re-examination of indene alkoxyfluorination reactions shows that the yield of alkoxyfluorination products drops as the acidity of the alcohols increases (Table 1). We believe the explanation for this observation involves polymerization of indene, as we observed with 2-fluoro-2,2-dinitroethanol.

As a final observation on the indene system, a novel result (solvent incorporation) was detected by capillary g.c.–m.s. in the acetonitrile solvent reaction. Three peaks from compounds with long retention times were identified as solvent adducts, 1,2-fluoroacetamido products.[11] This observation was verified using deuteriated solvent. The 'parent' peak was 176 (196 – HF) for each fluoroacetamido product along with an m/z peak at 46 (CD_3CO^+). The regio- and stereo-chemistry of the substituents are unknown at this time, but they are minor products compared with the polymer. Acetonitrile is clearly an unsuitable solvent [equation (1)].

Brief investigations with the energetic alcohols 2,2-dinitropropanol and 2,2,2-trinitroethanol afforded similar results. Thus we have been unable to generate significant yields of alkoxyfluorination products with indene and energetic alcohols due to the predominance of cationic polymerization of indene in methylene dichloride under these reaction conditions.

We currently favour cationic intermediates in these reactions based on the solvent incorporation (with acetonitrile), the stereochemical orientation of the difluoride isomers (minor products), and the fact that the reaction proceeds in the dark. We have not investigated the indene–energetic alcohol system further.

Experimental

Instrumentation.—^1H N.m.r. spectra were recorded on a Varian T60A (Point Loma Nazarene College), JEOL FX-90Q (Air Force Astronautics Laboratory), Chemagnetics A200 (California State University at San Diego), or a Nicolet NT-360 instrument (Colorado State University Regional NMR Center). ^1H and ^{13}C spectra are referenced relative to Me_4Si. Mass spectral analyses were obtained at 70 eV on a Hewlett–Packard 5890 GC interfaced with an HP 5970B mass-selective detector. A Hewlett–Packard 5750 GC (f.i.d. detector) interfaced to an HP 3380A integrator recorder was used to obtain analytical data. Preparative g.l.c. was carried out with a Hewlett–Packard 700 chromatograph (t.c. detector).

General Procedure.—Xenon difluoride and perfluoro-t-butyl alcohol were purchased from PCR/SCM Specialty Chemicals. 2-Fluoro-2,2-dinitroethanol[12] was a sample from Fluorochem, Inc. (Azusa); 2,2-dinitropropanol[13] was obtained from Aerojet Strategic Propulsion Company (Sacramento); 2,2,2-trinitroethanol, synthesized according to the literature,[14] was a gift of the F. J. Seiler Research Laboratory (US Air Force Academy). The remaining chemicals were from the Aldrich Chemical Company and were used as received except indene, which was distilled prior to use. The following procedure is representative. See below for the reaction of perfluoro-t-butyl alcohol.

To anhydrous alcohol (0.500 ml) in a dry round-bottom flask (5 ml) fitted with a drying tube and stirring bar at 0 °C was added XeF_2 (58.0 mg, 0.343 mmol). The alkene (0.686 mmol) and boron trifluoride–ether (0.343 mmol) when added, were introduced *via* separate syringes. The stirred mixture was allowed to warm to room temperature. When evolution of xenon gas ceased (5—30 min), the mixture was poured into aqueous sodium hydrogen carbonate, extracted three times with ether, dried ($MgSO_4$), and analysed by g.l.c. on the columns indicated.

Analytical data (Table 1) were obtained on a 17 ft × 1/8 in stainless steel column of 3% FFAP on 80—100 Chromosorb W. The products had the following retention times (min) at 130 °C [150 °C for (**18**)—(**21**)]: (**4**) (7.0), (**5**) (8.5), (**11**) (15), (**13**) (17), (**10**) (29), (**12**) (30); (**15**) (24), (**17**) (15), (**14**) (47), (**16**) (51.5); (**19**) (29), (**21**) (33), (**18**) (48), (**20**) (54), (**23**) (26), (**25**) (30), (**22**) (45), (**24**) (50); (**27**) (14), (**29**) (15), (**26**) (27), (**28**) (28); (**31**) (15), (**33**) (18), (**32**) (31). Yields (Table 1) were determined by n.m.r. with cyclohexane or toluene as internal standard. The products [except (**26**)—(**29**)] were isolated by column chromatography on silica gel with light petroleum (b.p. 35—60 °C) and light petroleum–diethyl ether as eluants. Products (**26**)—(**29**) were isolated by preparative g.l.c. on a 10 ft × 1/4 in stainless steel column of 5% SE-30 on 80—100 Chromosorb W at 60 °C. The *cis* and *trans* difluoro products (**4**) and (**5**) gave spectra identical to those reported in the literature.[10a] The remaining products gave spectral data similar to their methoxyfluorinated counterparts,[5] and their n.m.r. data are given in Table 2. Mass spectrum (70 eV), m/z (relative intensity): (**10**), 194 (M^+, 4%), 151 (55), 136 (55), 135 (100), 123 (4), and 43 (28); (**11**), 194 (M^+, 5%), 151 (57), 136 (57), 135 (100), 123 (4), and 43 (29); (**12**), 194 (M^+, 27%), 151 (9), 135 (10), 123 (100), 104 (64), and 43 (34); (**13**), 194 (M^+, 30%), 151 (7), 135 (16), 123 (100), 104 (62), and 43 (31); (**14**), 208 (M^+, 7%), 151 (46), 135 (68), 123 (2), and 57 (100); (**15**), 208 (M^+, 8%), 151 (43), 135 (65), 123 (1), and 57 (100); (**16**), 151 (11), 135 (1), 123 (12), 104 (13), and 57 (100); (**17**), 208 (M^+, 2%), 151 (1), 135 (18), 123 (12), 104 (12), and 57 (100); (**18**), 216 (M^+, 6%), 214 (19), 151 (22), 135 (100), 123 (5), 65 (5), and 63 (15); (**19**), 216 (M^+, 6%), 214 (18), 151 (20), 135 (100), 123 (4), 65 (5), and 63 (15); (**20**), 216 (M^+, 23%), 214 (75), 151 (32), 135 (81), 134 (67), 123 (100), 65 (21), and 63 (52); (**21**), 216 (M^+, 22%), 214 (69), 151 (27), 135 (78), 134 (60), 123 (100), 65 (16), and 63 (52); (**22**), 198 (M^+, 42%), 151 (30), 135 (100), 123 (6), and 47 (12); (**23**), 198 (M^+, 48%), 151 (31), 135 (100), 123 (6), and 47 (10); (**24**), (M^+, 100%), 178 (3), 151 (32), 135 (53), 134 (57), 131 (68), 123 (76), and 47 (16); (**25**), 198 (M^+, 54%), 178 (38), 151 (24), 135 (24), 134 (25), 131 (100), 123 (30), and 63 (43); (**26**), 234 (M^+, 67%), 151 (9), 135 (100), 123 (8), and 83 (10); (**27**), 234 (M^+, 70%), 151 (9), 135 (100), 123 (8), and 83 (10); (**29**), 234 (M^+, 100%), 151 (41), 135 (48), 134 (49), 131 (82), 123 (53), and 83 (14); (**31**), 370 (M^+, 47%), 135 (100), and 69 (39); (**32**), 370 (M^+, 100%), 135 (49), 123

(96), and 69 (50); (**33**), 370 (M^+, 100%), 135 (50), 123 (94), and 69 (35).

Reactions in perfluoro-t-butyl alcohol (pK_a 5.2) as solvent were too vigorous, but were alternatively carried out in solvent as follows. To XeF_2 (25.0 mg, 0.148 mmol) in methylene dichloride (0.125 ml) at 0 °C with stirring were added perfluoro-t-butyl alcohol (0.087 ml, 0.591 mmol) and indene (0.035 ml, 0.295 mmol). The mixture was stirred at 0 °C for 10 min and then allowed to warm to room temperature. After 30 min at room temperature, the mixture was worked up as above. G.l.c. analysis on the analytical column above gave (**31**), (**32**), and a trace of (**33**) with the retention times listed above. Products (**31**) and (**32**) were isolated by column chromatography as above. The n.m.r. data of (**31**) are listed in Table 2 but sample (**33**) thermally degraded before n.m.r. data could be obtained at the Colorado State University Regional Center. Product (**33**) could not be isolated, but g.c.–m.s. data were obtained (see above).

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