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Interaction of Fluoroxenonium Triflate, Fluorosulfate, and Nitrate with Alkenes. Stereochemical Evidence for the Electrophilic Noble Gas Cation Addition to the Carbon–Carbon Double Bond

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Reactions of fluoroxenonium triflate (1), fluorosulfate (2), and nitrate (3), prepared from XeF_2 and the corresponding acids in CH_2Cl_2 at −50 °C, with cyclohexene and 1-hexene result in β-fluoroalkyl triflates, fluorosulfates, and nitrates. Triflate **1** reacts with cyclohexene with exclusive formation of the cis isomer **5**; the analogous reactions of fluorosulfate **2** and nitrate **3** give mixtures of the corresponding cis and trans isomers. Reactions of 1-hexene with reagents **1**–**3** lead to mixtures of two regioisomers with domination of the Markovnikov type of addition. The stereochemical result of these reactions is rationalized in terms of an electrophilic attack by the positive xenonium ion on the π-electrons of the double bond with intermediate formation of organoxenonium species in analogy with the behavior of the isoelectronic iodine(III) species.

Since the discovery of first stable xenon compounds in 1962,[1] numerous new xenon(II) derivatives have been synthesized.[2,3] Among these are the relatively stable and readily obtainable xenon(II) derivatives of strong acids; fluorosulfonic,[3a–c] trifluoromethanesulfonic,[3a], perchloric,[3a] and nitric,[3d] with the general structure FXeOZ (Z = FSO_2, CF_3SO_2, ClO_3, NO_2). All of these compounds are prepared by low-temperature reactions of commercially available XeF_2 with the corresponding acids in HF; although most of them are unstable at room temperature, the structure of $FXeOSO_2F$ has been confirmed by X-ray analysis.[3c] Despite the ready availability of these new xenon reagents, their reactivity toward organic substrates has not been investigated.

Xenon(II) compounds are isoelectronic with iodine(III) species[4] and have many analogies in structure and properties. Recently we have prepared several iodine(III) derivatives of strong acids such as perchloric, sulfuric, triflic, substituted sulfonic, tetrafluoroboric, and others.[5] These compounds can be used as reagents for the preparation of covalent perchlorates, sulfates, triflates, tosylates,[5a–c] ring contraction reactions in cycloalkenes,[5d] new carbon–carbon bond formation,[5e–f] as well as the synthesis of a variety of previously unknown alkynyl esters.[5g]

Table I. Ratio of Products in the Reactions of Fluoroxenonium Triflate (1), Fluorosulfate (2), and Nitrate (3) with Alkenes

entry	alkene	reagent	products (ratio)[a]
1	cyclohexene	1	4 (only)
2	cyclohexene	2	5, 7 (3:1)
3	cyclohexene	3	6, 8 (1:1)
4	1-hexene	1	9, 12 (3:1)
5	1-hexene	2	10, 13 (2:1)
6	1-hexene	3	11, 14 (2:1)

[a] NMR data.

Therefore it might be expected that xenon(II) and iodine(III), as well as other 10-electron polyvalent species of nonmetals (for example, Se(IV) and Te(IV)) have similar chemical properties and reactivity, particularly as manifested by the strong electrophilic activity toward unsaturated compounds. We[5,6e] as well as Koser[6a–d] have demonstrated that derivatives of iodine(III), with good leaving

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groups in their structure (tosylate,[6a–d] triflate,[5a,b] perchlorate[5a,b] etc.) are strong electrophiles toward alkenes,[5a,b,6a] alkynes,[6b] and ketones.[6c–e] In the present paper we report the reactions of the analogous xenon(II) derivatives—triflate 1, fluorosulfate 2, and nitrate 3—with alkenes with the primary aim of comparing the chemical behavior of xenon(II) and iodine(III).[7]

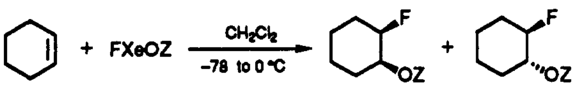
Results and Discussion

For the preparation of the fluoroxenonium reagents 1–3 (eq 1) we used the well known reaction of XeF_2 with 1 equiv of the corresponding acid.[3] However, instead of HF we employed the more convenient methylene chloride as a solvent; solutions of reagents 1–3 in *pure* CH_2Cl_2 are relatively stable up to −20 to −10 °C but decompose rapidly at higher temperature. The respective reagents were formed by addition of the corresponding acid to a stirred mixture of XeF_2 in CH_2Cl_2 at −50 °C, formation of a clear homogeneous solution indicated the end of the reaction, and the resulting solutions of reagents 1–3 were used without further purification or separation from HF.

The reaction of reagents 1–3 with cyclohexene (eq 2) and 1-hexene (eq 3) were investigated. Addition of the corresponding alkene to a solution of the xenonium reagent in CH_2Cl_2 at −78 °C resulted in rapid darkening of the reaction mixture, but Xe evolution and concomittant reaction was observed only upon warming the reaction mixture to −30 to −20 °C. The products 4–14 were isolated by column chromatography on silica gel. The ratio of isomers in the reaction mixtures were calculated from NMR data (Table I). The structure of the products was determined by NMR and mass spectra. The β-fluoroalkyl triflates and fluorosulfates obtained from 1 and 2 were relatively unstable at room temperature, and we could not obtain their mass spectra directly. Nevertheless these compounds were further characterized mass spectrometrically via transformation into stable β-fluoroalkyl bromides by reaction with KBr in acetone.

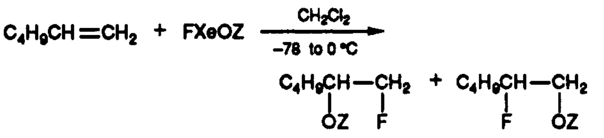
$$XeF_2 + HOZ \xrightarrow[-50\text{ to }-30\ °C]{CH_2Cl_2} FXeOZ + HF \qquad (1)$$

1, Z = Tf; 2, Z = SO_2F; 3, Z = NO_2



(2)

4–6 7–8



$$C_4H_9CH{=}CH_2 + FXeOZ \xrightarrow[-78\text{ to }0\ °C]{CH_2Cl_2} C_4H_9\underset{OZ}{CH}{-}\underset{F}{CH_2} + C_4H_9\underset{F}{CH}{-}\underset{OZ}{CH_2} \qquad (3)$$

9–11 12–14

4, 9, 12, Z = Tf; 5, 7, 10, 13, Z = SO_2F; 6, 8, 11, 14, Z = NO_2

Reaction of fluoroxenonium triflate 1 with cyclohexene gave only one product, *cis*-2-fluorocyclohexyl triflate 4, in 75% isolated yield. The cis configuration was established by the vicinal H–H and H–F couplings in the ^1H NMR spectra. The sum of J_{HH} for H1 or H2 is 13–14 Hz, which is typical for cis-substituted cyclohexanes.[8] The analogous reaction of fluoroxenonium fluorosulfate 2 gave mixtures of the cis and trans stereoisomers 5 and 7 in a ratio of 3:1. The spectral parameters (particularly, the coupling constants in the ^1H NMR for H-1 and H-2 and the chemical shift $\delta = -194$ ppm of the CHF signal in the ^{19}F NMR) of *cis*-fluorosulfate 5 were very similar to that of the corresponding triflate 4. The second product was identified as the trans isomer 7 by NMR data. The sum of the H–H coupling constants for H-1 and H-2 in 7 is 17–18 Hz, which is consistent with the trans arrangement of the substituents.[8] The chemical shift of the CHF fluorine in the ^{19}F NMR is about 16 ppm upfield in comparison with the cis isomers 4 and 5. Reaction of the fluoroxenonium nitrate 3 gave a mixture of two isomers 6 and 8 in low yield. In contrast to the corresponding fluorosulfates and triflates the nitrates were stable enough to be distilled, but we were unable to separate the individual isomers either by distillation or by chromatography. The two isomeric products 6 and 8 were identified as the cis and trans isomers by the chemical shifts of the CHF in the ^{19}F NMR −192.7 and −178.3, respectively. These values are similar to those found for the analogous triflate 4 and fluorosulfates 5 and 6.

Reaction of the xenonium reagents 1–3 with 1-hexene gave in each case mixtures of two regioisomers with domination of the Markovnikov type of addition. Each of the regioisomers was isolated in pure form and identified by NMR. In the ^{19}F NMR the Markovnikov regioisomers 9–11 all have the F signal as a doublet of triplets (δ = 220–222 ppm) with a geminal proton coupling of 48 Hz and a vicinal coupling of J_{HF} = 23 Hz, while for the anti-Markovnikov adducts (12–14) the signals are multiplets with a chemical shift of 181–187 ppm. The fluoronitrate 14 was additionally identified by comparison of its boiling point with literature data.[9]

The main stereochemical result of the present investigation is a stereospecific formation of cis adducts 4 and 5 in the reactions of triflate (1) and fluorosulfate (2) with cyclohexene, and predominant formation of Markovnikov adducts in the reactions of 1-hexene. The Markovnikov type of addition is consistent with a carbocationic mechanism involving "electrophilic" fluorine. Such a mechanism is congruent with literature rationalizations of XeF_2 and FXeOR reactions with unsaturated compounds.[10] However, this mechanism does not account for the selective formation of cis adducts 4 and 5. Therefore, in analogy with similar results on the stereochemistry of the reactions of iodine(III) trifate[5a,b] and perchlorate,[5a,b] which are isoelectronic with the xenonium reagents (1–3), with olefins we propose a new mechanism involving the initial electrophilic addition of xenonium ion to the double bond leading to an organoxenonium intermediate 15. This addition proceeds with trans stereoselectivity because of the participation of the xenon lone pairs in accord with the analogous iodine(III) reactions.[5a,b,6a] The existence of intermediates with a Xe–C covalent bond was confirmed recently by isolation of a relatively stable organoxenon compound.[11] In a second step a nucleophilic substitution

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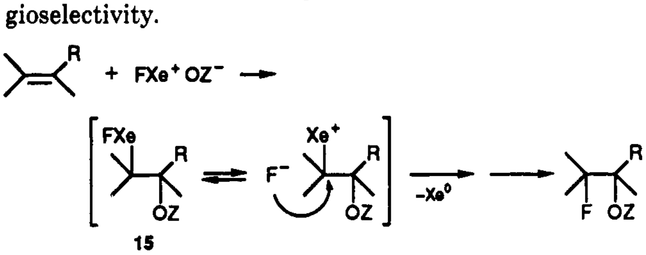
of Xe with the neighboring fluorine anion occurs. This is an S_N2 type process, which in case of the analogous reactions of iodine(III) proceeds stereospecificaly with inversion of configuration.[12] The final result of this process is the observed formation of cis product and Markovnikov regioselectivity.



It is important to emphasize that this mechanism can only apply to ionic xenonium reagents, bearing good leaving groups, such as triflate, fluorosulfate, perchlorate, but not alkoxy, nitrate, carboxylate, or halide derivatives. In the reagents employed, 1–3, ionic character decreases from triflate to nitrate, according to the known leaving group abilities,[13] and parallels the observed decreasing stereoselectivity of these reactions with alkenes. Likewise, iodonium reagents with nucleofugic triflate,[5a,b] perchlorate,[5a,b] and tosylate[6a–c] anions react with alkenes more selectively or even with opposite stereoselectivity than (diacetoxyiodo)benzene and (dichloroiodo)benzene.[4d,g]

In conclusion, new reactions of xenon(II) reagents leading to β-fluoroalkyl triflates, fluorosulfates, and nitrates are reported. The stereochemical result of these reactions can best be rationalized in terms of an electrophilic attack by the positive xenonium ion on the π-electrons of the double bond with concomittant formation of an organoxenonium intermediate. The similarity of these reactions to the analogous well-known reactions of iodine(III) species confirms the close resemblance in chemical properties of the isoelectronic iodine(III) and xenon(II) derivatives and opens the possibility to novel types of potentially stable organoxenon compounds.

Experimental Section

^1H and ^{19}F NMR spectra were recorded in the pulse Fourier transform mode on a Bruker WM-250 spectrometer (250.13 and 235.34 MHz, respectively) with Me_4Si or CCl_3F as an internal reference.

Mass spectra were obtained on a Varian MAT 44S and MAT CH-6 (electron impact, 75 eV; chemical ionization: isobutane plasma).

All materials used were commercially available. The methylene chloride was purified by double distillation over P_2O_5 and then over CaH_2.

General Procedure. To a stirred suspension of XeF_2 (1.7 g, 10 mmol) in methylene chloride (30 mL) was added the corresponding acid (9 mmol) at −50 °C. The reaction mixture was stirred at −30 °C for 30 min until formation of a colorless solution. The solution was cooled down to −70 °C, and a solution of the appropriate alkene (20 mmol) in methylene chloride (5 mL) was added. The reaction mixture was warmed up to 10 °C, washed with 50 mL of ice–water, dried with Na_2SO_4, and concentrated under vacuum at 0 °C. The products were separated by column chromatography on silica gel with 2:1 hexane–ether as eluent. The resulting β-fluoroalkyl triflates and fluorosulfates were unstable at room temperature and were identified by NMR spectra. Purity was determined by ^1H and ^{19}F NMR and judged to be 95% or greater. Their structure was additionally confirmed by transformation into β-fluorobromoalkanes by working up with NaBr in acetone. β-Fluoroalkyl nitrates were further purified by distillation and analyzed by NMR and mass spectra.

Reactions of β-Fluoroalkyl Sulfonates with NaBr. The appropriate sulfonate ester (50 mg) was added to a solution of NaBr (100 mg) in 1 mL of acetone. The mixture was stirred for 2 h at room temperature, the solvent was evaporated, and the residue was extracted with 5 mL of CH_2Cl_2. The extract was analyzed mass spectrometrically (electron impact, 75 eV), and the molecular peaks of the respective β-fluorobromoalkanes were observed in each case.

***cis*-1-Fluoro-2-[[(trifluoromethyl)sulfonyl]oxy]cyclohexane (4).** Reaction of 1.7 g of XeF_2, 1.35 g (0.8 mL) of triflic acid, and 1.64 g (2.02 mL) of cyclohexene gave 1.69 g (75%) of *cis*-triflate **4** as an unstable oil: ^1H NMR ($CDCL_3$) δ 5.05 (1 H, dddd, $^2J_{HF}$ = 17.1 Hz, $^2J_{HH}$ = 8.5, 2.6, and 2.6 Hz, $CHOSO_2CF_3$), 4.78 (1 H, dddd, $^1J_{HF}$ = 48.2 Hz, $^2J_{HH}$ = 8.1, 2.6, and 2.6 Hz, CHF), 2.3–1.2 (8 H, m, $4CH_2$); ^{19}F NMR ($CDCl_3$) δ −74.5 (3 F, s, CF_3SO_3), −194.2 (1 F, br s, CHF).

1-Fluoro-2-[[(trifluoromethyl)sulfonyl]oxy]hexane (9) and 2-Fluoro-1-[[(trifluoromethyl)sulfonyl]oxy]hexane (12). Reaction of 1.7 g of XeF_2, 1.35 g (0.8 mL) of triflic acid, and 1.68 g (2.5 mL) of 1-hexene gave 1.09 g (48%) of triflate **9** as an unstable oil [^1H NMR ($CDCl_3$) δ 4.8–4.2 [3 H, m, $CH(OSO_2CF_3)CH_2F$], 2.1–0.8 (9 H, m, C_4H_9); ^{19}F NMR ($CDCl_3$) δ −74.8 (3 F, s, CF_3SO_3), −221.8 (1 F, dt, $^1J_{HF}$ = 48 Hz, $^2J_{HF}$ = 48 Hz, $^2J_{HF}$ = 22 Hz, CH_2F)] and 0.34 g (15%) of triflate **12** as an unstable oil; ^1H NMR ($CDCl_3$) δ 4.8–4.2 [3 H, m, $CH(OSO_2CF_3)CH_2F$], 2.1–0.8 (9 H, m, C_4H_9); ^{19}F NMR ($CDCl_3$) δ −73.5 (3 F, s, CF_3SO_3), −181.5 (1 F, m, CHF).

***cis*-1-Fluoro-2-[(fluorosulfonyl)oxy]cyclohexane (5) and *trans*-1-Fluoro-2-[(fluorosulfonyl)oxy]cyclohexane (7).** Reaction of 1.7 g of XeF_2, 0.9 g (0.44 mL) of fluorosulfonic acid, and 1.64 g (2.02 mL) of cyclohexene gave 0.86 g (48%) of *cis*-fluorosulfate **5** as an unstable oil [^1H NMR ($CDCl_3$) δ 4.98 (1 H, dddd, $^2J_{HF}$ = 18 Hz, $^2J_{HH}$ = 7.9, 2.4, and 2.4 Hz, $CHOSO_2F$), 4.85 (1 H, dddd, $^1J_{HF}$ = 48.5 Hz, $^2J_{HH}$ = 7.5, 2.4, and 2.4 Hz, CHF), 2.3–1.3 (8 H, m, 4 CH_2); ^{19}F NMR ($CDCl_3$) δ −40.8 (1 F, s, FSO_3), −193.7 (1 F, br s, CHF)] and 0.29 g (16%) of *trans*-fluorosulfate **7** as an unstable oil: ^1H NMR ($CDCl_3$) δ 4.95 (1 H, dddd, $^2J_{HF}$ = 10 Hz, $^2J_{HH}$ = 7.5, 8.0, and 2.5 Hz, $CHOSO_2F$), 4.92 (1 H, dddd, $^1J_{HF}$ = 48 Hz, $^2J_{HH}$ = 7.5, 7.5, and 2.4 Hz, CHF), 2.3–1.3 (8 H, m, 4 CH_2); ^{19}F NMR ($CDCl_3$) δ −40.7 (1 F, s, FSO_3), −178.5 (1 F, br s, CHF).

1-Fluoro-2-[(fluorosulfonyl)oxy]hexane (10) and 2-Fluoro-1-[(fluorosulfonyl)oxy]hexane (13). Reaction of 1.7 g of XeF_2, 0.9 g (0.44 mL) of fluorosulfonic acid, and 1.68 g (2.5 mL) of 1-hexene gave 0.62 g (34%) of fluorosulfate **10** as an unstable oil [^1H NMR ($CDCl_3$) δ 4.8–4.2 [3 H, m, $CH(OSO_2F)$-CH_2F], 2.2–0.8 (9 H, m, C_4H_9); ^{19}F NMR ($CDCl_3$) δ −40.9 (1 F, s, FSO_3), −219.5 (1 F, dt, $^1J_{HF}$ = 48 Hz, $^2J_{HF}$ = 21 Hz, CH_2F)] and 0.31 g (17%) of fluorosulfate **13** as an unstable oil: ^1H NMR ($CDCl_3$) δ 4.8–4.2 [3, H, m, $CH(OSO_2F)CH_2F$], 2.2–0.8 (9 H, m, C_4H_9); ^{19}F NMR ($CDCl_3$) δ −40.8 (1 F, s, FSO_3), −182.4 (1 F, m, CHF).

***cis*- and *trans*-1-Fluoro-2-nitratocyclohexanes (6 and 8).** Reaction of 1.7 g of XeF_2, 0.57 g (0.36 mL) of 100% nitric acid, and 1.64 g (2.02 mL) of cyclohexene gave 0.34 g (25%) of mixture of isomers **6** and **8**: bp 98–102 °C (14 mm); ^1H NMR ($CDCl_3$) δ 5.2–4.2 (2 H, m, CHF and $CHONO_2$), 2.2–1.2 (8 H, m, $4CH_2$); ^{19}F NMR ($CDCl_3$) δ −178.3 (br s, CHF of trans isomer), −192.7 (br s, CHF of cis isomer). According to ^{19}F NMR the mixture contains cis and trans isomers in ratio of 1:1. MS (chemical ionization, CH_4) *m/e* 164 $[M + H]^+$, 163 $[M]^+$, 101 $[M - NO_3]^+$, 81 $[M - NO_3 - HF]^+$.

1-Fluoro-2-nitratohexane (11) and 2-Fluoro-1-nitratohexane (14). Reaction of 1.7 g of XeF_2, 0.57 g (0.36 mL) of 100% nitric acid, and 1.68 g (2.5 mL) of 1-hexene gave 0.27 g (18%) of nitrate **11** as an oil [bp 87–90 °C (14 mm); ^1H NMR ($CDCl_3$) δ 4.7–4.2 [3 H, m, $CH(ONO_2)CH_2F$], 1.9–0.9 (9 H, m, C_4H_9); ^{19}F NMR ($CDCl_3$) δ −219.9 (dt, $^1J_{HF}$ = 48 Hz,, $^2J_{HF}$ = 23 Hz; CH_2F); MS (chemical ionization, CH_4) *m/e* 166 $[M + H]^+$, 165 $[M]^+$, 103 $[M - NO_3]^+$, 83 $[M - NO_3 - HF]^+$] and 0.135 g (9%) of nitrate **14** as an oil: bp 80–85 °C (14 mm) (lit.[9] bp 83 °C (14.5 mm)); ^1H NMR ($CDCl_3$) δ 4.7–4.2 [3 H, m, $CH(ONO_2)CH_2F$], 1.9–0.9 (9 H, m, C_4H_9); ^{19}F NMR ($CDCl_3$) δ −187.7 (m, CHF); MS (chemical ionization, CH_4) *m/e* 166 $[M + H]^+$, 165 $[M]^+$, 103 $[M - NO_3]^+$, 83 $[M - NO_3 - HF]^+$.

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