

COMPETITIVE BINDING OF FLUOROSULFATE ANION
IN REACTIONS OF HALOGENS AND NITRONIUM
BOROFLUORIDE WITH OLEFINS

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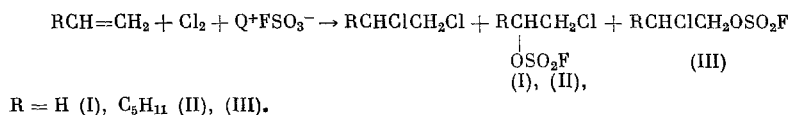
The fluorosulfate anion is one of the best leaving groups [1], i.e., it has a high nucleofugacity. It is therefore a superweak nucleophile and is not considered in any of the nucleophilicity scales [2-4]. The methods of functionalization of organic compounds with the formation of fluorosulfates are therefore limited to those processes in which the FSO_3^- anion is the only nucleophile in the reaction medium. In the case of olefins, reactions of addition of fluorosulfonic acid [5, 6], halofluorosulfates, and peroxydisulfuryl difluoride [7-11] are, in general, used for this purpose.

We have already found that those superweak nucleophiles, such as the ClO_4^- and CF_3SO_3^- anions, may react as nucleophiles at the concluding stage of Ad_E reactions, even under conditions of competition with other considerably more nucleophilic particles, to form the corresponding organic perchlorates [12-15] and triphthalates [16-17]. These data stimulated studies on possible competitive binding of the fluorosulfate anion.

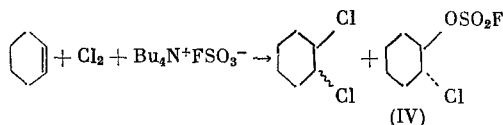
We used the reactions of the electrophilic addition of halogens and nitronium borofluoride to simple olefins (ethylene, 1-heptene, and cyclohexene) in the presence of equimolar amounts of tetraalkylammonium fluorosulfate salt Q^+FSO_3^- (where $\text{Q}^+ = \text{Et}_4\text{N}^+$ or Bu_4N^+). The reactions were carried out with cooling at -78 to 0°C , in aprotic solvents (CH_2Cl_2 , CHCl_3). The course of the reactions and the isolation of the products were controlled by chromatography on silica gel.

According to TLC and PMR spectral methods, in the reactions of the above olefins with Br_2 in the presence of fluorosulfonic salts, not only the products of normal addition - 1,2-dibromides - are formed, but also β -bromoalkyl fluorosulfates. The latter compounds could not be isolated from the reaction mixture by the method of adsorption chromatography because of their extremely low stability at $\sim 20^\circ\text{C}$ and high tendency to hydrolysis by atmospheric moisture.

The more stable esters of fluorosulfonic acid were obtained by the reaction of these alkenes with chlorine; the products could be isolated and completely characterized. The addition of chlorine to ethylene in the presence of $\text{Et}_4\text{N}^+\text{FSO}_3^-$ leads to 2-chloroethyl fluorosulfate (I) (yield 25%), which was identical with the compound described in [18]. In the case of 1-heptene, not only 1,2-dichloroheptane is obtained (yield 70%), but also a mixture of isomeric fluorosulfates (II) and (III) is formed in a ratio of 4:1 (according to PMR data).

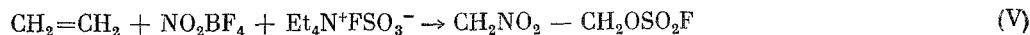


In the reaction of cyclohexene with chlorine and $\text{Bu}_4\text{N}^+\text{FSO}_3^-$, as in the preceding cases, besides 1,2-dichloride (yield 53%), a product of the participation of the fluorosulfate anion - trans-2-chlorocyclohexyl fluorosulfate (IV) - is also formed (yield about 20%). The trans configuration of (IV) has been established from the width of signals of methine protons (the W-parameter [19]), which is equal to 21.5 Hz.



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The reaction of nitronium borofluoride with ethylene in the presence of $\text{Et}_4\text{N}^+\text{F}\text{SO}_3^-$ at 25°C in CH_2Cl_2 gives one single product, 2-nitroethyl fluorosulfate (V) in a yield of 32%. The structure of this compound was confirmed by IR and NMR spectra



The compound is slightly stable at $\sim 20^\circ\text{C}$, and therefore satisfactory data of elemental analysis could not be obtained.

The formation of fluorosulfonic acid esters in the processes studied indicates that the fluorosulfate anion may play the role of a nucleophile at the concluding stage of the electrophilic addition to olefins. These processes proceed under the conditions of competition with other anion: the chloride ion that separates in an equivalent amount from chlorine, or the borofluoride ion that can produce the fluoride anion. These data require reexamination of the evaluation of the nucleophilic reactivity of the fluorosulfate anion as a superweak nucleophile. Together with the previously obtained results [12-17], these data also confirm the general character of the phenomenon of the competition binding of superweak nucleophiles in carbocation processes.

EXPERIMENTAL

The course of the reaction and the purity of the compounds were controlled by TLC on Silufol. The products were isolated by column chromatography (silica gel 40/100 μ). The IR spectra were run on a UR-10 spectrophotometer in thin layer, and the PMR spectra on Varian T60S and Tesla BS-497 spectrometers (100 MHz) in CCl_4 with reference to TMS as internal standard.

Tetraethyl- and tetrabutylammonium fluorosulfates were obtained by the method described in [20].

2-Chloroethyl Fluorosulfate (I). Ethylene and chlorine were simultaneously passed for 1 h at $\sim 20^\circ\text{C}$ through a solution of 3 g (10 mmoles) of tetraethylammonium fluorosulfate in 30 ml of absolute CH_2Cl_2 . A 70-ml portion of hexane was added to the mixture, and the precipitate was filtered. After evaporation of the solvent in vacuo, 0.31 g of (I) (25% based on the salt used) were obtained, bp 60°C (17 mm), R_f 0.32 (in a 1:6 ethyl acetate-hexane system). IR spectrum (ν , cm^{-1}): 1440, 1230, 820 (OSO_2F). PMR spectrum (δ , ppm): 4.7 t ($\text{CH}_2 \cdot \text{OSO}_2\text{F}$), 3.85 t (CH_2Cl).

Reaction of 1-Heptene with Cl_2 and $\text{Et}_4\text{N}^+\text{F}\text{SO}_3^-$. A dry current of chlorine was passed at 0°C through a solution of 1.7 g (17.3 mmoles) of 1-heptene and 4 g (17.5 mmoles) of tetraethylammonium fluorosulfate in 40 ml of CH_2Cl_2 up to the appearance of a stable yellow green color. An 80-ml portion of pentane was added to the mixture, and the precipitate was filtered. After evaporation of the solvent in vacuo, 3.25 g of an oil was obtained, which was chromatographed (eluent - pentane). Yield, 2 g (70%) of 1,2-dichloropentane, bp 190°C [21], R_f 0.82 (hexane) and 0.6 g (15%) of a mixture of 1-chloromethylhexyl fluorosulfate (II) and 2-chloroheptyl fluorosulfate (III), decomposes at 107°C , R_f 0.41 (a 1:6 ethyl acetate-hexane system). Found: C 36.85; H 6.78%. $\text{C}_7\text{H}_{14} \cdot \text{ClF}\text{O}_3\text{S}$. Calculated: C 36.13; H 6.02%. IR spectrum (ν , cm^{-1}): 1450, 1230, 820 (OSO_2F). PMR spectrum (δ , ppm): 0.7-2.0 m (C_7H_{14}), 3.8 d (CH_2Cl), 4.05 (CHCl), 4.53 d ($\text{CH}_2\text{OSO}_2\text{F}$), and 5.15 m (CHOSO_2F).

Reaction of Cyclohexene with Cl_2 and $\text{Bu}_4\text{N}^+\text{F}\text{SO}_3^-$. A current of chlorine was passed at 0°C through a solution of 1.25 g (15.2 mmoles) of cyclohexene and 5.3 g (15.5 moles) of tetrabutylammonium fluorosulfate in 30 ml of chloroform up to the appearance of a stable yellow color. An 80-ml portion of pentane was added to the mixture, and the precipitate was filtered. After evaporation of the solvent in vacuo, 2.8 g of an oil was obtained, which was chromatographed (eluent - pentane). Yield, 1.27 g (53%) of 1,2-dichlorocyclohexane, bp 188°C [22], R_f 0.42 (pentane) and 0.66 g (20%) of trans-2-chlorocyclohexyl fluorosulfate (IV), decomposes at 94°C , R_f 0.15 (pentane). Found: C 33.86; H 4.95%. $\text{C}_6\text{H}_{10}\text{ClF}\text{O}_3\text{S}$. Calculated: C 33.26; H 4.65%. IR spectrum (ν , cm^{-1}): 1450, 1230, 970, 820 (OSO_2F). PMR spectrum (δ , ppm): 4.65 m ($W = 21.5$ Hz, CHOSO_2F), 3.85 m (CHCl), 2.4-0.9 m (CH_2).

2-Nitroethyl Fluorosulfate (V). A slow current of ethylene was passed at $\sim 20^\circ\text{C}$ for 1.5 h through a solution of 1.8 g (7.9 mmoles) of tetraethylammonium fluorosulfate 1.5 g (11.3 mmoles) of nitronium borofluoride in 20 ml of CH_2Cl_2 . After evaporation of the solvent in vacuo, 0.44 g (32%) of (V) were obtained, R_f 0.26 (a 1:6 ethyl acetate-hexane system). IR spectrum (ν , cm^{-1}): 1560, 1370 (NO_2), 1440, 1230, 960, 830 (OSO_2F). ^1H NMR spectrum (δ , ppm): 4.75 s (cf. [15]). ^{19}F NMR spectrum (δ , ppm in CDCl_3 with reference to CFCl_3): -38.6 s (cf. [8]).

CONCLUSIONS

Reactions of olefins with chlorine in the presence of fluorosulfonic acid salts lead to β -chloroalkyl fluorosulfates together with 1,2-dichlorides. The addition of nitronium borofluoride to ethylene in the presence of

tetraethylammonium fluorosulfate gives 2-nitroethyl fluorosulfate. These reactions confirm the general character of the competitive binding of superweak nucleophiles in A_{D}^{E} reactions.

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