ELECTROPHILIC ALKENYLATION OF FLUOROOLEFINS BY PERFLUORO(2-ALKOXYPROPENES)

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UDC 66.095.253:547.413.5'161:547.371

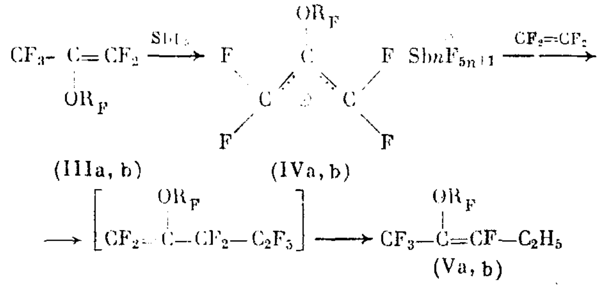
Perfluoro(2-alkoxypropenes) react with tetrafluoroethylene under mild conditions in the presence of SbF_5 to give the corresponding perfluoro(2-alkoxy-2-pentenes). 1-Trifluoromethoxyperfluoropropene is converted by the action of SbF_5 in SO_2ClF solution to the acid fluoride derivative of perfluoroacrylic acid.

In previous works [1, 2], we showed that both perfluoropropylene (I) and perfluoroisobutylene (II) readily undergo electrophilic alkenylation with fluorine-containing ethylenes in the presence of SbF_5 to give the corresponding higher fluoroolefins. This reaction involves the formation the perfluoroallyl (Ia) and perfluoromethallyl cations (IIa), respectively, which were detected and characterized by NMR spectroscopy [3, 4]. We have shown that perfluoro(2-alkoxypropenes) (IIIa) and (IIIb) gives the corresponding allyl cations (IVa) and (IVb) by the action of SbF_5 [5].

The relative stability of these cations was determined by the competitive reaction method. For this purpose, ^{19}F NMR spectra were taken for mixtures of (IIIa) and (I) as well as of (IIIa) and (II) with SbF_5 in SO_2ClF solution in 1:1:2 mole ratio. 2-Trifluoromethoxyperfluoroallyl cation (IVa) proved less stable than perfluoroallyl cation (Ia) and has approximately the same thermodynamic stability as perfluoromethallyl cation (IIa).

Hence, we might have expected that (IIIa) and (IIIb) also may be used as alkenylating agents in reactions with fluorine-containing ethylenes in the presence of SbF_5.

Perfluoroalkoxypropenes (IIIa) and (IIIb) react with tetrafluoroethylene in the presence of SbF_5 under mild conditions to give the corresponding 2-perfluoroalkoxyperfluoropentenes (Va) and (Vb), which were isolated as mixtures of E and Z isomers (the yield of a and b was 84%):



$R_F = CF_3$ (a), $n\text{-}C_3F_7$ (b).

As a consequence of the electronic properties of the trifluoromethoxy group and according to an MNDO SCF LCAO MO calculation [6], 1-trifluoromethoxyperfluoroallyl cation (VI) should be thermodynamically more stable than its 2-substituted analog, namely, cation (IVa). We might have expected that 1-trifluoromethoxyperfluoropropene (VII) would react with SbF_5 to give 1-OCF_3-perfluoroallyl cation (VI). However, (VI) could not be detected by ^{19}F NMR spectroscopy upon the action of SbF_5 on (VII) in SO_2ClF even at -60°C. Under these conditions, (VII) is fully converted to the acid fluoride derivative of acid (VIII). The yield of (VIII) was 77%:

A. N. Nesmeyanov Institute of Organometallic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1926-1928, August, 1991. Original article submitted December 30, 1990.

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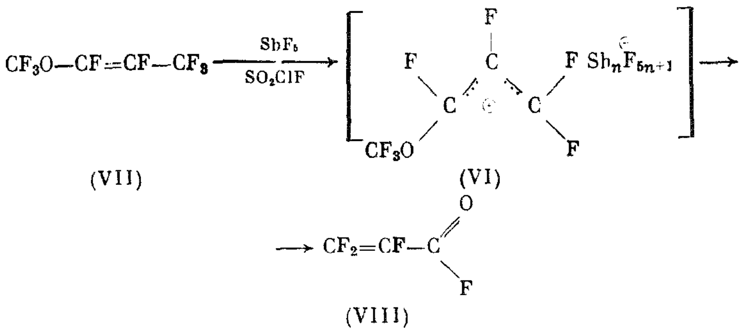


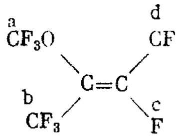
The analogous reaction for 1-methoxyperfluoropropene under more vigorous conditions has been observed by Abduganiev [7].

EXPERIMENTAL

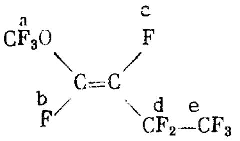
The ^{19}F NMR spectra were taken on a Bruker WP-200SY spectrometer with CF_3CO_2H as the internal standard. The chemical shifts are given in ppm, while the coupling constants are given in Hz. The Raman spectra were taken on a Ramanor HG-200S spectrometer with excitation by an argon laser at 514.5 nm. The mass spectra were obtained on a 6VG-7070E mass spectrometer at 70 eV.

2-Trifluoromethoxyperfluoro-2-pentene (Va). A mixture of 22.5 g (0.104 mole) (IIIa), 12 g (0.12 mole) tetrafluoroethylene, and 6 g ((0.03 mole) SbF_5 was heated for 5 h in a steel autoclave at 50°C. The autoclave was opened and the gaseous fraction was collected in a trap maintained at -78°C. The residue was poured into water at 5°C. The lower layer was separated, dried over $CaCl_2$, and distilled to give 10.5 g (IIIa) (55.6% conversion) and 15.4 g (84%) (Va) with bp 44-48°C. Raman spectrum: 1710 cm^{-1}. ^{19}F NMR spectrum of a 1:3 mixture of E and Z isomers: (δ, ppm, J, Hz):

E-isomer:

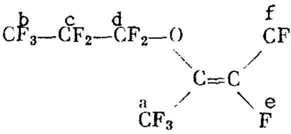


Z isomer:



E isomer: -16.9 ($3F^a$), -9.5 ($3F^b$), 8.3 ($3F^e$), 44.2 ($2F^d$), 55.8 (F^c), J_{b-c} 21, J_{a-d} 4, J_{c-d} 9.
Z isomer: -16.5 ($3F^a$), -13.4 ($3F^b$), 7.8 ($3F^e$), 42.8 ($2F^d$), 44.6 (F^c), J_{a-c} 10, J_{c-d} 17, J_{b-d} 16.
Mass spectrum m/z (I, %): $[M]^+$ 316 (14.2), $[M - F]^+$ 297 (23.8), $[M - C_2F_5]^+$ 197 (15.1), $[C_3F_7]^+$ 169 (33.8), $[C_2F_3O]^+$ 97 (7.3), $[CF_3]^+$ 69 (100).

2-Heptafluoropropoxyperfluoro-2-pentene (Vb). A mixture of 6 g (0.018 mole) (IIIb) and 6 g (0.03 mole) SbF_5 was placed into a two-necked flask equipped with a reflux condenser at -78°C. A sample of 10 g (0.1 mole) tetrafluoroethylene was passed through this mixture at 22°C with vigorous stirring for 3 h. The reaction mixture was poured into water at 5°C. The lower layer was separated, dried over $CaCl_2$, and distilled to give 2.1 g (IIIb) (65% conversion) and 4.3 g (84%) (Vb) with bp 77-80°C. Raman spectrum: 1709 cm^{-1}. ^{19}F NMR spectrum of a 1:6 mixture of the Z and E isomers (δ, ppm, J, Hz):



−11,8 ($3F^a$); 4,3 ($3F^b$); 6,5 ($2F^d$); 6,1 ($3F^g$); 42,2 ($2F^f$); 51,6 ($2F^c$); 52,0 (F^e); J_{a-e} = 19,7; J_{a-d} = 20.

Mass spectrum, m/z (I, %): $[M]^+$ 416 (4.2), $[M - F]^+$ 397 (2.8), $[M - C_2F_5]^+$ 297 (2.9), $[C_5F_7O]^+$ 209 (2.7), $[C_3F_7]^+$ 169 (100), $[C_2F_5]^+$ 119 (7.5), $[C_3F_3O]^+$ 109 (3.7), $[CF_3O]^+$ 85 (4.2), $[CF_3]^+$ 69 (99.4). Found: C, 22.94; F, 72.81%. Calculated for $C_8F_{16}O$: C, 23.08; F, 73.08%.

Acid Fluoride of Perfluoroacrylic Acid (VIII). A solution of 12 g (0.06 mole) 1-trifluoromethoxyperfluoro-1-propene (VII) in SO_2ClF was added to a two-necked flask equipped with a reflux condenser at -78°C. A sample of 3 g (0.01 mole) SbF_5 was then added dropwise with rapid stirring. The reaction was continued until a noncondensing gas was no longer evolved. The solvent was distilled off and the reaction mixture was poured with cooling into concentrated sulfuric acid at 5°C and distilled from concentrated sulfuric acid to give 5.4 g (77%) (VIII) with bp 28°C. Product (VIII) was identified by ^{19}F NMR spectroscopy.

The samples for recording the ^{19}F NMR spectra of the cations were prepared according to our previous procedure [8].

The authors express their deep gratitude to M. V. Galakhov for taking and interpreting the ^{19}F NMR spectra.

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