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REACTION OF INTERNAL FLUOROOLEFIN OXIDES WITH FLUOROSULFONIC ACID

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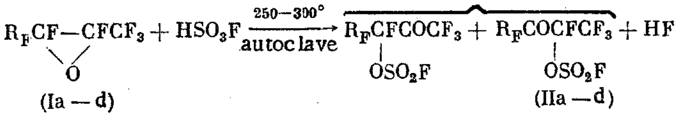
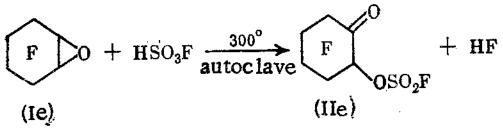
Previously it was shown [1] that hexafluoropropylene oxide (HFPO) reacts with the highly electrophilic reagent HSO_3F to give fluorosulfonoxypentafluoroacetone.

We established that internal fluoroolefin oxides (Ia-e) also react when heated with HSO_3F to give fluoroketones that contain a fluorosulfate group in the α-position (IIa-e):



$R_F = CF_3$ (a), C_2F_5 (b), n-C_3F_7 (c), $CF(CF_3)_2$ (d)



Perfluoro-2-butene oxide (Ia) forms a single ketone, namely 3-fluorosulfatoheptafluoro-2-butanone (IIa). Compound (IIa) was obtained previously [2] but not in the pure state. Similar to (Ia), perfluorocyclohexane oxide (Ie) forms one ketone, namely α-fluorosulfatoperfluorocyclohexanone (IIe).

Perfluoro-2-pentene oxide (Ib), perfluoro-2-hexene oxide (Ic), and perfluoro-4-methyl-2-pentene oxide (Id) when reacted with HSO_3F give a mixture of approximately equal amounts of isomeric ketones (IIb-d), but (IId) is formed in low yield, evidently due to steric hindrance. Perfluoro-2-methyl-2-pentene oxide does not react with HSO_3F even at 300°C.

It should be mentioned that the opening of the oxide ring of internal oxides by HSO_3F is not catalyzed by Cr^{3+} ions, which noticeably facilitate the opening of HFPO [1]. Thus, oxide (Ic) does not react with HSO_3F in the presence of Cr_2O_3 even at 150°C.

EXPERIMENTAL

The ^{19}F NMR spectra were recorded on Perkin–Elmer–Hitachi R-20 and Perkin–Elmer R-32 instruments (56.4 and 84.6 MHz) relative to CF_3COOH (external standard). The IR spectra were taken on a UR-20 instrument. The GLC analysis was run on a column packed with 5% SKTPT-100 deposited on Chromosorb G and 20% FS-1265 deposited on Chromosorb W.

Preparation of α-Fluorosulfatoperfluoroketones. A mixture of 0.05 mole of the oxide (Ia-e) and 45-50 ml of HSO_3F was heated in a rotated autoclave for 8-10 h at 250-300°C. The α-fluorosulfatoperfluoroketones were isolated from the reaction mixture by distillation.

3-Fluorosulfatoheptafluoro-2-butanone (IIa). The yield of (IIa) was 80%, bp 65-67°. Infrared spectrum (ν, cm^{-1}): 1490 (S=O), 1800 (C=O). Found, %: C 16.55; F 51.69; S 11.02.

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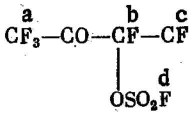
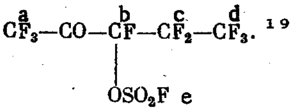
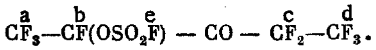
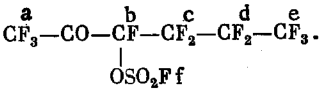
$C_4F_8SO_4$. Calculated, %: C 16.22; F 51.35; S 10.81.  $\overset{a}{CF_3}-CO-\underset{\substack{|\\ \overset{d}{OSO_2F}}}{\overset{b}{CF}}-\overset{c}{CF_3}$. ^{19}F NMR spectrum (δ, ppm): F_a −2.4; F_b 57.5; F_c 3.5; F_d −129.0; J_{ab} = 14.6, J_{ac} = 3.8, J_{bc} = 2.3, J_{bd} = 11 Hz.

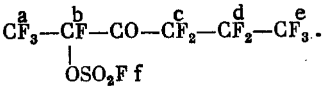
Reaction of HSO_3F with Perfluoropentene Oxide (Ib). The yield of (IIb) was 60%, bp 85-87°. Infrared spectrum (ν, cm^{-1}): 1490 (S=O), 1795 (C=O). Found, %: C 17.45; F 54.99. $C_5F_{10}SO_4$. Calculated, %: C 17.34; F 54.91.

3-Fluorosulfatoperfluoro-2-pentanone  $\overset{a}{CF_3}-CO-\underset{\substack{|\\ OSO_2F\ e}}{\overset{b}{CF}}-\overset{c}{CF_2}-\overset{d}{CF_3}$. ^{19}F NMR spectrum (δ, ppm): F_a −2.4; F_b 55.4; F_c 46.2; F_d 3.3 or 3.5; F_e −128.4 or −128.0; J_{ab} = 14.5, J_{ac} = 6.8, J_{be} = 11 Hz.

2-Fluorosulfatoperfluoro-3-pentanone  $\overset{a}{CF_3}-\overset{b}{CF}(OSO_2\overset{e}{F})-CO-\overset{c}{CF_2}-\overset{d}{CF_3}$. ^{19}F NMR spectrum (δ, ppm): F_a 5.5; F_b 57.2; F_c 42.7; F_d 3.3 or 3.5; F_e −128.4 or −128.0; J_{ab} = 2.2, J_{ac} = 6.4, J_{bc} = 23.5, J_{be} = 11 Hz.

Reaction of HSO_3F with Perfluoro-2-hexene Oxide (Ic). The yield of (IIc) was 55%, bp 104-106°. Infrared spectrum (ν, cm^{-1}): 1495 (S=O), 1795 (C=O). Found, %: C 18.04; F 57.62. $C_6F_{12}SO_4$. Calculated, %: C 18.18; F 57.68.

3-Fluorosulfatoperfluoro-2-hexanone  $\overset{a}{CF_3}-CO-\underset{\substack{|\\ OSO_2F\,f}}{\overset{b}{CF}}-\overset{c}{CF_2}-\overset{d}{CF_2}-\overset{e}{CF_3}$. ^{19}F NMR spectrum (δ, ppm): F_a −2.5; F_b 57.1; F_c 46.2; F_d 48.3; F_e 4.7; F_f −128.5 or −128.1; J_{ab} = 15.2, J_{ac} = 7.6, J_{bd} = 8.5, J_{be} = 2.3; J_{bf} = 11, J_{ce} = 10.4 Hz.

2-Fluorosulfatoperfluoro-3-hexanone  $\overset{a}{CF_3}-\underset{\substack{|\\ OSO_2F\,f}}{\overset{b}{CF}}-CO-\overset{c}{CF_2}-\overset{d}{CF_2}-\overset{e}{CF_3}$. ^{19}F NMR spectrum (δ, ppm): F_a 3.3; F_b 55.6; F_c 39.6; F_d 49.2; F_e 4.2; F_f −128.5 or −128.1; J_{ab} = 2.3, J_{bf} = 11, J_{ce} = 11 Hz.

Reaction of HSO_3F with Perfluoro-4-methyl-2-pentene Oxide (Id). The yield of (IId) was 9.6%, bp 108-109°. Infrared spectrum (ν, cm^{-1}): 1490 (S=O), 1810 (C=O). Found, %: C 17.95; F 57.45; S 7.98. $C_6F_{12}SO_4$. Calculated, %: C 18.18; F 57.58; S 8.08.

Reaction of HSO_3F with Perfluorocyclohexene Oxide (Ie). The yield of (IIe) was 37%, bp 113°. Infrared spectrum (ν, cm^{-1}): 1490 (S=O), 1812 (C=O). Found, %: C 20.32; F 52.91; S 9.11. $C_6F_{10}SO_4$. Calculated, %: C 20.11; F 53.07; S 8.94.

CONCLUSIONS

Internal perfluoroolefin oxides react with fluorosulfonic acid to give perfluoroketones that contain a fluorosulfate group in the α-position.

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