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SULFOTRIOXIDATION OF PERFLUOROISOPROPYL ALKENYL ETHERS

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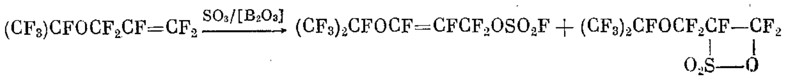
Reaction of hexafluoropropylene with SO_3 in the presence of catalytic amounts of boron compounds affords a mixture of perfluoroallyl fluorosulfate (I) and hexafluoropropane-β-sultone [1, 2] (in the absence of the catalyst, no (I) is formed] [3, 4]).

We here report a study of the reaction of SO_3 with perfluoroisopropyl allyl ether (II) (prepared as in [1]) and the isomeric perfluoroisopropyl propenyl ether (III). The ether (II), like many of its homologs [1], is a substituted perfluoroallyl system, and hence fluorosulfates, obtained from perfluoroallyl ethers, represent a considerable extension of the range of electrophilic fluoroalkylating agents.

Reaction of (II) with SO_3 in the presence of 2-3 mole % of B_2O_3 results in the formation of isomers of the fluorosulfate (IV) (a mixture of cis and trans in the ratio 6:4), together with the sultone (V):



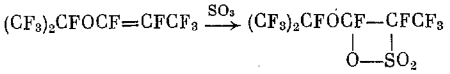
$$(CF_3)CFOCF_2CF{=}CF_2 \xrightarrow{SO_3/[B_2O_3]} (CF_3)_2CFOCF{=}CFCF_2OSO_2F + \begin{array}{c}(CF_3)_2CFOCF_2CF—CF_2\\ \qquad\qquad\quad | \quad\ \ | \\ \qquad\qquad\quad O_2S—O\end{array}$$

(II) (IV) (V)

In the absence of B_2O_3, the sultone (V) is formed nearly exclusively.

The fluorosulfate (IV) appears to be formed by the reaction sequence proposed for the synthesis of perfluoroallyl fluorosulfate [2], If the alternative route, involving a six-membered transition state [5], were operative, much greater stereoselectivity would be expected.

The pathway involving preliminary electrophilic isomerization of (II) to (III) followed by insertion of SO_3 into the C−F bond of the CF_3 group can also be excluded; we have previously demonstrated the possibility of such a process in the case of 1,1,2-trichloro-3,3,3-trifluoropropene [6]. It was found that the ether (III) reacts readily with SO_3, but the sole reaction product is the sultone (VI):

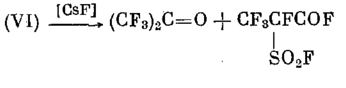


$$(CF_3)_2CFOCF{=}CFCF_3 \xrightarrow{SO_3} \begin{array}{c}(CF_3)_2CFOCF—CFCF_3\\ \qquad\quad | \quad\ \ | \\ \qquad\quad O—SO_2\end{array}$$

(III) (VI)

The ether (III) was obtained by isomerizing (II) with SbF_5. The stereoisomeric composition of (III) (cis:trans = 4:6) suggests that the reaction proceeds via the isomerization of perfluoroallylbenzene to cis- and trans-perfluoropropenylbenzenes [7].

The orientation of the addition of SO_3 to the ether (III) is confirmed by the reaction of the sultone (VI) with nucleophiles. Thus, the sultone (VI) reacts with CsF in diglyme, undergoing cleavage to form hexafluoroacetone and α-fluorosulfonyltetrafluoropropionyl fluoride.



$$(VI) \xrightarrow{[CsF]} (CF_3)_2C{=}O + \begin{array}{c}CF_3CFCOF\\ | \\ SO_2F\end{array}$$

However, on reaction with a weaker nucleophile (H_2O), the C−O−C bond is retained, and the sultone (VI) merely rearranges to perfluoroisopropyl α-fluorosulfonyltetrafluoropropionate (VII):

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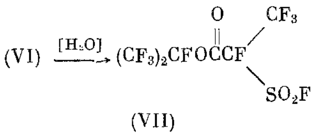


$$(VI)\xrightarrow{[H_2O]}(CF_3)_2CFOC(=O)CF(CF_3)(SO_2F)$$

(VII)

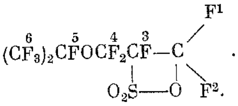
Like other fluorinated alken-2-yl fluorosulfates [1, 2, 5], the fluorosulfate (IV) is a powerful alkylating agent and may be used to introduce the perfluoro-γ-isopropoxyallyl group. Thus, reaction of (IV) with potassium hexafluoroisopropoxide gives satisfactory yields of perfluoroisopropyl γ-isopropoxyallyl ether (VIII)

$$(IV)\xrightarrow[-FSO_2OK]{(CF_3)_2CFOK}(CF_3)_2CFOCF{=}CFCF_2OCF(CF_3)_2$$

(VIII)

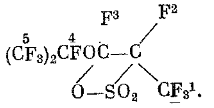
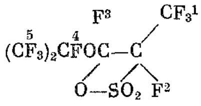
EXPERIMENTAL

^{19}F NMR spectra were obtained on a Perkin–Elmer R-32 NMR spectrometer (84.6 MHz), external standard CF_3COOH; the mass spectra, on a Varian CH-5 mass spectrometer.

Reaction of (II) with SO_3. A mixture of 4 g (13 mmole) of (II) and 1.2 g (15 mmole) of SO_3 was heated in a sealed ampul for 4 h at 100°C. The reaction mixture was distilled to give 4.9 g (94%) of the sultone (V) containing, according to GLC, ~4% of the fluorosulfate (IV); repeated distillation gave pure (V), bp 107-109°C. Found: C 18.22; F 57.00%, $C_6F_{12}O_4S$. Calculated: C 18.18; F 57.58%.  . ^{19}F NMR spectrum (δ, ppm): 5.7 d.d.t (F^1), 12.4 d.t (F^2), 74.7 d.t (F^3), −2.7 m ($CF_2{}^4$), 67.8 t.m (F^5), 4.0 br. s ($CF_3{}^6$), $J_{1-2}=109$, $J_{1-3}=6.6$, $J_{1-4}=2.5$, $J_{2-4}=13.2$, $J_{3-4}=6.6$, $Z_{4-5}=22.6$ Hz.

Reaction of (II) with $SO_3/[B_2O_3]$. A mixture of 20 g (60 mmole) of (III), 5 g (60 mmole) of SO_3, and 0.1 g (1.6 mmole) of B_2O_3 was kept in a sealed ampul for 3 days at 20°C, heated for 12 h at 100°C, the reaction mixture distilled, and the fraction bp 105-130°C collected. There was obtained 18.3 g of a mixture containing, according to GLC, 79% of (IV), 20% of (V), and ~1% of (VI); the yields of (IV) and (V) were 58 and 7.3%, respectively. Further fractionation gave (IV), bp 120-122°C. Found: C 18.19; S 7.70%, $C_6F_{12}O_4S$. Calculated: C 18.18; S 8.08%. trans-$(C\overset{6}{F}_3)_2C\overset{5}{F}OC\overset{4}{F}{=}C\overset{3}{F}C\overset{2}{F}_2OSO_2F^1$. ^{19}F NMR spectrum (δ, ppm): −125.3 t (F^1), −4.4 d.d.d (F^2), 96.9 d.m (F^3), 25.3 d.m (F^4), 62.8 m (F^5), 4.0 br. s (F^6), $J_{1-2}=7.6$, $J_{2-4}=28.3$, $J_{3-4}=122$ Hz. cis-$(C\overset{6}{F}_3)_2C\overset{5}{F}OC\overset{4}{F}{=}C\overset{3}{F}C\overset{2}{F}_2OSO_2\overset{1}{F}$: −125.5 t ($F^1$), −4.9 m ($F^2$), 92.7 d.t ($F^3$), 12 m ($F^4$), 61.3 d.m ($F^5$), 3.2 br. s ($F^6$), $J_{1-2}=9.4$, $J_{2-3}=19.4$, $J_{3-4}=32.9$ $J_{4-5}=15$ Hz.

Perfluoroisopropyl Isopropenyl Ether (III). To 0.6 g (2.7 mmole) of SbF_5 was added 10 g (30 mmole) of the ether (II). When the exothermic reaction was complete, the reaction mixture was distilled to give 9.4 g (94%) of (III) (mixture of cis and trans isomers, 4:6), bp 58-60°C. trans-$(C\overset{5}{F}_3)_2C\overset{4}{F}OC\overset{3}{F}{=}C\overset{2}{F}C\overset{1}{F}_3$. ^{19}F NMR spectrum (δ, ppm): −6.2 d.d (F^1), 99.5 d.m (F^2), 29.5 d.m (F^3), 63.8 d.d.m (F^4), 4.6 d.d.d (F^5), $J_{1-2}=11.3$, $J_{1-3}=22.6$, $J_{2-3}=122$, $J_{3-4}\approx J_{2-4}\approx 9.4$, $J_{2-5}\approx J_{3-5}\approx J_{4-5}\approx 2.8$ Hz, cis-$(C\overset{5}{F}_3)_2C\overset{4}{F}OC\overset{3}{F}{=}C\overset{2}{F}C\overset{1}{F}_3$. ^{19}F NMR spectrum (δ, ppm): −6.8 m (F^1), 95.2 d.q.m (F^2), 16.1 m (F^3), 62 d.m (F^4), 4 d.d.d.q (F^5), $J_{2-3}=32$, $J_{1-2}=10.4$, $J_{3-4}=14$, $J_{1-5}\approx J_{5-2}\approx J_{3-5}\approx J_{4-5}\approx 2.8$ Hz.

Sultone (VI). To 9 g (28 mmole) of (III) was added 2.3 g (29 mmole) of freshly distilled SO_3. When the exothermic reaction was complete, conc. sulfuric acid was added, volatile products distilled off at 10-12 mm, and the distilate redistilled to give 11.0 g (98%) of (VI) (mixture of erythro and threo isomers), bp 105-107°C. Found: C 18.19; F57.58; S 8.07%. $C_6F_{12}O_4S$. Calculated: C 18.18; F 57.58; S 8.08%.  ^{19}F NMR spectrum (δ, ppm): −3.0 d.d (F^1), 73 d.q (F^2), 7.1 m (F^3), 66.5 d.m (F^4), 3.9 m (F^5), $J_{1-2}=7$, $J_{2-3}=4$, $J_{1-3}=1.5$, $J_{3-4}=21$ Hz.  . −2.9 d.d (F^1), 72.7 d.q (F^2), 1.5 m (F^3), 66.8 d.m (F^4), 3.4 m (F^5), $J_{1-2}=8.5$, $J_{1-3}=1.5$, $J_{2-3}=3.8$, $J_{3-4}=19$ Hz.

Ester (VII). A mixture of 2.4 g (60 mmole) of (VI) and 10 ml of cold water was stirred for 1 h, the organic layer separated, and distilled over conc. sulfuric acid to give 2.1 g (87.5%) of (VII), bp 21°C (20 mm). Found: C 18.19; S 8.00; F 57.67%. $C_6F_{12}O_4S$. Calculated: C 18.18; F 57.58; S 8.08% $(C\overset{5}{F}_3)_2C\overset{4}{F}OC(O)C\overset{3}{F}(C\overset{2}{F}_3)SO_2\overset{1}{F}$. ^{19}F NMR spectrum (δ, ppm): −129.5 d.q (F^1), −3.3 d.d (F^2), 83.5 d.q (F^3), 65 br. s (F^4), 2.9 br. s (F^5), $J_{1-2}=8$, $J_{1-3}=7$, $J_{2-3}=3.2$ Hz.

Ether (VIII). To a solution of potassium heptafluoroisopropoxide [from 4 g (24 mmole) of HFA and 1.2 g (20 mmole) of KF] in 20 ml of diglyme was added gradually over 20 min 5 g (9 mmole) of 75% fluorosulfate (IV) containing 25% of the sultone (V)], the mixture stirred for 4 h, the lower layer separated, and distilled over conc. sulfuric acid at 20 mm Hg. Redistillation of the distillate afforded 1.8 g (39%) of (VIII) (mixture of cis and trans isomers), bp 110-111°C. Found: C 22.43; F 71.00%. $C_9F_{18}O_2$. Calculated: C 22.41; F 70.95%. $(C\overset{1}{F}_3)_2C\overset{2}{F}OC\overset{3}{F}=C\overset{4}{F}C\overset{5}{F}_2OC\overset{6}{F}(C\overset{7}{F}_3)_2$. ^{19}F NMR spectrum (δ, ppm): trans isomer: 3.9 m (F^1), 63.1 d.d.m (F^2), 96.4 d.m (F^3), 27.8 d.m (F^4), −7.6 m (F^5), 68.4 t (F^6), 4.4 m (F^7), $J_{2-4}=9.5$, $J_{2-3}=9.5$, $J_{3-4}=128$; $J_{6-5}=22$ Hz. cis-Isomer: 3.1 m (F^1), 61.1 d.m (F^2), 92.4 d.m (F^3), 15.6 d.m (F^4), −7.6 d.m (F^5), 68.4 t (F^6), 4.4 m (F^7), $J_{2-4}=15$, $J_{3-4}=34$, $J_{6-5}=22$ Hz.

CONCLUSIONS

The reactions of perfluoroisopropyl allyl (I) and perfluoroisopropyl propenyl ethers with SO_3 have been examined. In the presence of B_2O_3, (I) forms perfluoro-γ-isopropoxyallyl fluorosulfate, which is an alkylating agent.

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