ACID FLUORIDES OF PERFLUORO-α,β-UNSATURATED ACIDS

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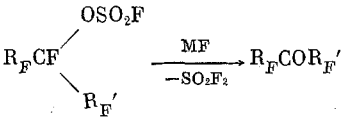
Polyfluoroalkyl fluosulfates are easily cleaved by alkali metal fluorides at the O–S bond to give, depending on the structure of the starting compounds, the corresponding acid fluorides and ketones [1-4].



R_F = F, fluoroalkyl.

At the same time, perfluoroallyl fluosulfate, when treated with CsF in monoglyme, is cleaved at the C–O bond to give perfluoropropylene [5]. It seemed of interest to study the reaction of other $\Delta^{2,3}$-perfluoroalkenyl fluosulfates, the homologs of perfluoroallyl fluosulfate, with alkali metal fluorides.

It proved that the perfluorohexen-2-yl and perfluoro-4-methyl-penten-2-yl fluosulfates [6] when treated with CsF easily form the acid fluorides of the corresponding α,β-unsaturated acids.

$$\underset{\text{(I)}}{R_FCF{=}CFCF_2OSO_2F} \xrightarrow[-SO_2F_2]{CsF} \underset{\text{(II)}}{R_FCF{=}CFCOF}$$

$R_F = n\text{-}C_3F_7$ (Ia), (IIa); $(CF_3)_2CF$ (Ib), (IIb)

The methanolysis of acid fluorides (II) leads quantitatively to esters (III); the same esters can also be obtained in high yield directly from fluosulfates (II) by reaction with MeOH in the presence of CsF.

$$\text{(IIa, b)} \xrightarrow{MeOH} \underset{\text{(IIIa, b)}}{R_FCF{=}CFCOOMe} \xleftarrow[-SO_2F_2]{MeOH/CsF} \text{(Ia, b)}$$

As a result, the cleavage of perfluoroalken-2-yl fluosulfates using either CsF or MeOH/CsF expands the existing methods for the synthesis of fluorinated derivatives of α,β-unsaturated acids [7-19].

EXPERIMENTAL

The ^{19}F NMR spectra were taken on a Perkin-Elmer R-32 NMR spectrometer (84.6 MHz) using CF_3COOH as the external standard (Table 1). The IR spectra were taken on a UR-20 spectrophotometer.

Reaction of Fluosulfates (I) with CsF. A mixture of 10.5 g (0.0276 mole) of (Ia) and 6 g (0.0395 mole) of freshly ignited CaF was heated at 50-80°C for 1 h, the volatile products were distilled off at 12 mm, and the distillate was distilled to give 5.9 g (78%) of acid fluoride (IIa), bp 79-80°. Found: C 25.90; F 68.25%. $C_6F_{10}O$. Calculated: C 25.89; F 68.34%. Infrared spectrum (ν_{max}, cm^{-1}): 1691 w (C=C), 1842 s (C=O). In a similar manner, from (Ib) and CsF we obtained acid fluoride (IIb) in 83% yield, bp 74-76°. Found: C 25.83; F 68.39%. $C_6F_{10}O$. Calculated: C 25.89; F 68.34%. Infrared spectrum (ν_{max}, cm^{-1}): 1693 w (C=C), 1838 s (C=O).

Reaction of Fluosulfates (I) with MeOH and CsF. To a solution of 5.2 g (0.0137 mole) of (Ia) in 11 ml of MeOH was gradually added 2.4 g (0.0158 mole) of freshly ignited CsF and,

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TABLE 1. ^{19}F NMR Spectra of Compounds (II, b) and (IVa, b)

Compound	δ, m.d, J, Hz
$CF_3CF_2CF_2CF=CFCOF$ (1 2 3 4 5 6)	δ_1=4,9 t (3F), δ_2=51,8 d.d (2F), δ_3=42,9 d.d.q (2F) δ_4=63,7 d.d.m (1F), δ_5=78,8 d.d.t.t (1F), δ_6=−103,6 d.d (1F); J_{1-3}=8,5, J_{2-4}=5,6, J_{2-5}=8, $J_{3,4}$=8,5, J_{3-5}=27,3, $J_{4,5}$=135,6, J_{4-6}=56,5, J_{5-6}=20,7
$CF_3CF_2CF_2CF=CFCOOMe$ (1 2 3 4 5)	δ_1=4,9 t (3F), δ_2=52,0 d.d (2F), δ_3=42,2 d.d.q (2F), δ_4=72,7 d.m (1F), δ_5=74,9 d.t.t (1F); J_{1-3}=9, $J_{3,4}\cong$ $\cong$8, $J_{2-4}\cong$8, $J_{2-5}\cong$7, J_{3-5}=23,5, $J_{4,5}$=139
$(CF_3)_2CFCF=CFCOF$ (1 2 3 4 5)	δ_1=−1,1 d.d.d (6F), δ_2=110,7 d.d. hept (1F), δ_3= =62,4 d.d.d, hept(1F), δ_4=77,4 d.d.d. hept(1F), δ_5= =−103,3 d.d (1F); $J_{1,2}$=6, J_{1-3}=8,4, J_{1-4}=5,6, J_{2-3}= =10,3, J_{2-4}=48, $J_{3,4}$=139, J_{3-5}=56,5, $J_{4,5}$=22,6
$(CF_3)_2GFCF=CFCOOMe$ (1 2 3 4)	δ_1=−1,2 d.d.d (6F), δ_2=109,4 d.d.hept (1F), δ_3= =71,3 d.d.hept (1F), δ_4=75 d.d.hept (1F); $J_{1,2}$=8,3, J_{1-3}=8,3, J_{1-4}=6,7, $J_{2,3}$=8,3, J_{2-4}=46, $J_{3,4}$=139

at the end of gas evolution, the mixture was refluxed for 5-8 min, poured into water, and the oil was separated, dried over $MgSO_4$, and distilled to give 3.3 g (83%) of ester (IIIa), bp 130-131°. Found: C 28.95; H 1.08; F 58.90%. $C_7H_3F_9O_2$. Calculated: C 28.96; H 1.03; F 58.96%. Infrared spectrum (ν_{max}, cm^{-1}): 1694 w (C=C), 1753 s (C=O). In a similar manner, from (Ib), MeOH and CsF we obtained ester (IIIb) in 85% yield, bp 124-126°. Found: C 28.88; H 1.08; F 59.00%. $C_7H_3F_9O$. Calculated: C 28.96; H 1.03; F 58.96%. Infrared spectrum (ν_{max}, cm^{-1}): 1695 w (C=C), 1756 s (C=O).

CONCLUSIONS

The perfluorohexen-2-yl and perfluoro-4-methylpenten-2-yl fluosulfates are cleaved by CsF to give the acid fluorides of the corresponding perfluoro-α,β-unsaturated acids.

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