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REACTIONS OF HEXAFLUOROPROPENE OLIGOMERS WITH CARBOXYLATE ANIONS

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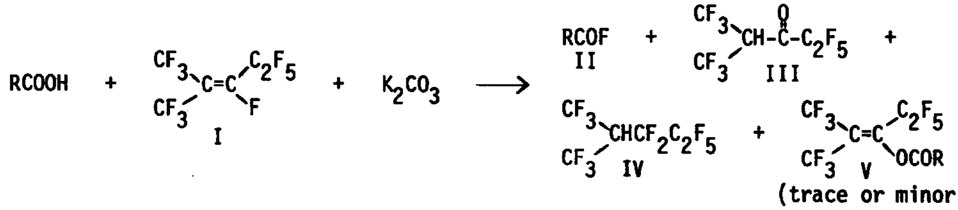
Various reactions of cyclic and acyclic perfluoroalkenes with strong nucleophiles such as phenolate[1,2] and alkoxide ions[3,4] and amines[5] have been widely investigated.[6-8] We have now found that carboxylate anions, which are rather weak nucleophiles, also react with perfluoro-2-methyl-2-pentene(I), a dimer of hexafluoropropene,[9] in an aprotic polar solvent(DMF, DMSO, acetone or acetonitrile), giving acid fluorides(II) in fair to good yields with the formation of the ketone(III), the HF addition product(IV) and the esters(V) as follows(Table 1);



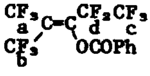
The acid fluorides(II) were confirmed by ir(1810-1850 cm^{-1}) and mass spectra, and the ketone (III), the addition product(IV) and the esters(V) were isolated respectively by the preparative glpc(Silicone SE-30 10% on Diasolid L(60-80 mesh), 4 mm x 1.5 m) and spectroscopically identified; III,[10] ir(NaCl cell 0.025 mm): 1770 cm^{-1}(C=O); ^1H-nmr(acetone, ppm(TMS)): 6.24 (septet); ^{19}F-nmr($CF_2ClCFCl_2$, 50% as a mixture with IV, ppm($CFCl_3$)), $(\underset{a}{CF_3})_2CHCO\underset{c}{CF_2}\underset{b}{CF_3}$: 64.3(a, 6F, doublet of multiplet), 82.8(b, 3F, multiplet), 123.5(c, 2F, multiplet), J_{FaH}=7.5 Hz; mass (m/e(rel int.)(fragmentation)): 179(100)(M-C_2F_5), 159(26)(M-HF-C_2F_5), 147(11)(M-C_3F_6H), 119(15) (C_2F_5), 113(6)(C_3F_4H), 91(8)(C_3F_2HO), 69(17)(CF_3). IV, ir(NaCl cell 0.025 mm): 2950 cm^{-1}(C-H) ^1H-nmr(acetone, ppm(TMS)): 5.56(triplet of septet); ^{19}F-nmr($CF_2ClCFCl_2$, 50%, ppm($CFCl_3$)), $(CF_3)_2CHCF_2CF_2CF_3$: 62.6(a, 6F, multiplet), 81.4(b, 3F, triplet), 112.7(c, 2F, multiplet), 126.4 (d, 2F, multiplet), J_{FaH}=7.5 Hz, J_{ac}=J_{bd}=12.5 Hz, J_{FdH}=12 Hz, J_{ab}=J_{bc}≃0 Hz; mass(m/e(rel int.) (fragmentation)): 301(3)(M-F), 281(5)(M-HF-F), 231(3)(M-HF-CF_3), 213(12)(M-CF_4-F), 201(10) (M-C_2F_5), 193(1)(M-CF_4-HF), 181(23)(M-HF-C_2F_5), 169(10)(C_3F_7), 163(3)(M-C_2F_6-F), 143(1.5)(C_4F_5), 131(1)(C_3F_5), 119(3)(C_2F_5), 113(19)(M-CF_4-C_2F_5), 100(3)(C_2F_4), 93(4)(C_3F_4), 69(100)(CF_3). V(R=Ph), ir(neat): 1775 cm^{-1}(C=O), 1665 cm^{-1}(C=C); ^{19}F-nmr($CF_2ClCFCl_2$, 50% as a mixture with PhCOF, ppm($CFCl_3$)),  $(\underset{a}{CF_3})(\underset{b}{CF_3})C{=}C(\underset{d}{CF_2}\underset{c}{CF_3})(OCOPh)$: 57.2(a, 3F, multiplet), 61.5(b, 3F, quartet of triplet),

Table 1. Preparation of Acid Fluorides(II) with Perfluoro-2-methyl-2-pentenein Aprotic Polar Solvents

Carboxylic Acids	Solvent	Reaction Time(hr) a)	Yield (%) b)	By-products Identified
C_6H_5COOH	Acetone	5	35	III, V(R=Ph), VI
	Acetone	c)	46d)	
	DMSO	6	58	
$CH_3(CH_2)_{10}COOH$	Acetonitrile		59	III, IV(trace), VI
	DMF	3	70	V(R=$C_{11}H_{23}$)
$CH_3(CH_2)_4COOH$	Acetone	3	50	III, V(R=C_5H_{11})
	Acetonitrile	3	81	III, V(R=C_5H_{11})
CH_3CH_2COOH	Acetonitrile	3	e)	
	DMF	3	e)	
$C_6H_5CH=CHCOOH$	Acetone	3	23	
$HOOCCH_2CH_2COOH$	Acetonitrile	2	25	III, IV, Succinic Anhydride
$C_7F_{15}COOH$	Acetone	6	0f)	

a). Reaction temp., r.t.~60°C. b). Crude yields. c). Until the peak due to the ester V(R=Ph) disappeared. d). Glpc yield. e). Identified by ir. f). The potassium salt was recovered.

Table 2. Phase-transfer Reactions of Hexafluoropropene Dimer[a)] or Trimers[b)] with Carboxylate Anions

Carboxylic c) Acid(mole)	Solvent (ml)	Phase-transfer Catalyst(g)(mole%) d)	Reaction time(hr)	Yields(%) e) II	V & VII	Total
C_6H_5COOH (0.01)	CH_2Cl_2 (30 ml)	$(C_8H_{17})_3NCH_3Cl$ (0.45 g)(11 %)	2	39	48	87
"	"	18-crown-6 (0.45 g)(17 %)	8	57	35	92
"	"	"	47	56	36	92
"	"	18-crown-6 (1.0 g)(38 %)	24	81	13	94
p-$NO_2C_6H_4COOH$ (0.01)	"	18-crown-6 (0.5 g)(18 %)	24	f)		
n-$C_5H_{11}COOH$ (0.02)	CH_2Cl_2 (50 ml)	18-crown-6 (0.8 g)(15 %)	8	ca,61	ca.9	
CH_3COOH (0.03)	C_6H_6 (50 ml)	18-crown-6 (0.5 g)(18 %)	12	g)		
C_6H_5COOH b) (0.01)	C_6H_6 (30 ml)	18-crown-6 (0.5 g)(18 %)	8	14	g)	
C_6H_5COOH b) (0.01)	CH_2Cl_2 (30 ml)	18-crown-6 (0.5 g)(18 %)	8	29	g)	
n-$C_7F_{15}COOH$	CH_2Cl_2	18-crown-6	24	no reaction h)		

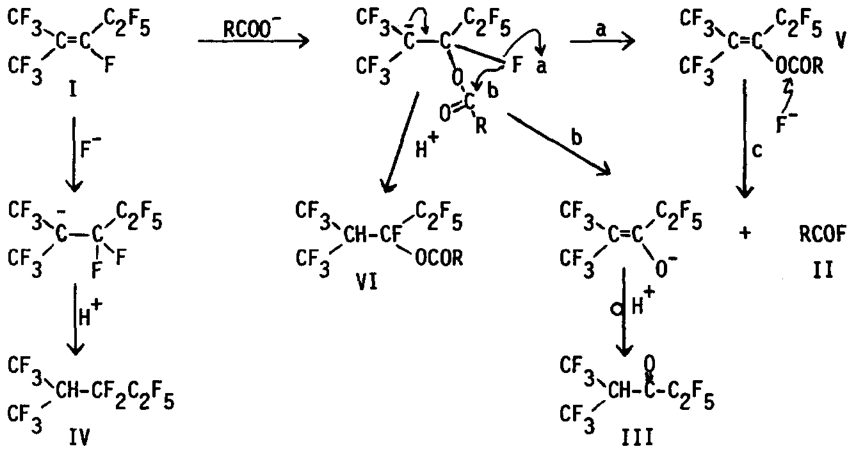
a). Perfluoro-2-methyl-2-pentene was used. b). The mixture of the trimers was used.[13)] c). Mole ratios acid:oligomer:K_2CO_3=1:1:0.5. d). Based on acid or oligomer. e). Determined by glpc of the distillate. f). The mixture of the acid fluoride(II, R=p-$NO_2C_6H_5$) and the ester(V, R=p-$NO_2C_6H_5$)(1.5 g) was isolated(II/V=2~3). h). The potassium salt was recovered.

82.5(c, 3F, quartet of triplet), 115.4(d, 2F, quartet of septet), J_{ad}=22 Hz, J_{ab}=11 Hz, J_{ac}=5 Hz, J_{bd}=2 Hz, J_{bc}≃0 Hz, J_{cd}=2 Hz; mass(m/e(rel int.)(fragmentation)): 402(0.1)(M), 383(0.6)(M-CF_3), 262(0.2)(M-$C_6H_5CO_2$-F), 181(0.3)(C_4F_7), 169(6)(C_3F_7), 124(6)(C_6H_5F), 77(55)(C_6H_5), 69(8)(CF_3), 51(22)(CF_2H), 50(6)(CF_2), 44(1.5)(CO_2), 28(4)(CO).

The reaction with succinic acid in acetonitrile gave not only succinyl difluoride but also succinic anhydride and the addition product(IV) was formed in preference to the ketone(III).

Generally the crude acid fluorides thus obtained darken on long standing. Further it was ascertained by glpc analysis that acetone reacts slowly with the dimer(I) in the presence of K_2CO_3[11,12] and that the ester(IV, R=Ph) once formed undergoes further reaction in acetone,[12] giving the unidentified products having the larger retention volume of glpc(The silicone SE-30 column). To avoid these undesirable and ambiguous side reactions in aprotic polar solvents, the reaction was carried out in dichloromethane or benzene using a phase-transfer catalyst. Without phase-transfer catalysts, no reaction was observed. However, the addition of 18-crown-6 or trioctylmethylammonium chloride caused a gradual reaction, yielding the acid fluorides(II) and the esters V(major) and VI(trace) with the deposition of potassium fluoride and potassium hydrogenfluoride(Table 2). The ester VI(R=Ph) was speculated on the basis of mass and ir spectra; mass(m/e(rel int.)(fragmentation): 422(1)(M), 402(12)(M-HF), 383(1)(M-HF-F), 333(4)(M-CF_4-H), 281(1)(M-$C_6H_5CO_2$-HF), 181(6)(C_4F_7), 124(10)(C_6H_5COF), 119(1)(C_2F_5), 105(100)(C_6H_5CO), 96(6)(C_6H_5F), 77(33)(C_6H_5), 69(17)(CF_3), 51(12)(CF_2H), 50(5)(CF_2), 44(9)(CO_2), 28(8)(CO); ir(neat): 1770 cm^{-1}. It should be noted that at the biginning of the reaction, the reaction mixture constitutes a tri-phase, e.g. the perfluoroalkene(II), potassium carbonate or benzoate, and the solvent.

The overall reactions above-mentioned can be depicted as follows;



In the reaction of potassium benzoate using 18-crown-6 in dichloromethane, neither the prolonged reaction time nor the presence of additional potassium fluoride enhanced the yield of benzoyl fluoride(See Table 2). However, when the amount of 18-crown-6 was doubled, the yield increased to 81%. These facts imply that the acid fluorides may be formed via the path b rather than the path c.

When a mixture of the trimers of hexafluoropropene13) was reacted with potassium benzoate under the comparable conditions, benzoyl fluoride and the corresponding ester(V) were also formed, although the yields were low.14)

Potassium perfluorooctanoate did not react neither in acetone nor in dichloromethane-18-crown-6 system.

These reactions are the first examples to use the perfluoroalkenes as fluorinating agents and provide a facile preparation of aliphatic and aromatic acid fluorides.

References and Footnotes

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6) R. D. Chambers and R. H. Mobbs, "Advances in Fluorine Chemistry", vol. 4., M. Stacey, J. C. Tatlow and A. G. Sharpe, ed., Butterworths, Washington, D. C., 1965, p63.
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9) Hexafluoropropene dimerizes in acetonitrile in the presence of KF, giving perfluoro-2-methyl-3-penetene, which undergoes isomerization to perfluoro-2-methyl-2-pentene(I) by reflux in sulforane in the presence of KF; N. Ishikawa and T. Mizuno, Japan Kokai, 49-134,614(1974), T. Mizuno, N. Ishikawa and S. Nakamura, Japan Kokai, 50-117,705(1975).
10) Martini has recently reported that the ketone III produces by the reaction of I with water in the presence of triethylamine followed by treatment with mineral acids. T. Martini, J. Fluorine Chem., 8, 535(1976).
11) The lower yields in acetone(See Table 1) might be partly due to this side reaction.
12) The reaction via the enolate anion, $CH_2=C(CH_3)O^-$, is conceivable.
13) The composition was established as follows; I'a: $(CF_3)_2C=C(C_2F_5)CF(CF_3)_2$, I'b: $CF_3CF=C[CF(CF_3)_2]_2$, I'c: $(CF_3)_2CFCF=C(CF_3)(C_3F_7)$(cis and trans)(minor). S. P. v. Halasz, K. Kluge and T. Martini, Chem. Ber., 106, 2950(1973), T. Martini and S. P. v. Halasz, Tetrahedron Lett., 1974, 2129.
14) The low yields might be attributable to the lower electrophilicity of the trimers I'a and I'b than the dimer I. N. Ishikawa and J. Maruta and S. Hayashi, The 34th National Meeting of the Chemical Society of Japan, Hiratsuka, April, 1976, 2C08.

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