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SHORT COMMUNICATION

Diacyl Perfluoroesters

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Recently, the condensation of fluoroacetones with oxalyl fluoride and potassium fluoride in a heated pressure reactor was shown to lead to 2,2-di(fluoroalkyl)-5,5-difluoro-1,3-dioxolan-4-ones [1]. With perfluorodiacyl fluorides, the possibility then existed that higher ring systems could be formed under similar conditions. Since potassium heptafluoroisopropoxide might also be present [2], it was conceivable that perfluoroesters would be prepared instead, especially in view of the recent report of perfluoromonoacyl heptafluoroisopropoxide esters [3].

With these considerations in mind, 2-2-difluoropropanedioyl fluoride, 2,2,3,3-tetrafluorobutanedioyl fluoride, 2,2,3,3,4,4-hexafluoropentanedioyl fluoride, 3-oxa-2,2,4,4-tetrafluoropentanedioyl fluoride, and 4-oxa-2,2,3,3,5,5,6,6-octafluoroheptanedioyl fluoride were heated in separate reactions with hexafluoroacetone and potassium fluoride in a Hoke stainless steel reactor. No ring compounds were noted; instead, varying yields of mono- and di-heptafluoroisopropoxide esters were formed. Separation of

the products from the excess potassium fluoride was achieved as soon as possible by immediately cooling the heated reactor with liquid nitrogen and allowing the products to vaporize into cooled traps. No attempt was made to examine the temperature effects on the yields or products. All of the products had the characteristic carbonyl absorption at about 5.40μ in the infrared spectra and the expected ^{19}F NMR pattern at 142.5 Ø* for the methine fluorine [3].

$$FOC(CF_2)_nCOF \xrightarrow[CF_3COCF_3]{\Delta/KF} FOC(CF_2)_nCO_2CF(CF_3)_2 + (CF_2)_n[CO_2CF(CF_3)_2]_2$$

For	n=1	I	II
	n=2	III	IV
	n=3	V	VI

$$O[(CF_2)_nCOF]_2 \xrightarrow[CF_3COCF_3]{\Delta/KF} FOC(CF_2)_nO(CF_2)_nCO_2CF(CF_3)_2 + O[(CF_2)_nCO_2CF(CF_3)_2]_2$$

For	n=1	VII	VIII
	n=2	IX	X

The temperature involved in this study, i.e. $>100°$, was above that at which potassium heptafluoroisopropoxide has been reported to be completely decomposed[4]. Further, the reactions leading to the alkali metal salts of fluoroalkoxides are described to be possible only in a solvent [5]. Evidently, confinement in a pressure reactor established the adduct equilibrium sufficiently so that ester formation could take place.

EXPERIMENTAL

^{19}F NMR spectra were recorded on a Varian V-4300-2 spectrometer at 40.0 MHz utilizing fluorotrichloromethane as solvent and internal standard. The infrared spectra were measured on a Perkin-Elmer Model 21 and product analyses and separations were carried out on a Perkin-Elmer Model 154 gas chromatograph employing a 12 ft by 3/8 in column packed with 33% FS-1265 on Chrom P. The fluoro intermediates used along with appropriate references are summarized as follows: hexafluoroacetone, 2,2,3,3-tetrafluorobutanedioic acid and 2,2,3,3,4,4-hexafluoro-

TABLE I

Infrared and Analytical Properties of Fluoroesters

Compd.	Yield %	IR	%C		%F	
		C=O (μ)	Calc.	Found	Calc.	Found
I	10	5.30 5.42	23.3	23.1	61.3	61.5
II	3	5.38	22.7	22.6	63.9	63.7
III	10	5.26 5.38	23.3	23.6	63.3	62.8
IV	64	5.38	22.8	22.6	65.0	64.9
V	78	5.30 5.40	23.4	23.5	64.9	64.6
VI	10	5.39	22.9	22.8	66.0	66.0
VII	42	5.30 5.40	22.3	22.3	60.6	60.2
VIII	4	5.40	22.1	22.1	63.1	62.6
IX	90	5.34 5.42	22.7	22.5	63.9	63.5
X	5	5.42	22.4	22.3	65.1	64.9

pentanedioyl fluoride (PCR, INC.), 3-oxa-2,2,4,4-tetrafluoropentanedioyl fluoride [6], 4-oxa-2,2,3,3,5,5,6,6-octafluoroheptanedioyl fluoride [7] and 2,2-difluoropropanedioyl chloride [8]. The application of known procedures led to the acyl fluorides where necessary. Analytical and spectral data for these new fluoroesters are tabulated in Tables I and II.

TABLE II

NMR Spectra of Fluoroesters

Compd	Ø*	Group	Coupling[a]	Ø*	Group	Coupling[a]
I	-20.3	COF	t,J=10.1	142.3	CF	m[b],J=2.4
	111.5	CF_2	d,J=10.1	79.2	CF_3	d,J= 2.4
II	111.4	CF_2	s	142.2	CF	m[b]
				79.2	CF_3	broad
III	-23.8	COF	m	142.2	CF	m[b],J=2.0
	118.7;119.2	CF_2	m;m	79.1	CF_3	d,J=2.0
IV	118.5	CF_2	s	142.3	CF	m[b],J=2.1
				79.1	CF_3	d,J= 2.1
V	-24.0	COF	m[c],J=5.7	142.6	CF	m[b],J=2.1
	118.0;123.4	CF_2	s	79.2	CF_3	d,J=2.1
VI	118.0;123.2	CF_2	s	142.7	CF	m[b],J=1.9
				79.3	CF_3	d,J=1.9
VII	-13.0	COF	m	142.5	CF	m[b],J=2.0
	76.7;77.3	CF_2	m	79.0	CF_3	d,J=2.0
VIII	77.4	CF_2	s	142.8	CF	m[b],J=1.9
				79.2	CF_3	d,J=1.9
IX	-23.5	COF	t,J=8.3	142.3	CF	m[b],J=1.9
	85.6;121.3;, 121.6	CF_2	m	79.2	CF_3	d,J=1.9
X	85.3;121.2	CF_2	m	142.3	CF	m[b],J=1.9
				79.2	CF_3	d,J=1.9

[a] in Hertz [b] 7-fold [c] 5-fold

General Procedures - All of the reactions were carried out in essentially the same manner by heating a slight excess of perfluoroacetone with the perfluorodiacyl fluoride and a three fold excess of dried potassium fluoride in a preevacuated Hoke stainless steel reactor at 120° to 150° for ca. 16 hr. After immediate cooling, the products were allowed to vaporize into two evacuated traps connected in series in a standard vacuum line, cooled to -40° and -196°, respectively, as the temperature of the reactor rose from -196° to 150°C. Isolation of the pure compounds was achieved from the product mixtures in the -40° trap by glpc techniques. It should be noted that the yields of the products obtained. I to X (all nc), were highly variable.

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