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THE PERFLUORO-t-BUTANOL DERIVATIVES OF PHOSPHORYL CHLORIDE

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SUMMARY

The reaction of phosphoryl chloride with sodium perfluoro-t-butoxide gives
the new compounds $OP(OC_4F_9)Cl_2$ and $OP(OC_4F_9)_2Cl$, which have been isolated and
characterized by infra-red and mass spectrometric techniques.

INTRODUCTION

The perfluorinated aromatic esters of phosphoryl halides [1,2] and
phosphoric acid [3,4] are known. Although the partially fluorinated alkyl
phosphate esters tris(2,2,2-trifluoroethyl)phosphate and
tris(3,3,3,2-pentafluoropropyl) phosphate have been successfully prepared
[5,6], no fully fluorinated alkyl phosphate esters have been reported. Because
primary perfluoroalcohols are unstable, it is not possible to use them for the
synthesis of phosphorus esters. However, as the trifluoromethoxides are
slightly stable [7], it is possible that tris(trifluoromethyl) phosphate could
be prepared. The tertiary alcohol, perfluoro-t-butanol, forms a stable alkoxide
[8].

    This paper describes the substitution reactions of $t-C_4F_9O$ Na with $POCl_3$ to
form $(t-C_4F_9O)POCl_2$ and $(t-C_4F_9O)_2POCl$ and also reports an attempt to prepare
the phosphate $OP(OC_4F_9)_3$.

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EXPERIMENTAL

General

Reactants and products were transferred under vacuum for weighing
and spectral studies. Operations not done under vacuum were carried out in a
dry glove box. Infra-red spectra were recorded on a Perkin-Elmer 225
spectrometer using 10 cm gas cells fitted with either AgCl or KBr windows and
PTFE valves. Mass spectra were recorded at 70 eV on AEI MS3 and AEI MS9 mass
spectrometers. For the determination of metastable peaks, the latter was
operated at a source temperature of 50°C.

Reagents

Perfluoro-t-butanol (PCR Research Chemicals Inc.) and phosphoryl
chloride (BDH Chemicals) were distilled under vacuum prior to use. Particular
attention was paid to removing HCl from the POCl$_3$. Sodium perfluoro-t-butoxide
was prepared by the method of Dear *et al.* [9]. Samples of this salt were
transferred to weighed reaction tubes and resublimed under dynamic vacuum before
re-weighing.

Preparation of perfluoro-to-butoxy phosphoryl dichloride

In a typical reaction, 1 mmol (153 mg) of phosphoryl chloride was distilled
on to 1 mmol (258 mg) of sodium perfluoro-t-butoxide in an evacuated tube fitted
with a PTFE valve. The mixture was refluxed at 90°C for 30 minutes. Vacuum
distillation at -10°C gave 213 mg (65% yield) of (t-C$_4$F$_9$O)POCl$_2$. The remaining
volatile liquid appeared to be the disubstituted compound (t-C$_4$F$_9$O)$_2$POCl and a
small amount of (t-C$_4$F$_9$O)POCl$_2$. In the temperature range -8 to 22°C,
(t-C$_4$F$_9$O)POCl$_2$ has a vapour pressure defined by the equation $\log_{10} P_{(Pa)} =$
$- \dfrac{1909}{K} + 9.66$. The compound was characterized by mass spectrometry and
infra-red spectroscopy. Maintenance of a good vacuum during preparation and
handling was essential owing to the extreme sensitivity of this compound to
moisture. Hydrolysis produces the parent alcohol which is readily detected by
its characteristic infra-red absorptions at 3620 and 955 cm^{-1}.

Preparation of bis(perfluoro-t-butoxy phosphoryl chloride)

2.63 mmol (680 mg) of t-C$_4$F$_9$O Na and 1.2 mmol (184 mg) of phosphoryl
chloride were refluxed in an evacuated tube for 30 minutes. After pumping under
vacuum for five minutes at -10°C to remove traces of (t-C$_4$F$_9$O)POCl$_2$, 210 mg (31%
yield) of (t-C$_4$F$_9$O)$_2$POCl were distilled off. A white non-voltile residue (apart
from NaCl) remained. The vapour pressure of (t-C$_4$F$_9$O)$_2$POCl was 467 Pa at 22°C.
This compound also hydrolyzes rapidly in air.

Attempted preparation of tris(perfluoro-t-butyl)phosphate

The disubstituted compound $(t-C_4F_9O)_2POC\ell$ was heated at $150^\circ C$ for 72 hours with a large excess of $t-C_4F_9O$ Na. However, this procedure failed to produce a compound with the expected volatility, and a white non-volatile residue remained. Infra-red spectroscopy showed this to be identical with the residue observed in the preparation of the disubstituted compound.

RESULTS AND DISCUSSION

Mass Spectra

$(t-C_4F_9O)POC\ell_2$

Ion fragments and their relative intensities are shown in Fig.1. In common with phosphoryl chloride [10], the most abundant ion in the spectrum is m/e 117, corresponding to $OP^{35}C\ell^{35}C\ell$. For ions containing two chlorine atoms, the characteristic chlorine isotope pattern of 100:65:10 was observed. Metastable ions and the probable processes by which they originate are summarized in Table 1.

Metastable ions indicate the following pathways of fragmentation of the molecular ion m/e 352 :

(i) The loss of a CF_3 radical to give the 283 amu ion.

(ii) Loss of $C\ell^\cdot$ to give the 317 amu ion, which then loses the neutral fragment $OPF_2C\ell(120)$ to give the 197 amu ion (a metastable ion exists for the latter process).

(iii) A rearrangement process in which a $CF_3\cdot$ migrates to the phosphorus atom with subsequent elimination of $C_3F_6O(166)$ to give the 186 amu ion.

(iv) Loss of $F^\cdot$ to form the 333 amu ion which then rearranges with transfer of a CF_2 to the phosphorus atom, followed by elimination of the neutral fragment $C_3F_6O(166)$, (a metastable ion exists for the latter process).

Using the processes suggested in Table 1 for the metastable transitions, the decomposition scheme shown in Fig.1 is proposed, in which metastable transitions are indicated by an asterisk.
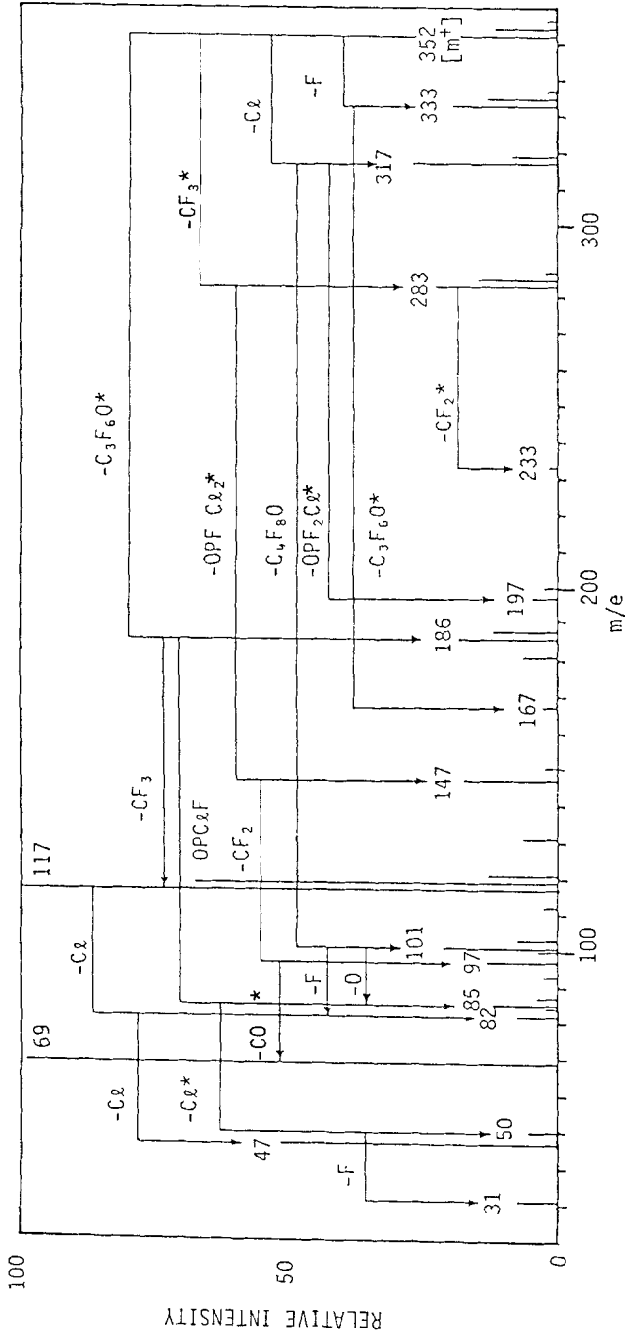
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Fig. 1. The 70 eV mass spectrum of Perfluoro-t-butoxy phosphoryl dichloride

$(t-C_4F_9O)_2POC\ell$

Ion fragments and their relative intensities are shown in Fig.2, and metastable ions and probable processes are listed in Table 2. The most intense ion is m/e 69(CF$_3$).

The fragmentation pattern of this compound shows that of the five processes by which the molecular ion m/e 552 fragments, four are similar to those observed for the mon-compound with respect ot the neutral fragment eliminated or the rearrangement involved.

TABLE 1

Metastable Peaks (amu)	
227.5, 229.4, 231.4	OPCℓ_2(OC$_4$F$_9$)$^+$(352) ──>OPCℓ_2(OC$_3$F$_6$)$^+$(283)+CF$_3^{\cdot}$(69)
122.5, 121.7	OPCℓ(OC$_4$F$_9$)$^+$(317) ──>C$_4$F$_7$O$^+$(197)+OPF$_2$C$\ell^{\cdot}$(120)
98.3, 99.8, 101.4	OPCℓ_2(OC$_4$F$_9$)$^+$(352) ──>OPCℓ_2CF$_3$(186)+C$_3$F$_6$O$^{\cdot}$(166)
83.8#	OPCℓ_2(OC$_4$F$_8$)$^+$(333) ──>OPCℓ_2CF$_2$(167)+C$_3$F$_6$O$^{\cdot}$(166)
76.4, 75.8, 75.3	OPCℓ_2(OC$_3$F$_6$)$^+$(283) ──>C$_3$F$_5$O$^+$(147)+OPFCℓ_2(136)
191.8, 193.7, 195.7	OPCℓ_2(OC$_3$F$_6$)$^+$(283) ──>OPCℓ_2(OC$_2$F$_4$)$^+$(233)+CF$_2^{\cdot}$(50)
49.1	C$_2$F$_3$O$^+$(97) ──>CF$_3$(69)+CO$^{\cdot}$(28)
29.5#	CF$_2$Cℓ^+(85) ──>CF$_2$(50)+C$\ell^{\cdot}$(35)
and/or	PFCℓ^+(85) ──>PF$^+$(50)+C$\ell^{\cdot}$(35)

#These metastable peaks were of very low intensity and metastable ions for the other isotope combinations were not confirmed.

The following processes are indicated by metastable ions
(i) Loss of neutral CF$_3^{\cdot}$(69).
(ii) Loss of C$\ell^{\cdot}$(35) (the subsequent process has a metastable ion).
(iii) A rearrangement transferring a CF$_3$ to the phosphorus atom with elimination of neutral C$_3$F$_6$O(166).
(iv) The loss of F$^{\cdot}$(the subsequent process has a metastable ion).
The fifth fragmentation of the parent ion not common to the mono-compound involves exchange of Cℓ on the phosphorus atom with a fluorine atom and elimination of C$_4$F$_8$CℓO$^{\cdot}$(251).

As was expected, many of the decompositions of the fragment ions occurred by identical processes observed for the monosubstituted compound. Figure 2 shows a suggested decomposition scheme for the parent molecule ion.
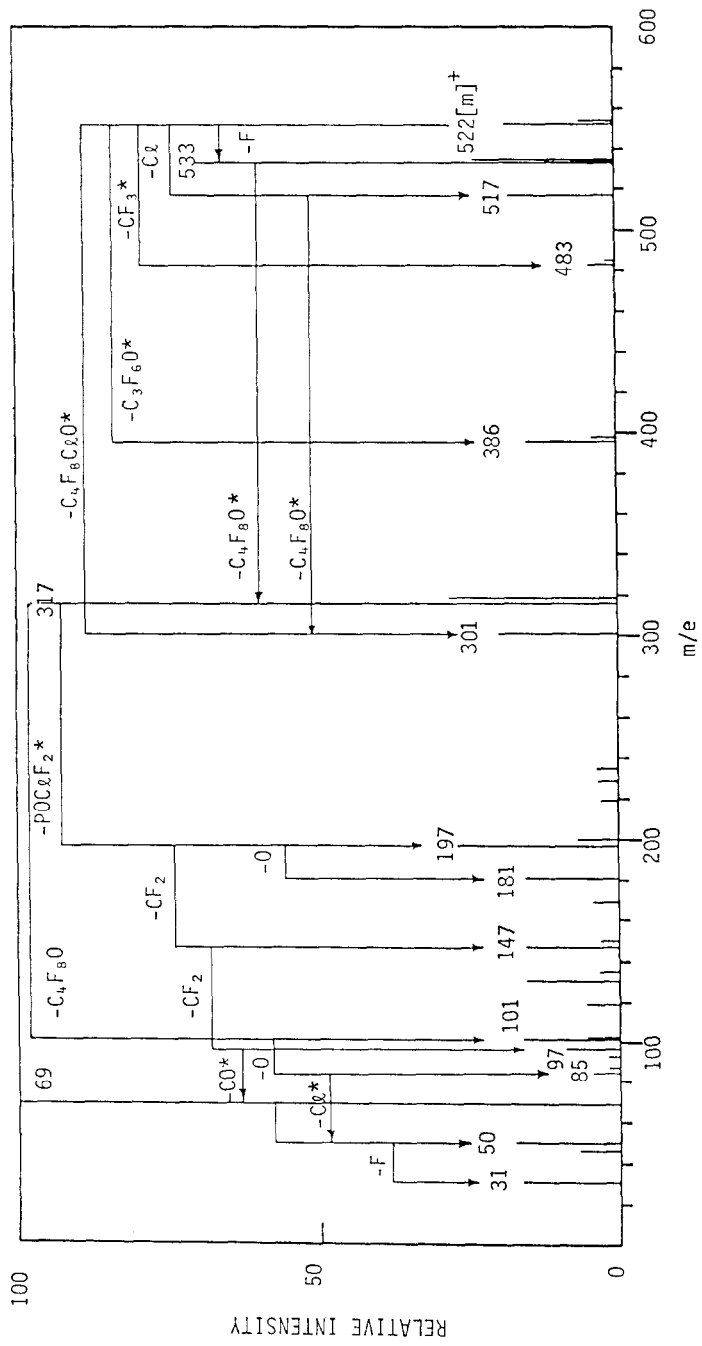
Fig.2 The 70 eV Mass spectrum of bis(perfluoro-t-butoxy)phosphoryl chloride

TABLE 2

Metastable Peaks (amu)	Probable Process
422.6, 424.6	$OPCl(OC_4F_9)_2^+(552) \longrightarrow OP(OC_4F_9)^+(483)+CF_3^{\cdot}(69)$
175.3	$OP(OC_4F_9)_2^+(517) \longrightarrow OPF(OC_4F_9)^+(301)+C_4F_8O^{\cdot}(216)$
269.9, 271.7	$OPCl(OC_4F_9)^+(552) \longrightarrow OPCl(OC_4F_9)(CF_3)^+(386)+C_3F_6O^{\cdot}(166)$
188.4, 190.2	$OPCl(OC_4F_9)(OC_4F_8)^+(533) \longrightarrow OPCl(OC_4F_9)^+(317)+C_4F_8O^{\cdot}(216)$
164.1#	$OPCl(OC_4F_9)_2(552) \longrightarrow OPF(OC_4F_9)^+(301)+C_4F_8ClO^{\cdot}(251)$
122.5, 121.7	$OPCl(OC_4F_9)^+(317) \longrightarrow C_4F_7O^+(197)+POClF_2^+(120)$
49.2	$(C_2F_3O)^+(97) \longrightarrow CF_3^+(69)+CO^{\cdot}(28)$
29.5	$CF_2Cl^+(85) \longrightarrow CF_2^+(50)+Cl^{\cdot}(35)$
and/or	$PFCl^+(85) \longrightarrow PF^+(50)+Cl^{\cdot}(35)$

#The metastable ion for ^{37}Cl species was not detected.

Infra-red-Spectra

The major peaks in the gas phase infra-red spectra of $(t-C_4F_9O)POCl_2$ and $(t-C_4F_9O)_2POCl$ are listed in Table 3. Data for phosphoryl chloride [11] and the parent alcohol [12] have been included for comparison.

The most notable differences with the spectra of the parent alcohol $t-C_4F_9OH$ and phosphoryl chloride ($POCl_3$) are the absence of the 955 cm^{-1} ν_s (skel) vibration from the alcohol and the appearance of P=O stretches at 1343 cm^{-1} and 1361 cm^{-1} for the monosubstituted and disubstituted compounds.

Both compounds exhibit a strong absorption at 613 cm^{-1} attributable to the P-Cl stretch. Absorptions at 1145 cm^{-1} for $(t-C_4F_9O)POCl_2$ and 1178 cm^{-1}(w) and 1127 cm^{-1}(s) for $(t-C_4F_9O)_2POCl$ are due to CF_3 vibrations. C-F stretching occurs at 1203-1310 cm^{-1} for both compounds, the same range as that observed in theparent alcohol. The absorptions at 892 and 915 cm^{-1} are probably due to P-O-C vibrations. Similar absorptions have been observed for the compounds $(t-C_4F_9O)VOCl_2$ and $(t-C_4F_9O)_2VOCl$ [13]. Additionally, neither the free alcohol nor the oxide halides $POCl_3$ and $VOCl_3$ exhibit absorptions in the 800-950 cm^{-1} region.

The non-volatile product observed in the preparation of $(t-C_4F_9O)_2POCl$ and the attempted preparation of $(t-C_4F_9O)_3PO$, has an infra-red spectrum similar to $(t-C_4F_9O)POCl_2$ and $(t-C_4F_9O)_2POCl$ with bands at 986 cm^{-1}(m), 883 cm^{-1}(w) and 736 cm^{-1}(s). Absorptions at 1268 cm^{-1}(s), 1158 cm^{-1}(m) and 610 cm^{-1}(w) are broad with shoulders, unlike similar absorptions in the other compounds which are sharp. The broad absorption at 610 cm^{-1} suggests the presence of bridging O-P-O

TABLE 3

Infra-red Absorption Frequencies

$POC\ell_3[11]$	$(t-C_4F_9O)POC\ell_2$	$(t-C_4F_9O)_2POC\ell$	$t-C_4F_9OH[12]$
1290(s)(P=O)	1343(m)	1361(m)	
	1309(m)	1310(m)	1313(s)
	1286(s)	1285(s)	1288(s)
	1275(s)	1275(s)	1270(s) (CF)
	1203(w)	1203(w)	1260(s)
			1209(w)
	1145(s)	1178(w)	1155(s) ($-CF_3$)
		1127(s)	
	986(s)	988(s)	979)s) (Skel.)
			958(s) (Skel.)
			955(s) (Skel.)
	892(m)	915(m)	
	732(s)	733(s)	730(s) (CF_3)
581(s)(P-Cℓ)	613(s)	613(s)	

bonds [14]. This fact, and its involatility suggest that the compound is polymeric.

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