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Polyfluoroalkyl Dibasic Acid Phosphates, Bis(polyfluoroalkyl) Monobasic Acid Phosphates, and Their Precursors

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The new dibasic acid phosphates $R_fOP(O)(OH)_2$ ($R_f = (CF_3)_2CH$ and $CF_3(CH_3)CH$) and monobasic acid phosphates $(R_fO)_2P(O)OH$ ($R_f = CF_3(CH_3)CH$, $(CF_3)_2CH$, $(CF_3)_2CH_3C$, $CF_3(CH_3)_2C$), as well as new routes to $CF_3CH_2OP(O)(OH)_2$, $(CF_3CH_2O)_2P(O)OH$, and $[H(CF_2)_4CH_2O]_2P(O)OH$, are reported. When heated in the presence of water at 80–100 °C, $(R_fO)_2P(O)OH$ is hydrolyzed to $R_fOP(O)(OH)_2$, which is converted to H_3PO_4 at higher temperatures. The dibasic acid phosphates $R_fOP(O)(OH)_2$ ($R_f = (CF_3)_2CH_3C$, $CF_3(CH_3)_2C$) undergo dehydration to form $[R_fOP(O)(OH)]_2O$. Additionally, the chloro precursors to these acids have been synthesized, including the (polyfluoroalkyl) dichlorophosphinites, R_fOPCl_2 ($R_f = CF_3CH_2$, $CF_3(CH_3)CH$, $(CF_3)_2CH$, $(CF_3)_2CH_3C$, $CF_3(CH_3)_2C$), and bis(polyfluoroalkyl) chlorophosphonites, $(R_fO)_2PCl$ ($R_f = CF_3CH_2$, $(CF_3)_2CH_3C$, $CF_3(CH_3)_2C$). If dinitrogen tetraoxide is used as an oxidant, the former are converted to $R_fOP(O)Cl_2$ and the latter to $(R_fO)_2P(O)Cl$. Lithium polyfluoroalkoxides with PCl_3 give tris(polyfluoroalkyl) phosphites, $(R_fO)_3P$ ($R_f = CF_3(CH_3)CH$, $(CF_3)_2CH_3C$, $CF_3(CH_3)_2C$, CF_3CH_2, $(CF_3)_2CH$), which can be oxidized to $(R_fO)_3PO$ phosphates with N_2O_4. In some cases, $(R_fO)_2PCl$ ($R_f = (CF_3)_2CH_3C$, $CF_3(CH_3)_2C$) gives tetrakis(polyfluoroalkyl) diphosphates, $(R_fO)_2P(O)OP(O)(OR_f)_2$, and $CF_3CH_2OPCl_2$ gives $CF_3CH_2OP(O)(\mu\text{-}O)_2P(O)OCH_2CF_3$. The $(R_fO)_3P$ phosphites ($R_f = CF_3CH_2$, $CF_3(CH_3)CH$, $(CF_3)_2CH_3C$, $CF_3(CH_3)_2C$) undergo Arbuzov rearrangements with Cl_2 to form $(R_fO)_2P(O)Cl$. Hydrogen chloride converts $[CF_3(CH_3)_2CO]_3P$ to $[CF_3(CH_3)_2CO]_2P(O)H$, which with chlorine forms $[CF_3(CH_3)_2CO]_2P(O)Cl$.

Introduction

Very few polyfluoroalkyl acid phosphates have been reported. Since it is likely that these compounds may have characteristics which will make them competitive with phosphoric acid as electrolytes for fuel cells, it was appropriate to synthesize several of them for further testing. To accomplish this goal, it was necessary to synthesize a large number of new materials as precursors to the acid phosphates. This resulted in the syntheses and characterization of bis(polyfluoroalkyl) chlorophosphonites, polyfluoroalkyl dichlorophosphinites, tris(polyfluoroalkyl) phosphites, bis(polyfluoroalkyl) chlorophosphonates, polyfluoroalkyl dichlorophosphinates, tris(polyfluoroalkyl) phosphates and tetrakis(polyfluoroalkyl) pyrophosphates. These materials were then treated as required to form the new mono- and dibasic acid phosphates.

The results obtained when selected compounds are tested to determine their cell characteristics will be reported in due course.

Results and Discussion

Lithium salts of the polyfluorinated alcohols CF_3CH_2OH, $(CF_3)_2CHOH$, $CF_3(CH_3)CHOH$, $(CF_3)_2CH_3COH$, and $CF_3(CH_3)_2COH$ were prepared by the reaction of BuLi and the corresponding alcohols by allowing the mixture to warm from −196 to +25 °C and remain there for about 1 h. Each of the lithium alkoxides is a stable white solid at 25 °C. The reaction of $(CF_3)_2CO$ with NaH in the presence of $Al(C_2H_5)_3$ has been used to form $(CF_3)_2CHONa$.[1] The perfluoro-*tert*-butoxide salt was obtained earlier from the alcohol and an alkali metal (Li, Na, K) or an alkali-metal hydride (LiH, NaH, KH).[2,3]

We have used the lithium salts of the polyfluorinated alcohols in neat reactions with PCl_3 to form polyfluoroalkyl dichlorophosphinites at 25 °C.

$$R_fOLi + PCl_3 \xrightarrow[10\ \text{h}]{-196\ \text{to}\ +25\ °\text{C}} R_fOPCl_2 + LiCl$$

R_f (% yield) = CF_3CH_2 (65), $(CF_3)_2CH$ (60),
$CF_3(CH_3)CH$ (85), $(CF_3)_2CH_3C$ (~100), $CF_3(CH_3)_2C$ (90)

The polyfluoroalkyl dichlorophosphinites were formed preferentially relative to the bis(polyfluoroalkyl)chlorophosphonites and tris(polyfluoroalkyl) phosphites when the R_f group contained a tertiary carbon, e.g., when $R_f = (CF_3)_2CH_3C$ or $CF_3(CH_3)_2C$. When there was an α-secondary or primary carbon present in the R_f group, the yields of the chlorobis(polyfluoroalkyl)phosphites and of the tris(polyfluoroalkyl)phosphites increased, e.g., when $R_f = CF_3(CH_3)CH$, $(CF_3)_2CH$, or CF_3CH_2. Since we did not use a solvent, separation of these compounds was easily accomplished by using trap-to-trap distillation.

Table I. N_2O_4 Oxidation of Dichlorophosphinites

R_f	*T*, °C	*t*, h	yield, %
CF_3CH_2	−45	3	75
$(CF_3)_2CH$	−45	3	75
$CF_3(CH_3)CH$	−45	0.6	81
$(CF_3)_2CH_3C$	−25	24	70
$CF_3(CH_3)_2C$	−25	24	74

Table II. Hydrolyses of Bis(polyfluoroalkyl) Chlorophosphonates

R_f	*T*, °C	*t*, h	yield, %
CF_3CH_2	25	36	89
$CF_3(CH_3)CH$	50	48	85
$(CF_3)_2CH_3C$	65	240	40
$CF_3(CH_3)_2C$	68	72	55

Table III. Hydrolyses of Tris(polyfluoroalkyl) Phosphates

R_f	*T*, °C	*t*, h	yield, %
CF_3CH_2	48	72	82
$(CF_3)_2CH$	25	72	70
$CF_3(CH_3)CH$	75	64	70

Some of these dichloro compounds can also be made by reacting PCl_3 with the respective alcohols at, e.g., −15 °C, but the yields are lower and the product mixture contains the bis(polyfluoroalkyl) chlorophosphonite and the tris(polyfluoroalkyl) phosphite. Even after 36 h all of the PCl_3 is not completely consumed. Moreover, as the temperature of the reaction is increased, the HCl that is formed in the reaction tends to react with $(R_fO)_3P$ via an Arbuzov rearrangement.

$$R_fOH + PCl_3 \rightarrow R_fOPCl_2 + (R_fO)_2PCl + (R_fO)_3P + HCl$$

$$(R_fO)_3P + HCl \rightarrow (R_fO)_2P(O)H + R_fCl$$

However, alcohols, such as $(CF_3)_2CHOH$ and $(CF_3)_2CCH_3OH$, did not react with PCl_3 at 25 °C with or without solvent. Reaction with the former alcohol commenced at 60 °C, but after 7 days at 75–80 °C, the reaction was not complete. However, $(CF_3)_2CHOPCl_2$ was the only product formed. On the other hand, $(CF_3)_2CH_3COH$ did not react with PCl_3 even at 90 °C.

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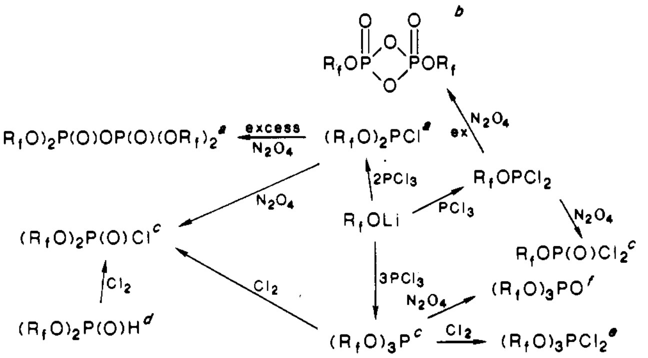
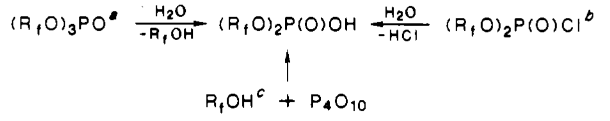
Scheme I



[a] R_f = $(CF_3)_2CH_3C$, $CF_3(CH_3)_2C$. [b] R_f = CF_3CH_2. [c] R_f = CF_3CH_2, $(CF_3)_2CH$, $CF_3(CH_3)CH$, $(CF_3)_2(CH_3)C$, $CF_3(CH_3)_2C$. [d] R_f = $CF_3(CH_3)_2C$. [e] R_f = $(CF_3)_2CH$. [f] R_f = CF_3CH_2, $(CF_3)_2CH$, $CF_3(CH_3)CH$.

Scheme II



[a] R_f = CF_3CH_2, $(CF_3)_2CH$, $CF_3(CH_3)CH$, $H(CF_2)_4CH_2$. [b] R_f = CF_3CH_2, $(CF_3)_2CH_3C$, $CF_3(CH_3)_2C$, $CF_3(CH_3)HC$. [c] R_f = CF_3CH_2.

There are a variety of methods reported for the preparation of alkyl dichlorophosphinites.[4,5]

$$2PCl_3 + (RO)_3P \rightarrow 3ROPCl_2$$

$$R = n\text{-}C_4H_9,\ C_8H_{17},\ C_6H_5$$

Although dialkyl chlorophosphonites and alkyl dichlorophosphinites have been known for a long time, only one fluorinated analogue has been reported.[6-8] Trialkyl phosphites can be isolated in systems where HCl is formed when the latter is allowed to escape.[4,7,9,10] The first reported example of a tris(polyfluoroalkyl) phosphite was $(CF_3CH_2O)_3P$.[11]

$$3R_fCH_2OH + PCl_3 \xrightarrow[4\ h]{80-90\ °C} (R_fCH_2O)_3P + 3HCl\uparrow$$

$$R_f = CF_3,\ C_3F_7$$

Just as is the case for $(RO)_3P$,[7,9] $(CF_3CH_2O)_3P$ can be reacted with bromine.[11]

$$(CF_3CH_2O)_3P + Br_2 \rightarrow (CF_3CH_2O)_2P(O)Br + CF_3CH_2Br$$

In this work, we have reacted tris(polyfluoroalkyl) phosphites with chlorine

$$(R_fO)_3P + Cl_2 \rightarrow (R_fO)_2P(O)Cl + R_fCl$$

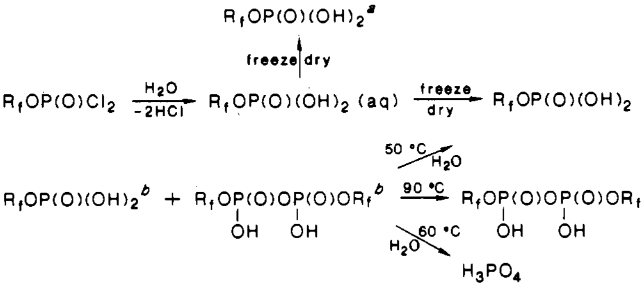
$$R_f = CF_3CH_2,\ CF_3(CH_3)CH$$

but when R_f = $(CF_3)_2CH_3C$ or $CF_3(CH_3)_2C$, the chloroalkane is unstable with respect to loss of HCl and olefin formation.

$$(CF_3)_2CH_3CCl \rightarrow (CF_3)_2C{=}CH_2 + HCl$$

$$(CF_3)(CH_3)_2CCl \rightarrow (CF_3)(CH_3)C{=}CH_2 + HCl$$

Scheme III



[a] R_f = CF_3CH_2, $(CF_3)_2CH$, $CF_3(CH_3)CH$. [b] R_f = $(CF_3)_2CH_3C$, $CF_3(CH_3)_2C$.

It is interesting to note that oxidative addition of chlorine to $((CF_3)_2CHO)_3P$ gave a stable dichlorophosphorane;[12,13] i.e., Arbuzov rearrangement did not occur even after 12 h at 60 °C. The stability of the dichlorophosphorane is enhanced by the greater electronegativity of the $(CF_3)_2CHO$ group when compared with the other polyfluoroalkoxy groups examined.[13]

The method described in the literature for the preparation of bis(2,2,2-trifluoroethyl) chlorophosphonite in 66% yield involved heating $(CF_3CH_2O)_3P$ with PCl_3 at 90 °C.[14] We were able to isolate bis(polyfluoroalkyl) chlorophosphonites by controlling the stoichiometry of the neat reaction

$$2R_fOLi + PCl_3 \xrightarrow{25\ °C} (R_fO)_2PCl + 2LiCl$$

$$R_f\ (\%\ \text{yield}) = (CF_3)_2CH_3C\ (92),\ CF_3(CH_3)_2C\ (90)$$

The bis(polyfluoroalkyl) chlorophosphonates, $(R_fO)_2P(O)Cl$, were prepared from bis(polyfluoroalkyl) phosphonites, $(R_fO)_2P(O)H$, and chlorine on the basis of literature methods for dialkylchlorophosphonates.[15,16] This process probably occurs via a four-center intermediate.[17]

$$(CF_3(CH_3)_2CO)_2P(O)H + Cl_2 \xrightarrow[10\ h]{-196\ \text{to}\ +25\ °C} (CF_3(CH_3)_2CO)_2P(O)Cl + HCl$$

Most of the methods reported in the literature for oxidation of trialkylphosphites involve air,[18] ozone,[19] hydrogen peroxide,[20] organic peroxides such as *tert*-butyl peroxide,[21] dinitrogen tetraoxide in a solvent (CH_2Cl_2) at −78 °C,[22] or mercury(II) oxide.[23] We have used dinitrogen tetraoxide without solvent to oxidize tris(polyfluoroalkyl) phosphites

$$2(R_fO)_3P + N_2O_4 \xrightarrow{-196\ \text{to}\ +25\ °C} \underset{\sim 100\%}{2(R_fO)_3PO} + 2NO$$

$$R_f = CF_3CH_2,\ (CF_3)_2CH,\ CF_3(CH_3)CH$$

at 25 °C and polyfluoroalkyl) dichlorophosphinites

$$R_fOPCl_2 + N_2O_4\ (1{:}1) \xrightarrow[t]{T} R_fOP(O)Cl_2$$

at reduced temperature as given in Table I. In the case of R_f

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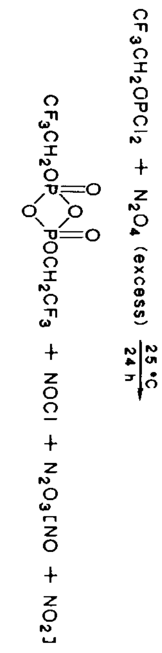
Table IV. Reactants, Yields, and NMR Spectral Data for Phosphorus(V) Acid Precursors

				^{1}H NMR			^{19}F NMR			
	compd (T_{trap}, °C)	reactants (amt, mmol)	yield, %	δ	J_{H-F}, Hz	J_{H-P}, Hz	ϕ	J_{F-P}, Hz	^{31}P{^{1}H} NMR δ	^{31}P NMR
1	$CF_3CH_2OPCl_2$ (−45)	CF_3CH_2OLi (20) PCl_3 (20)^a	65	4.5 (dq)	7.93	8.6	−72.1 (t)		180.9 (br)	
2	$(CF_3)_2CHOPCl_2$ (−45) $[(CF_3)_2CHO]_2PCl$ (−25) $[(CF_3)_2CHO]_3P$ (−25)	(a) $(CF_3)_2CHOLi$ (20) PCl_3 (20)^a	60	5.13 (sept, d)	5.37	13.8	−70.9 (dd)	1.46	187.0 (s)	dm
		(b) $(CF_3)_2CHOH$ (5) PCl_3 (5)^b	70							
3	$(CF_3)_2CH_3COPCl_2$ (−35)	$(CF_3)_2CH_3COLi$ (5) PCl_3 (5)^a	~100	1.9 (sept, d)	1.1	2.56	−77.95 (qd)	9.77	203.5 (m)	m
4	$CF_3(CH_3)_2COPC_2$ (−35)	$(CF_3)(CH_3)_2COLi$ (20) PCl_3 (20)^a	90	1.74 (p)	0.97	1.0	−81.4 (sept, d)	8.79	192.1 (br)	br
5	$CF_3(CH_3)CHOPCl_2$ (−30)	$CF_3(CH_3)CHOLi$ (20) PCl_3 (20)^a	85	5.02 (m) 1.58 (qd)	0.73	12 6.59 (J_{H-H})	76.97 (m)		180.3 (m)	dm
6	$[(CF_3)_2CH_3CO]_2PCl$ (−5)	$CF_3(CH_3)CHOLi$ (2) PCl_3 (1)^a	92	1.84 (br)			−78.7 (d)	9.76	173.5 (sept)	br, sept
7	$[CF_3(CH_3)_2CO]_2PCl$ (−5)	$CF_3(CH_3)_2COLi$ (2) PCl_3 (1)^a	90	1.63 (s) 1.58 (s)			−84.6 (d) −84.4 (d)	8.3	168.97 (sept)	br, sept
8	$[(CF_3)_2CHO]_3P$ (−15) $[(CF_3)_2CHO]_2PCl$ (−35) $[(CF_3)_2CHO]PCl_2$ (−35)	$(CF_3)_2CHOLi$ (3) PCl_3 (1)^a	92	4.77 (d, sept)	5.49	9.76	−75.87 (dd)	6.59	139.46 (m)	m
9	$[(CF_3)_2CH_3CO]_3P$ (0)^c	$(CF_3)_2CH_3COLi$ (3) PCl_3 (1)^a	93	1.78 (d)		1.10	−78.24 (d)	10.74	142.69 (m)	br
10	$[CF_3(CH_3)_2CO]_3P$ (−4)	$CF_3(CH_3)_2COLi$ (3) PCl_3 (1)^a	~100	1.51			−85.02 (d)	8.3	139.46 (dec)	br
11	$[CF_3(CH_3)CHO]_3P$ (−4)	(a) $CF_3(CH_3)CHOLi$ (3) PCl_3 (1)^a	90	1.28 (d)		5.62 (J_{H-H})	−80.67 (m)	6.1	142.37 (sept)	
		(b) $CF_3(CH_3)CHOH\cdot Et_3N$ (3) PCl_3 (1)^a	80	4.4 (m)			−81.02 (m)	6.1	140.30 (sept)	
12	$(CF_3CH_2O)_3PO$	$(CF_3CH_2O)_3P$(5) N_2O_4 (2.5)^a	~100	4.8 (p)	7.81	8.79	−75.9 (t)		−2.8 (s)	sept
13	$[(CF_3)_2CHO]_3PO$	$[(CF_3)_2CHO]_3P$ (5) N_2O_4 (2.5)^a	~100	6.2 (m)	4.76	11.72	−74.48 (d)		−4.64 (br)	q
14	$[CF_3(CH_3)CHO]_3PO$ (0)	$[CF_3(CH_3)CHO]_3P$ (5) N_2O_4 (2.5)^a	~100	4.78 (m) 1.46 (d) 1.465 (d) 1.469 (d)	5.79 5.72 (J_{H-H})	9.19 9.04	−79.03 (d) −79.10 −79.17 (d) −79.22 (d)		−3.98 (s) −5.49 (s)	q q
15	$CF_3CH_2OP(O)Cl_2$ (−35)	$CF_3CH_2OPCl_2$ (10) N_2O_4 (5)^d	75	4.5 (qd)	7.57	10.98	−74.65 (t)		10.12 (m)	tr
16	$(CF_3)_2CHOP(O)Cl_2$ (−30)	$(CF_3)_2CHOPCl_2$ (10) N_2O_4 (5)^d	76	5.38 (sept, d)	5.37	15.87	−72.45 (d)		13.89 (br)	dbr
17	$[(CF_3)_2CH_3CO]P(O)Cl_2$ (−10)	$(CF_3)_2CH_3COPCl_2$ (10) N_2O_4(5)^a	70	2.06 (sept, d)	1.17	1.1	−77.78 (dq)	0.48	4.51 (br)	br
18	$CF_3(CH_3)_2COP(O)Cl_2$ (−30)	$CF_3(CH_3)_2COPCl_2$ (10) N_2O_4 (5)^a	74	1.78 (q)	0.98		−85.83) (d, sept)	~1.0	3.66 (br)	br
19	$CF_3(CH_3)CHOP(O)Cl_2$ (−25)	$CF_3(CH_3)CHOPCl_2$ (10) N_2O_4 (5)	81	4.98 (m) 1.61 (q) 1.52 (q)	0.73	12.45	−76.97 (d, q)		9.26 (br)	d
20	$(CF_3CH_2O)_2P(O)Cl$ (−35)	$(CF_3CH_2O)_3P$ (5) Cl_2 (5)^a	~100	4.36 (dq)	7.81	9.53	−76.22 (t)		5.06 (br)	p
	CF_3CH_2Cl (−116)			3.75 (q)	8.42		−72.7 (t)			

21	$[CF_3(CH_3)_2CO]_2P(O)Cl$ (−5) $CF_3(CH_3)C{=}CH_2$ (−116)	(a) $(CF_3(CH_3)_2CO)_3P$ (5) Cl_2 (5)[a]	~100	1.63	0.98		−84.09 (d, sept)	~1.0	−6.25	br
22	$[(CF_3(CH_3)_2CO)_2P(O)]_2O$	(b) $[CF_3(CH_3)_2CO]_2PCl$ (10) N_2O_4 (5)[a]	70	1.65			−84.09		−25.42 (br)	br
		(c) $[CF_3(CH_3)_2CO]_2P(O)H$ (5) Cl_2 (5)[a]	~100							
23	$[CF_3(CH_3)_2CO]_2P(O)H$ (−20) $\{CF_3(CH_3)_2CO]_3P$ (0) $CF_3(CH_3)C{=}CH_2$ (−116)[e]	$CF_3(CH_3)_2COH$ (15) PCl_3 (5)[a]	75 20	1.7 (s) 1.42 (d)		728.52	−83.05	1.76	−2.79 (sept)	−2.79 (sept, d)
24	$[(CF_3)_2CH_3CO]_2P(O)Cl$ (−5) $[[(CF_3)_2CH_3CO]_2P(O)]_2O$	$[(CF_3)_2CH_3CO]_2PCl$ (10) N_2O_4 (5)[a]	71	1.98 (m)			−78.4 (m)		−6.8 (br)	br
25	$[(CF_3)_2CH_3CO]_2P(O)Cl$ (−5) $(CF_3)_2C{=}CH_2$ (−196)[f]	$[(CF_3)_2CH_3CO]_3P$ (5) Cl_2 (5)[a]	~100				−78.56 (dm) −78.66 (d, q)			
26	$[CF_3(CH_3)CHO]_2P(O)Cl$ (−15) $CF_3(CH_3)CHCl$	$[CF_3(CH_3)CHO]_3P$ (5) Cl_2 (5)[a]	~100	4.8 (m) 1.61 (d)	5.72	6.29 (J_{H-H})	−78.82 (d, m) −78.90 (d)		4.52 (br) 3.34 (br)	m m
27	$[(CF_3)_2CHO]_3PCl_2$ (−20)	$[(CF_3)_2CHO]_3P$ (5) Cl_2 (5)[a]	~100	5.4 (d, sept)	5.37	19.78	−74.30 (d)		−56.54 (br)	q

[a] Reaction temperature 25 °C. [b] Reaction temperature 80 °C. [c] Sublimed at 25 °C (0.1 Torr). [d] Reaction temperature −45 °C. [e] Reference 39. [f] Reference 40.

= CF_3CH_2, a heterocyclic compound has been characterized in addition to 2,2,2-trifluoroethyl dichlorophosphinate.



The oxidation of bis(polyfluoroalkyl) chlorophosphonites with N_2O_4 at low temperatures gave the new bis(polyfluoroalkyl) chlorophosphonates as well as the first examples of the tetra(polyfluoroalkyl) diphosphates.

$$(R_fO)_2PCl + N_2O_4 \rightarrow (R_fO)_2P(O)Cl + (R_fO)_2P(O)OP(O)(OR_f)_2 + NOCl$$

R_f (% yield) = $(CF_3)_2CH_3C$ (67), $CF_3(CH_3)_2C$ (60)

Some of the methods for the preparation of tetraalkyl diphosphates include reactions of CS_2 with a silver salt, e.g., with $(C_6H_5O)_2PO_2Ag$,[24] the reaction of a dialkyl phosphorochloridate with a dialkyl hydrogen phosphorate in the presence of a base,[25] e.g.

$$(RO)_2P(O)Cl + (RO)_2P(O)OH \xrightarrow{B} (RO)_2P(O)OP(O)(OR)_2$$

ROH = β-dinaphthol

or the reaction of diphenyl phosphorochloridate and the silver salt of dibenzyl hydrogen phosphorate.[26] Thermal decomposition of a mixture of a dialkyl phosphorochloridate and a trialkyl phosphate[27] also gave the nonfluorinated tetraalkyl diphosphate.

Our method is superior to the reported methods for the preparation of both the bis(polyfluoroalkyl) chlorophosphonates and tetraalkyl diphosphates in that it utilizes milder conditions.

Hydrolysis of the polyfluoroalkyl dichlorophosphinates, $R_fOP(O)Cl_2$, was carried out as reported for chloroalkyl phosphates[28,29] with the exception that the former compounds were isolated and purified before they were hydrolyzed with a slight excess of distilled water at 25 °C. Upon freeze-drying, the acids were isolated.

$$R_fOP(O)Cl_2 + H_2O \xrightarrow[-HCl]{25\ °C} R_fOP(O)(OH)_2(aq) \xrightarrow[dry]{freeze} \underset{\text{white solid}}{R_fOP(O)(OH)_2}$$

R_f (% yield) =
CF_3CH_2 (~80), $(CF_3)_2CH$ (75), $CF_3(CH_3)CH$ (90)

However, when $R_f = (CF_3)_2CH_3C$ and $CF_3(CH_3)_2C$, a mixture of polyfluoroalkyl dihydrogen phosphate and bis(polyfluoroalkyl) dihydrogen diphosphate esters was formed. They were characterized by measuring their $^{31}P\{^1H\}$ NMR spectra and by comparing these spectra with the $^{31}P\{^1H\}$ NMR spectra reported for alkyl diphosphate esters.[30]

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Table V. Reactants, Yields, and NMR Spectral Data for Phosphorus(V) Acids

				^{1}H NMR			^{19}F NMR			
	compd (T_{trap}, °C)	reactants (amt, mmol)	yield, %	δ	J_{H-F}, Hz	J_{H-P}, Hz	ϕ	J_{F-P}, Hz	^{31}P{^{1}H} NMR δ	^{31}P NMR
1	$(CF_3CH_2O)_2P(O)OH$	(a) $(CF_3CH_2O)_2P(O)Cl$ (10)	89	14.74 (s; OH)			−73.61 (t)		−3.34 (br)	p
		H_2O (11)^a		4.4 (dq)	8.79	7.81				
		(b) CF_3CH_2OH (10)	60							
		P_4O_{10} (10)^a								
		(c) $(CF_3CH_2O)_3PO$ (10)	82							
		H_2O (11)^b								
2	$[H(CF_2)_4CH_2O]_2P(O)OH$^{c}	$[H(CF_2)_4CH_2O]_3PO$ (4)	~100	9.1 (s; OH)						
		H_2O (4)^a		7.0 (tt)	50.21		−120.5 (p)		−3.1 (s)	p
					6.86		−124.9 (t)			
				4.51 (td)	14.29	7.33	−129.8 (m)			
							−138.7 (dm)	7.4		
3	$[(CF_3)_2CHO]_2P(O)OH$^{d}	$[(CF_3)_2CHO]_3PO$ (10)	70	11.2 (s; OH)			−73.84 (d)		−4.85	tm
		H_2O (11)		5.5 (sept, d)	6.35	12.66				
4	$[CF_3(CH_3)CHO]_2P(O)OH$^{c}	(a) $[CF_3(CH_3)CHO]_3PO$ (10)	70	11.5 (s; OH)			−79.26 (d)		3.64	tr
		H_2O (11)^e		4.79	6.41		−79.17 (d)		3.76	tr
				(d, sept)	(J_{CH-F})					
		(b) $[CF_3(CH_3)CHO]_2P(O)Cl$ (10)	85	1.37 (d)	6.41	9.40				
		H_2O (11)^f			(J_{CH_3-CH})					
5	$[CF_3(CH_3)_2CO]_2P(O)OH$	$[CF_3(CH_3)_2CO]_2P(O)Cl$ (10)	55	13.5 (s; OH)			−83.69 (br)		−10.88 (br)	br
		H_2O (11)^f		1.57 (s)						
6	$[(CF_3)_2CH_3CO]_2P(O)OH$^{g}	$[(CF_3)_2CH_3CO]_2P(O)Cl$ (10)	40	14.75 (s; OH)			−77.95 (br)		−13.78 (br)	br
		H_2O (11)^f		1.9 (br)						
7	$CF_3CH_2OP(O)(OH)_2$^{h}	$CF_3CH_2OP(O)Cl_2$ (10)	85	11.5 (s; OH)						
		H_2O (25)^a		4.33 (dq)	8.78	7.32	−74.19 (t)		−1.72 (s)	t
8	$(CF_3)_2CHOP(O)(OH)_2$^{i}	$(CF_3)_2CHOP(O)Cl_2$ (10)	80	11.9 (s; OH)						
		H_2O (25)^a		5.7 (m)	6.34	13.18	−73.44 (d)		−2.4 (s)	d, m
9	$CF_3(CH_3)CHOP(O)(OH)_2$^{j}	$CF_3(CH_3)CHOP(O)Cl_2$ (10)	78	11.76 (s; OH)						
		H_2O (25)^a		4.7	6.73	10.01	−78.93 (d)		−2.4 (br)	d
				(d, sept)	(J_{CH-F})					
				1.36 (d)	6.73					
					(J_{CH_3-C-H})					
10	$CF_3(CH_3)_2COP(O)(OH)_2$	$CF_3(CH_3)_2COP(O)Cl_2$ (10)	80	12.5 (s; OH)			−81.1 (m)		−4.9 (br)	br
		H_2O (25)^a		1.56						
11	$[CF_3(CH_3)_2COP(O)(OH)]_2O$		75	13.1 (s; OH)			−83.3 (br)		−19.28 (br)	br
				1.6 (m)						
12	$(CF_3)_2CH_3COP(O)(OH)_2$	$(CF_3)_2CH_3COP(O)Cl_2$ (10)	90	12.84 (s; OH)			−77.95 (br)		−7.0 (br)	br
		H_2O (25)^a		1.9 (m)						
13	$[(CF_3)_2CH_3COP(O)(OH)]_2O$			13.87 (s; OH)			−77.89 (br)		−20.35 (br)	br
				1.9 (m)						
14	$CF_3CH_2OP(O)(\mu\text{-}O)_2P(O)OCH_2CF_3$ (−30)	$CF_3CH_2OPCl_2$ (5)	~100	4.3 (p)	7.81	7.81	−76.16 (tr)		−3.2	tr
		N_2O_4^{a}								

[a] Reaction temperature 25 °C. [b] Reaction temperature 48 °C. [c] Nonvolatile liquid. [d] Sublimed at 35 °C (0.1 Torr). [e] Reaction temperature 75 °C. [f] Reaction temperature 50 °C. [g] Mp: 75 °C. [h] Sublimed at 130 °C (0.1 Torr). [i] Sublimed at 70 °C (0.1 Torr). [j] Sublimed at 80 °C (0.1 Torr).

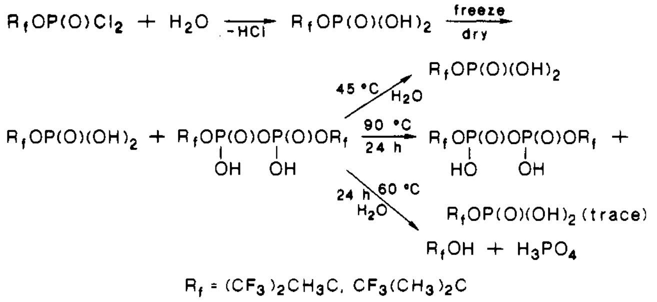
Table VI. Infrared Spectral Data for Phosphorus(V) Acid Precursors (cm^{-1})

compd	IR
$CF_3CH_2OPCl_2$	2973 w, 1480 w, 1455 m, 1296 vs, 1183 vs, 1080 vs, 966 m, 853 m, 825 m, 658 w, 553 w, 510 m, 483 s
$(CF_3)_2CHOPCl_2$	2957 w, 1355 s, 1290 vs, 1245 vs, 1205 vs, 1105 s, 1085 vs, 895 m, 870 m, 846 m, 730 w, 688 m, 556 w, 545 m, 500 vs, 377 w
$(CF_3)_2CH_3COPCl_2$	3007 w, 1455 m, 1303 s, 1227 vs, 1148 s, 1098 w, 998 m, 970 s, 878 w, 810 m, 706 m, 634 w, 546 m, 503 s
$CF_3(CH_3)_2COPCl_2$	3001 m, 2958 w, 1473 m, 1398 m, 1378 m, 1318 m, 1238 m, 1194 vs, 1188 vs, 1178 vs, 1138 vs, 1028 vs, 963 vs, 918 s, 795 m, 728 w, 610 m, 528 s, 498 vs, 470 vs
$CF_3(CH_3)CHOPCl_2$	3003 w, 2978 w, 1458 w, 1378 m, 1280 s, 1201 vs, 1170 vs, 1115 m, 1080 vs, 1028 m, 975 vs, 811 w, 790 m, 748 w, 670 w, 549 m, 508 s, 490 s
$[(CF_3)_2CH_3CO]_2PCl$	3006 w, 1457 m, 1390 m, 1308 s, 1260 m, 1240 vs, 1225 vs, 1210 m, 1128 s, 1090 s, 1008 m, 968 s, 878 w, 808 m, 705 m, 638 w, 540 m
$[CF_3(CH_3)_2CO]_2PCl$	2997 m, 2960 m, 2935 m, 2885 w, 1460 m, 1395 m, 1377 m, 1297 s, 1218 s, 1188 vs, 1130 s, 1028 s, 980 m, 910 m, 791 w, 698 w, 601 w, 530 m, 494 m, 470 m
$CF_3CH_2OP(O)Cl_2$	2980 w, 1460 w, 1319 s, 1294 s, 1189 vs, 1081 vs, 968 w, 851 w, 669 w, 618 s, 594 vs, 554 m, 485 w
$(CF_3)_2CHOP(O)Cl_2$	2988 m, 1375 br, s, 1318 s, 1300 br, s, 1270 w, 1250 s, 1210 s, 1118 s, 1085 s, 895 vs, 870 m, 740 w, 690 vs, 620 vs, 570 s, 520 m, 412 m, 392 m
$(CF_3)_2CH_3COP(O)Cl_2$	3017 w, 1458 m, 1398 w, 1313 br, s, 1238 vs, 1120 m, 1100 br, m, 1008 vs, 870 w, 848 m, 658 s, 638 s, 610 vs, 580 m, 560 m, 520 m, 400 m
$CF_3(CH_3)_2COP(O)Cl_2$	3001 w, 1471 w, 1398 w, 1378 w, 1350 w, 1310 s, 1245 w, 1192 vs, 1135 s, 1020 s, 930 w, 630 m, 605 s, 548 m
$CF_3(CH_3)CHOP(O)Cl_2$	3005 w, 2975 w, 1457 w, 1388 m, 1340 br, 1308 s, 1288 vs, 1205 vs, 1178 vs, 1118 m, 1070 vs, 1030 s, 988 vs, 839 m, 801 w, 778 m, 620 vs, 590 w, 498 w
$(CF_3CH_2O)_2P(O)Cl$	2980 w, 1463 m, 1318 s, 1290 s, 1188 vs, 1113 m, 1080 vs, 969 m, 899 w, 853 w, 669 w, 615 m, 559 w, 489 w
$[CF_3(CH_3)_2CO]_2P(O)Cl$	3008 w, 2960 w, 1476 m, 1402 m, 1382 w, 1335 m, 1299 m, 1236 w, 1172 vs, 1140 s, 1129 s, 932 w, 797 w, 632 m, 588 m, 477 w
$[(CF_3)_2CH_3CO]_2P(O)Cl$	3027 w, 2980 w, 1463 m, 1402 w, 1320 s, 1269 w, 1237 vs, 1174 m, 1136 s, 1098 s, 1013 s, 968 s, 880 w, 837 w, 705 s, 640 m, 611 m, 586 w, 538 w, 477 m
$[CF_3(CH_3)CHO]_2P(O)Cl$	3008 w, 2960 w, 1462 m, 1393 m, 1344 m, 1279 s, 1193 s, 1168 s, 1121 m, 1075 s, 1034 s, 997 s, 848 w, 821 w, 802 w, 672 m, 590 m
$[(CF_3)_2CHO]_3PCl_2$	2977 w, 1378 m, 1304 s, 1274 m, 1248 vs, 1221 s, 1189 w, 1123 s, 1095 s, 995 m, 907 w, 741 w, 692 m, 600 w, 503 w

Table VII. Elemental Analysis Data[a]

	anal.				
compd	% C	% H	% Cl	% F	% P
$(CF_3)_2CH_3COPCl_2$	17.06 (16.96)	1.10 (1.06)	24.95 (25.08)	40.0 (40.28)	10.83 (10.95)
$CF_3(CH_3)_2COPCl_2$	21.88 (21.05)	2.74 (2.63)	26.98 (30.70)	26.1 (25.00)	13.64 (13.60)
$CF_3(CH_3)CHOPCl_2$	16.94 (16.74)	1.93 (1.86)	32.87 (33.02)	26.2 (26.51)	14.36 (14.48)
$(CF_3)_2CH_3COP(O)Cl_2$	16.14 (16.05)	1.08 (1.00)	23.64 (23.75)		
$CF_3(CH_3)_2COP(O)Cl_2$	20.16 (19.59)	2.52 (2.45)	28.22 (28.97)		12.75 (12.65)
$CF_3(CH_3)CHOP(O)Cl_2$	16.77 (15.58)	1.87 (1.73)	28.18 (30.73)		13.66 (13.41)
$(CF_3CH_2O)_2P(O)OH$	18.90 (18.32)	2.03 (1.91)			11.50 (11.83)
$[H(CF_2)_4CH_2O]_2P(O)OH$	19.86 (22.81)	1.52 (1.33)			5.68 (5.89)
$[(CF_3)_2CHO]_2P(O)OH$	17.70 (18.09)	0.80 (0.75)			7.06 (7.79)
$[CF_3(CH_3)CHO]_2P(O)OH$	23.82 (24.82)	3.17 (3.10)			11.02 (10.68)
$[CF_3(CH_3)_2CO]_2P(O)OH$	29.09 (30.18)	3.65 (4.08)			10.46 (9.74)
$[(CF_3)_2CH_3CO]_2P(O)OH$	22.73 (22.53)	1.63 (1.64)			7.38 (7.27)
$CF_3CH_2OP(O)(OH)_2$	14.18 (13.33)	2.33 (2.22)			16.08 (17.22)
$(CF_3)_2CHOP(O)(OH)_2$	14.68 (14.51)	1.36 (1.20)			12.32 (12.50)
$CF_3(CH_3)CHOP(O)(OH)_2$	18.91 (18.55)	3.21 (3.09)			15.57 (15.97)

[a] Calculated values in parentheses.



There are several methods reported in the literature for the preparation of dialkyl diphosphate esters.[31-35] The preparation of polyfluoroalkyl acid phosphates, $R_fOP(O)(OH)_2$, and their ammonium salts has been reported by the stepwise reaction of $X(CF_2)_nCH_2OH$ ($X = H, F$; $n = 1-12$) with $OPCl_3$ or P_4O_{10}[36] with subsequent conversion to their respective ammonium salts.[36,37]

We attempted the reaction of P_4O_{10} and R_fOH at 25 °C.

$$R_fOH + P_4O_{10} \xrightarrow{25\ °C} R_fOP(O)(OH)_2 + (R_fO)_2P(O)OH$$

$$R_f = CF_3CH_2,\ (CF_3)_2CH,\ CF_3(CH_3)CH,\ (CF_3)_2CH_3C,\ CF_3(CH_3)_2C$$

In all cases, we have detected the presence of the monobasic acid phosphates, $(R_fO)_2P(O)OH$, and the dibasic acid phosphates, $R_fOP(O)(OH)_2$, by their characteristic chemical shifts in the $^{31}P\{^1H\}$ NMR spectra, but were unable to isolate the pure acid phosphates with the exception of $(CF_3CH_2O)_2P(O)OH$. It was purified by Kugelrohr distillation at 52 °C (0.1 Torr). This

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Table VIII. Hydrolytic Stabilities of $(R_fO)_2P(O)OH$ and $R_fOP(O)(OH)_2$

acid	reacn conditions 50 °C/20 h	75 °C/3 h	100 °C/36 h	150 °C/48 h
$CF_3CH_2OP(O)(OH)_2$	stable	10% H_3PO_4	$H_3PO_4 + CF_3CH_2OH$	
$CF_3(CH_3)CHOP(O)(OH)_2$	stable	stable	stable	$H_3PO_4 + CF_3(CH_3)CHOH$
$(CF_3)_2CHOP(O)(OH)_2$	stable	stable	$H_3PO_4 + (CF_3)_2CHOH$	
$(CF_3)_2CH_3COP(O)(OH)_2$	$H_3PO_4 + (CF_3)_2CH_3COH$			
$CF_3(CH_3)_2COP(O)(OH)_2$	$H_3PO_4 + CF_3(CH_3)_2COH$			
$[(CF_3)_2CH_3COP(O)O(OH)]_2$	stable	H_3PO_4 + (CF3)2CH_3COH		
$[CF_3(CH_3)_2COP(O)O(OH)]_2$	stable	$H_3PO_4 + CF_3(CH_3)_2COH$		
$[CF_3(CH_3)CHO]_2P(O)(OH)$	stable	stable	$CF_3(CH_3)CHOP(O)(OH)_2 + CF_3(CH_3)CHOH$	$H_3PO_4 + CF_3(CH_3)CHOH$
$[(CF_3)_2CHO]_2P(O)(OH)$	stable	stable	$H_3PO_4 + (CF_3)_2CHOH$	
$(CF_3CH_2O)_2P(O)(OH)$	stable	stable	stable	$H_3PO_4 + CF_3CH_2OH$
$[(CF_3)_2CH_3CO]_2P(O)OH$	stable	stable	stable	H_3PO_4 (~2%)
$[CF_3(CH_3)_2CO]_2P(O)(OH)$	stable	stable	stable	H_3PO_4 (~2%)
$[H(CF_2)_4CH_2O]_2P(O)(OH)$	$H(CF_2)_4CH_2OP(O)(OH)_2$ (~15%) + $[H(CF_2)_4CH_2O]_2P(O)(OH)$ + $H(CF_2)_4CH_2OH + H_3PO_4$	$H(CF_2)_4CH_2OP(O)(OH)_2$ (~25%) + $[H(CF_2)_4CH_2O]_2P(O)$ + $H(CF_2)_4CH_2OH + H_3PO_4$	$H_3PO_4 + H(CF_2)_4CH_2OH$	

technique was not successful with the other acid phosphates due to their decomposition when heated with P_4O_{10}.

$$CF_3CH_2OH + P_4O_{10} \xrightarrow{25\ °C} (CF_3CH_2O)_2P(O)OH + CF_3CH_2OP(O)(OH)_2 \xrightarrow{52\ °C\ (0.1\ Torr)} (CF_3CH_2O)_2P(O)OH$$

The bis(polyfluoroalkyl) acid phosphates were synthesized by the aqueous hydrolysis of bis(polyfluoroalkyl) chlorophosphonates (Table II).

$$(R_fO)_2P(O)Cl + H_2O \xrightarrow[t]{T} (R_fO)_2P(O)OH + HCl$$

Similar results are obtained from the hydrolyses of tris(polyfluoroalkyl) phosphates. (Table III).

$$(R_fO)_3PO + H_2O \xrightarrow[t]{T} (R_fO)_2P(O)OH + R_fOH$$

The precursors to polyfluoroalkyl or bis(polyfluoroalkyl) acid phosphates that were synthesized in this work are summarized in Scheme I.

In Schemes II and III, the syntheses of bis(polyfluoroalkyl) acid phosphates and polyfluoroalkyl acid phosphates are outlined. In Table IV are found the reactants and conditions as well as the NMR spectral data for the phosphorus(V) acid precursors reported in this paper. In Table V are data for the new acids. In Table VI are infrared spectral data for the acid precursors. In Table VII are found elemental analysis data. Essentially every compound exhibits a molecular ion in its positive chemical ionization mass spectrum. Each mass spectrum contained fragments appropriate to the suggested structure. In the infrared spectra, absorption bands in the 470–500-cm^{-1} region have been assigned to $\nu_{P(III)-Cl}$, in the 600–620-cm^{-1} region to $\nu_{P(V)-Cl}$, and in the 1310–1340-cm^{-1} region to $\nu_{P=O}$.[38-40]

Hydrolysis studies of the acids in water show that while the majority of them are stable in water at 50 °C for 20 h, approximately 50% of the acids are decomposed after 3 h at 75 °C, and after 48 h at 150 °C all are decomposed to H_3PO_4 and the respective parent alcohol. These data are given in Table VIII.

Experimental Section

Starting Materials. N_2O_4 (Air Products), Cl_2 (Linde), PCl_3 (Baker), BuLi (Aldrich), and CF_3CH_2OH, $(CF_3)_2CHOH$, $(CF_3)_2CH_3COH$, $CF_3(CH_3)_2COH$, and $(H(CF_2)_4CH_2O)_3PO$ (PCR), were used as received. Et_3N (Baker) was dried on KOH, and $CF_3(CH_3)CHOH$ was dried over molecular sieves before use.

General Procedures. A conventional Pyrex-glass vacuum line apparatus equipped with a Heise Bourdon tube gauge was used for manipulation of gases and volatile materials. Trap-to-trap distillation was carried out to accomplish separation of volatile products. Infrared spectra were obtained on a Perkin-Elmer 599B spectrometer or Perkin-Elmer 1710 Fourier transform infrared spectrometer by using a 10-cm cell fitted with KBr windows. ^1H, ^{19}F, and ^{31}P NMR spectra were recorded on a JEOL FX90Q Fourier transform spectrometer with CCl_3F or H_3PO_4 (85%) as external reference and $CDCl_3$ as the internal reference for polyfluoroalkyl dichlorophosphinites, bis(polyfluoroalkyl)chlorophosphonites, tris(polyfluoroalkyl) phosphites, and tris(polyfluoroalkyl) phosphates. Dimethyl-d_6 sulfoxide was used as the internal reference for polyfluoroalkyl acid phosphates and bis(polyfluoroalkyl) acid phosphates. Negative values were assigned to signals that were upfield of the reference. Mass spectra were recorded on a VG 7070HS mass spectrometer. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

Preparation of CF_3CH_2OLi. The lithium salts of all the polyfluoroalkyl alcohols were prepared similarly. *n*-BuLi (20 mmol, 12.5 mL of a 1.6 M solution) in hexane was transferred via a syringe into a 1000-mL round-bottomed flask equipped with a Teflon stopcock in a drybox. This flask was evacuated at −196 °C, and then CF_3CH_2OH (21 mmol, 2.1 g) was condensed into it. The flask was allowed to warm slowly to 25 °C

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where an exothermic reaction occurred. After 1 h at 25 °C, all volatile materials were evacuated to leave a white solid, CF_3CH_2OLi (20 mmol, 2.1 g, ~100%).

Preparation of 2,2,2-Trifluoroethyl Dichlorophosphinite, $CF_3CH_2OPCl_2$. Onto CF_3CH_2OLi (20 mmol, 2.1 g) in a 1000-mL round-bottomed Pyrex flask at −196 °C, was condensed PCl_3 (20 mmol, 2.75 g). This flask was warmed to and held at 25 °C for 10 h. Trap-to-trap distillation gave $CF_3CH_2OPCl_2$ (13 mmol, 2.6 g, 65% yield) in a trap at −45 °C, PCl_3 in a trap at −120 °C, and a mixture of $(CF_3CH_2O)_2PCl$ and $(CF_3CH_2O)_3P$ in a trap at −30 °C.

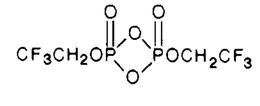
Preparation of Bis(polyfluoroalkyl) Chlorophosphonites, $(R_fO)_2PCl$, or Tris(polyfluoroalkyl) Phosphites, $(R_fO)_3P$. This preparation can be carried out as described above for polyfluoroalkyl dichlorophosphinites, except the stoichiometry of the reaction is 2:1 of R_fOLi to PCl_3 or 3:1 of R_fOLi to PCl_3.

Preparation of $(R_fO)P(O)Cl_2$, $(R_fO)_2P(O)Cl$, and $(R_fO)_3PO$. The compound, R_fOPCl_2 or $(R_fO)_2PCl$ (5 mmol), was transferred into a 100-mL flask equipped with a Teflon stopcock. Stoichiometric amounts of N_2O_4 were condensed at −196 °C onto the compound. The oxidation was complete at low temperatures from −50 to −20 °C. The trap-to-trap distillation gave the products in their respective traps. For $(R_fO)_3P$, the starting material was transferred to the 100-mL flask under an inert atmosphere. After the flask was evacuated at −196 °C, the stoichiometric amount of N_2O_4 was transferred and the temperature was raised from −196 to +25 °C slowly. After 1 h the volatile materials, including NO, were removed, leaving behind a very slightly volatile liquid or solid.

Preparation of $(R_fO)_2P(O)Cl$ from $(R_fO)_3P + Cl_2$. The tris(polyfluoroalkyl) phosphites (5 mmol) were transferred into a 100-mL round-bottomed flask under an inert atmosphere. After the flask was evacuated at −196 °C, Cl_2 (5 mmol) was condensed in. The temperature was raised to 25 °C slowly and left there for a few hours. The trap-to-trap distillation gave the $(R_fO)_2P(O)Cl$ compounds in their respective traps as described earlier.

Hydrolysis of Polyfluoroalkyl Dichlorophosphinates ($R_fOP(O)Cl_2$), Bis(polyfluoroalkyl) Chlorophosphonates ($(R_fO)_2P(O)Cl$), and $(R_fO)_3PO$. The hydrolysis of these phosphates to form acid phosphates, $(R_fO)_2P(O)OH$, was carried out by condensing distilled water onto the dichlorophosphinates, chlorophosphonates, or tris(polyfluoroalkyl) phosphates. The reaction proceeded smoothly for the dichlorophosphinates at room temperature, whereas the reaction between $(R_fO)_2P(O)Cl$ and H_2O took place in the range of 50–64 °C. The reaction was also smooth between $[(CF_3)_2CHO]_3PO$ and water at ambient temperature, and for $[CF_3(CH_3)CHO]_3PO$ and H_2O at 68 °C. Freeze-drying gave the acid phosphates $R_fOP(O)(OH)_2$ and $(R_fO)_2P(O)OH$.

Preparation of $CF_3CH_2OP(O)(\mu\text{-}O)_2P(O)OCH_2CF_3$. $CF_3CH_2OPCl_2$ (1.0 g, 5 mmol) was transferred into a 1000-mL round-bottomed flask equipped with a Teflon stopcock at −196 °C. Then N_2O_4 (1.12 g, 12 mmol) was condensed onto the $CF_3CH_2OPCl_2$. The reaction mixture was warmed to and left at 25 °C overnight. The trap-to-trap distillation gave NOCl in a trap at −196 °C, N_2O_3 at −140 °C, and



in a trap at −25 °C in ~100% yield. This compound was characterized by its ^1H, ^{19}F and ^{31}P NMR spectra as well as by its mass spectrum.

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Registry No. $(CF_3CH_2O)_2P(O)OH$, 40547-38-4; $[H(CF_2)_4CH_2O]_2P(O)OH$, 2794-65-2; $[(CF_3)_2CHO]_2P(O)OH$, 103981-52-8; $[CF_3(CH_3)CHO]_2P(O)OH$, 103981-53-9; $[CF_3(CH_3)_2CO]_2P(O)OH$, 103981-54-0; $[(CF_3)_2CH_3CO]_2P(O)OH$, 103981-55-1; $CF_3CH_2OP(O)(OH)_2$, 2805-15-4; $(CF_3)_2CHOP(O)(OH)_2$, 101686-67-3; $CF_3(CH_3)CHOP(O)(OH)_2$, 103981-56-2; $CF_3(CH_3)_2COP(O)(OH)_2$, 103981-57-3; $[CF_3(CH_3)_2COP(O)(OH)]_2O$, 103981-58-4; $(CF_3)_2CH_3COP(O)(OH)_2$, 104013-77-6; $[(CF_3)_2CH_3COP(O)(OH)]_2O$, 103981-59-5; $CF_3CH_2OP(O)(\mu\text{-}O)_2P(O)OCH_2CF_3$, 103981-60-8; $(CF_3CH_2O)_2P(O)Cl$, 381-44-2; CF_3CH_2OH, 75-89-8; $(CF_3CH_2O)_3PO$, 358-63-4; $[H(CF_2)_4CH_2O]_3PO$, 355-86-2; $[(CF_3)_2CHO]_3PO$, 66489-68-7; $[CF_3(CH_3)CHO]_3PO$, 103981-61-9; $[CF_3(CH_3)CHO]_2P(O)Cl$, 103981-62-0; $[CF_3(CH_3)_2CO]_2P(O)Cl$, 103981-63-1; $[(CF_3)_2CH_3CO]_2P(O)Cl$, 103981-64-2; $CF_3CH_2OP(O)Cl_2$, 462-56-6; $(CF_3)_2CHOP(O)Cl_2$, 103981-65-3; $CF_3(CH_3)CHOP(O)Cl_2$, 103981-66-4; $CF_3(CH_3)_2COP(O)Cl_2$, 103981-67-5; $(CF_3)_2CH_3COP(O)Cl_2$, 103981-68-6; $CF_3CH_2OPCl_2$, 103981-69-7; $(CF_3)_2CHOPCl_2$, 67091-84-3; $[(CF_3)_2CHO]_2PCl$, 67091-85-4; $[(CF_3)_2CHO]_3P$, 66470-81-3; $(CF_3)_2CH_3COPCl_2$, 103981-70-0; $CF_3(CH_3)_2COPCl_2$, 103981-71-1; $CF_3(CH_3)CHOPCl_2$, 103981-72-2; $[(CF_3)_2CH_3CO]_2PCl$, 103981-73-3; $[CF_3(CH_3)_2CO]_2PCl$, 103981-74-4; $[(CF_3)_2CH_3CO]_3P(O)$, 103981-75-5; $[CF_3(CH_3)_2CO]_3P$, 103981-76-6; $[CF_3(CH_3)CHO]_3P$, 79155-02-5; $[(CF_3(CH_3)_2CO)_2P(O)]_2O$, 103981-77-7; $(CF_3(CH_3)_2CO)_2P(O)H$, 103981-78-8; $[(CF_3)_2CHO]_3PCl_2$, 66559-58-8; CF_3CH_2OLi, 69163-14-0; $(CF_3)_2CHOLi$, 29649-10-3; $(CF_3)_2CHOH$, 920-66-1; $(CF_3)_2CH_3COLi$, 98171-13-2; $(CF_3)(CH_3)_2COLi$, 102828-97-7; $CF_3(CH_3)CHOLi$, 103981-79-9; $CF_3(CH_3)_2COLi$, 102828-97-7; $CF_3(CH_3)CHOH$, 374-01-6; $(CF_3CH_2O)_3P$, 370-69-4; $[CF_3(CH_3)_2CO]_2P(O)H$, 103981-78-8; $CF_3(CH_3)_2COH$, 507-52-8; $[(CF_3)_2CH_3CO]_3P$, 103981-80-2; CF_3CH_2Cl, 75-88-7; $CF_3(CH_3)C{=}CH_2$, 374-00-5; $[[(CF_3)_2CH_3CO]_2P(O)]_2O$, 103981-81-3; $(CF_3)_2C{=}CH_2$, 382-10-5; $CF_3(CH_3)CHCl$, 460-35-5.

Notes

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Direct Evidence for an S_N1CB Mechanism. 4. Crystal and Molecular Structure of Chloro(bis(8-quinolinyl)amido-N^1,N^2,N^3)copper(II), a Metal Chelate Containing an sp^2-Hybridized Deprotonated Amine

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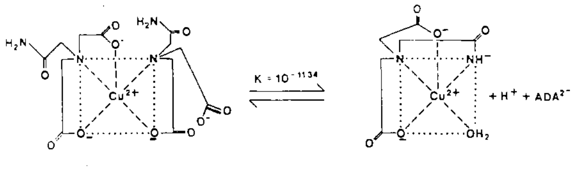
As possible models for substrate release at metalloenzyme centers, we have reported aminoacidate dechelation upon amide deprotonation[1] in the bis(N-acetamidoiminodiacetato)copper(II) chelate $[Cu(ADA)_2{}^{2-}]$ (eq 1), upon hydroxy group ionization[2] in the bis(N,N-bis(2-hydroxyethyl)glycinato)copper(II) chelate (eq 2), and upon peptide proton ionization[3] in the mixed-ligand chelate (N,N-bis(carboxymethyl)glycylglycinato)(glycinato)copper(II) (eq 3). Recently, we have observed[4] the buildup of $[Cu(H_{-1}ADA(\beta\text{-ala})^{2-}]$ (β-ala = β-alanine), a deprotonated mixed-ligand chelate, in solution prior to the release of β-alanine. This work was predicated on the belief that the S_N1CB mechanism,



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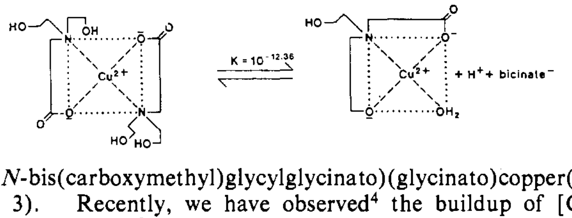

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