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The synthesis and reactions of dialkyl fluoroalkyl phosphates

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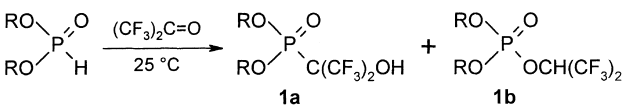
Abstract

Dimethyl and diethyl fluoroalkyl phosphates were prepared from (1) a dialkyl phosphite with a fluoroalcohol, triethylamine and carbon tetrachloride, (2) a dialkyl chlorophosphate with a fluoroalcohol and triethylamine, and (3) a dialkyl chlorophosphate with the sodium salt of a fluoroalcohol. Dimethyl and diethyl (2,2,2-trifluoroethyl) phosphates reacted with bromotrimethylsilane (TMSBr) in chloroform to give two products with loss of alkyl bromide. The major product was an alkyl (trifluoroethyl) trimethylsilyl phosphate, RO(TMSO)-$P(O)OCH_2CF_3$ and the minor product was a bis(trimethylsilyl) trifluoroethyl phosphate, $(TMSO)_2P(O)OCH_2CF_3$. The mechanism presumably involves initial attack of an alkoxy oxygen atom on the silicon atom of bromotrimethylsilane. Diethyl (2,2,2-trifluoroethyl) phosphate is resistant to chlorination. It did not react with oxalyl or thionyl chloride in chloroform under prolonged reflux. Unlike triethyl phosphate, it did not react with phosphorus oxychloride in chloroform under reflux.

Keywords: Dialkyl fluoroalkyl phosphates; Fluorinated phosphate; Fluoroalchol; Phosphate; Todd–Atherton reaction

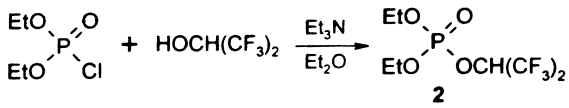
1. Introduction

Symmetrical fluorine-containing trialkyl phosphates have been made from phosphorus oxychloride [1] or phosphorus pentachloride/pentabromide [2] with fluoroalcohols or by oxidation of fluoroalkyl phosphites with dinitrogen tetraoxide [3]. Similar methods have been used to prepare alkyl [4] and aryl bis(fluoroalkyl) phosphates [5], dialkyl fluoroaryl phosphates [6], diaryl fluoroalkyl and tris(fluoroalkyl) phosphates [7]. Of the few dialkyl fluoroalkyl phosphates described in the literature, most contain a hexafluoroisopropyl group derived from hexafluoroacetone. Reaction of dialkyl phosphite with this ketone gives a mixture of phosphonate **1a** and phosphate **1b** [8–10].



1a **1b**

Conversion of **1a** to the thermodynamically more stable **1b** occurs on heating to 100°C with 1,4-diazabicyclo(2,2,2)octane and yields are usually no more than 40% [8]. The volatility (bp −27°C) and toxicity of hexafluoroacetone[1], and the likelihood of obtaining product mixtures, has prompted the development of alternative routes to hexafluoroisopropyl phosphates **1b** and unbranched fluoroalkyl homologues which cannot be derived from fluoroketones. One alternative route, the reaction of a dialkyl chlorophosphate with a fluoroalcohol and a base, has been used to make diethyl hexafluoroisopropyl phosphate **2** [9]. Little is known about dialkyl fluoroalkyl phosphates having linear fluorocarbon side-chains.



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We now report the preparation of dimethyl and diethyl fluoroalkyl phosphates having linear and branched fluorocarbon side-chains. The reactivities of selected phosphates with bromotrimethylsilane (TMSBr) and various chlorinating agents are also discussed.

2. Results and discussion

2.1. Synthesis of dialkyl fluoroalkyl phosphates

Dialkyl fluoroalkyl phosphates were prepared by three routes (Fig. 1). The first route involved reaction of a dialkyl phosphite with a fluoroalcohol, carbon tetrachloride and triethylamine in chloroform (Method A). This is a modified Todd–Atherton procedure [12] where the dialkyl chlorophosphate intermediate couples with the alcohol. The second

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[1]Hexafluoroacetone has a moderate order of acute inhalation toxicity (LD_{50} is 300 ppm for rats exposed for 4 h) [11].

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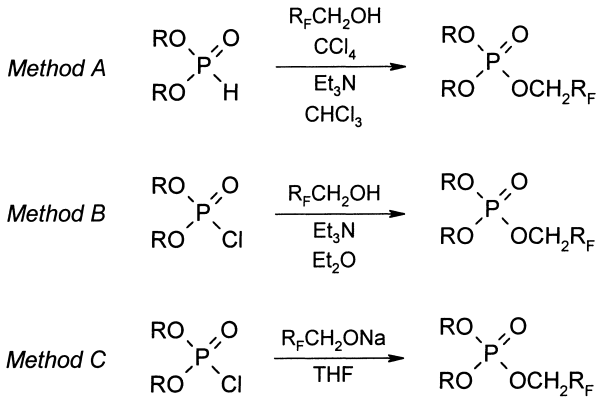


Fig. 1. Methods of Preparation.

route involved reaction of a dialkyl chlorophosphate with a fluoroalcohol and triethylamine in diethyl ether (Method B). The third route involved the reaction between a dialkyl chlorophosphate and the sodium salt of a fluoroalcohol in tetrahydrofuran (Method C). The methods of preparation and yields of dialkyl fluoroalkyl phosphates **3**–**12** are given in Table 1.

Method A was of general applicability to the synthesis of dialkyl fluoroalkyl phosphates and was very useful for large-scale work (50 g or more). Method B was also general in scope but the yields depended on the combination of the dialkyl chlorophosphate and fluoroalcohol. Under such conditions, the long-chain alcohol $HOCH_2(CF_2)_3CF_2H$ reacted poorly with dimethyl chlorophosphate, but well with diethyl chlorophosphate (41% yield). Dimethyl phosphate **7** was therefore best prepared using Method C. Generally the yields of dimethyl fluoroalkyl phosphates were lower than those of the diethyl homologues. The former had a tendency to pyrolyse more readily on distillation.

Dimethyl and diethyl fluoroalkyl phosphates are mobile colourless liquids that have fairly high boiling points (Table 1). Spectroscopic data are given in Tables 2 and 3. Infrared bands appear at 1292–1269 (P=O), 1038–1032 (P–OEt), 1059–1053 (P–OMe) and 1132–1105 cm^{-1} (P–O-R_F). The frequency of the P=O and P–OR vibrations increase as the electronegativity of the substituents attached to the phosphorus atom increase [13,14]. For example: $(EtO)_2P(O)OCH_2CF_3$ ($\nu_{P=O}$ 1271,ν_{P-OEt} 1036 cm^{-1}) and $(EtO)_3P{=}O$($\nu_{P=O}$ 1264, ν_{P-OEt} 1033 cm^{-1}). Phosphorus chemical shifts for dialkyl fluoroalkyl phosphates were between −3.4 and −0.3 ppm.

2.2. Reaction of dialkyl (2,2,2-trifluoroethyl) phosphates with bromotrimethylsilane

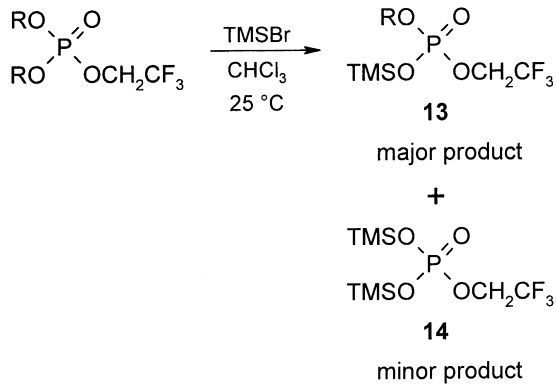
Reaction of alkoxy-substituted phosphoryl compounds with TMSBr often results in formation of a trimethylsilyl phosphorus ester with loss of alkyl bromide [15]. Dimethyl and diethyl (trifluoroethyl) phosphates reacted with TMSBr

Table 1
Experimental data for dialkyl fluoroalkyl phosphates $(RO)_2P(O)OR_F$

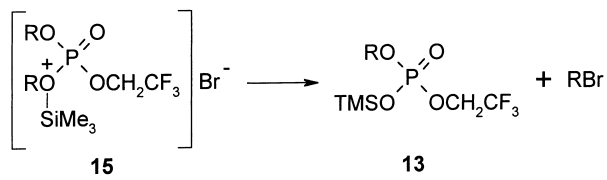
Compound	R	R_F	Method	Yield (%)	Bp (°C/mm Hg)
3	Me	CH_2CF_3	A	54[a]	54/1.8
4	Me	$CH_2CF_2CF_3$	B	40	61/1
5	Me	$CH(CF_3)_2$	B	39	50/6
6	Me	$CH_2CF_2CF_2CF_3$	B	30	42/0.06
7	Me	$CH_2CF_2CF_2CF_2CF_2H$	C	30	66/0.08
8	Et	CH_2CF_3	A	30	60–66/0.05
9	Et	$CH_2CF_2CF_3$	A	49[b]	90/12
10	Et	$CH(CF_3)_2$	B	60[c]	56/0.5
11	Et	$CH_2CF_2CF_2CF_3$	A	56	88/8
12	Et	$CH_2CF_2CF_2CF_2CF_2H$	B	41	111/3.5

[a] Compound **3** has been previously prepared in 63% yield from dimethyl phosphite and hexafluoroacetone; bp 59–60°/8 mm Hg [9].
[b] We also prepared compound **9** by route B in 39% yield.
[c] Compound **10** has been made in 88% yield from diethyl phosphite and hexafluoroacetone at −196°C [8] and in 53% yield from diethyl chlorophosphate, hexafluoroisopropanol and triethylamine in ether; bp 71–74 Hg/10 mm [9].

in chloroform at room temperature. The trifluoroethyl group was retained in preference to the unfluorinated alkyl groups. Reaction mixtures were found by GC–MS analysis to contain alkyl (trifluoroethyl) trimethylsilyl phosphate **13** as the major product (55–60%) and bis(trimethylsilyl) trifluoroethyl phosphate **14** as the minor product (5–10%)[2]. No attempt was made to isolate the two products.



The reaction most likely involves initial attack of alkoxy oxygen on TMSBr to give oxonium intermediate **15**. Dealkylation by bromide ion furnishes the monosilyl ester **13** with loss of alkyl bromide.



[2]Silyl esters, $(RO)(TMSO)P(O)OCH(CF_3)_2$ and $(TMSO)_2P(O)OCH(CF_3)_2$ have been prepared from hexafluoroacetone and silyl phosphites, (RO)(TMSO)P(O)H and $(TMSO)_2P(O)H$, respectively (R=Me or Et) [8].

Table 2
Spectroscopic data for dimethyl fluoroalkyl phosphates ($CDCl_3$ solvent)

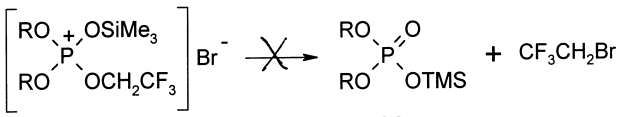
Product	^{1}H NMR δ, J (Hz)	^{13}C NMR δ, J (Hz)	^{19}F NMR δ, J (Hz)	^{31}P NMR δ	IR(ν,cm^{-1})	HRMS analysis
3	4.46 (dq, 2 H, J=8.2, OCH_2), 3.83 (d, 6 H, J=11.3, CH_3)	122.5 (dq, 1 C, J=9, 277, CF_3), 63.5 (dq, 1 C, J=6, 38, OCH_2), 54.7 (d, 2 C, J=7, CH_3)	−74 (m, 3 F, CF_3)	−0.4	2920, 2848, 1298, 1277 (P=O), 1178, 1109 (P–O–CH_2R_F), 1055 (P–OMe), 964, 858	Calc. $C_4H_8O_4F_3P$ 208.0112, found 208.0045 (error 32.3 ppm)
4	4.45 (dt, 2 H, J=7.6, 12.5, OCH_2), 3.85 (d, 6 H, J=11.3, CH_3)	118 (m, 1 C, CF_3), 112 (m, 1 C, CF_2), 62.8 (dt, 1 C, J=4.4, 29, OCH_2), 54.8 (d, 2 C, J=7, CH_3)	−82.6 (m, 3 F, CF_3), −123.8 (m, 2 F, CF_2)	−0.6	2922, 2912, 2848, 1284 (P=O), 1207, 1157, 1113, (P–O–CH_2R_F), 1053 (P–OMe), 937	Calc. $C_5H_8O_4F_5P$ 258.0080, found 258.0023 (error 22.2 ppm)
5	5.12 (dsep, 1 H, J=5.5, CH), 3.82, (d, 6 H, J=11.4, CH_3)	120 (q, 2 C, J=282, CF_3), 71.7 (dsep, 1 C, J=4, 35, CH), 55.1 (d, 2 C, J=7, CH_3)	−73.5 (m, 6 F, CF_3)	−1.1	2918, 2848, 1385, 1277 (P=O), 1236, 1203, 1115 (P–O–CH_2R_F), 1059 (P–OMe), 903, 868, 688	Calc. $C_5H_7O_4F_6P$ 275.9986, found 275.9968 (error 6.5 ppm)
6	4.50 (dtt, 2 H, J=7.6, 13.2, 1.2, OCH_2), 3.85 (d, 6 H, J=11.2, CH_3)	117 (tq, 1 C, J=33, 287, CF_3), 114 (dtt, 1 C, J=10, 35, 257, CF_2), 108.5 (tq, 1 C, J=257, 287, CF_2), 62.8 (dt, 1 C, J=3.1, 28, OCH_2), 54.7 (d, 2 C, J=6.3, CH_3)	−80.2 (m, 3 F, CF_3), −120.8 (m, 2 F, CF_2) −126.7 (m, 2 F, CF_2)	−0.3	2966, 1456, 1356, 1292 (P=O), 1232, 1188, 1132 (P–O–CH_2R_F), 1059 (P–OMe), 1016, 966, 928, 858, 760	Calc. $C_6H_8O_4F_7P$ 308.0048, found 307.9877 (error 55.8 ppm)
7	6.06 (tt, 1 H, J=5.3, 51.9, CF_2H), 4.5, (dt, 2 H, J=7.3, 13.4, OCH_2), 3.82 (d, 6 H, J=8.3 Hz, CH_3)	115 (m, 1 C, $CH_2CF_2CF_2$), 112 (m, 1 C, CF_2CF_2H), 110 (m, 1 C, CH_2CF_2), 107.5 (m, 1 C, CF_2H), 62.9 (dt, 1 C, J=3.1, 26, OCH_2), 54.7 (d, 2 C, J=5.7, CH_3)	−120 (m, 2 F, CF_2CF_2H), −124 (m, 2 F, CF_2) −128 (m, 2 F, CH_2CF_2), −136.1 (m, 2 F, CF_2H)	−0.4	2966, 2917, 1454, 1286 (P=O), 1175, 1131 (P–O–CH_2R_F), 1054 (P–OMe), 961, 904, 858, 808	Calc. $C_7H_9O_4F_8P$ 340.0111, found 340.0114 (error −0.9 ppm)

Table 3
Spectroscopic data for diethyl fluoroalkyl phosphates ($CDCl_3$ solvent)

Product	^{1}H NMR δ, J (Hz)	^{13}C NMR δ, J (Hz)	^{19}F NMR δ, J (Hz)	^{31}P NMR δ	IR(ν, cm^{-1})	HRMS analysis
8	4.35 (dq, 2 H, J=8.2, OCH_2CF_3), 4.16 (m, 4 H, J=7, OCH_2), 1.36 (dt, 6 H, J=1, 7, CH_3)	122.5 (dq, 1 C, J=9, 277, CF_3), 64.6 (d, 2 C, J=6, OCH_2), 63.5 (dq, 1 C, J=4, 37, OCH_2CF_3), 16.05 (d, 2 C, J=7, CH_3)	−74.4 (m, 3 F, CF_3)	−2.6	2922, 2914, 2848, 1294, 1271 (P=O), 1174, 1109 (P–O–CH_2R_F), 1036 (P–OEt), 966	Calc. $C_6H_{12}O_4F_3P$ 236.0425, found 236.0649 (error −94.9 ppm)
9	4.42 (dtq, 2 H, J=10.9, 7, 0.9, OCH_2CF_2), 4.16 (dq), 4 H, J=7.2, OCH_2), 1.36 (dt, 6 H, J=1.1, 7.2, CH_3)	118.5 (tq, 1 C, J=148, 286, CF_3), 110 (dq, 1 C, J=9.3, 255, CF_2), 62.8 (d, 1 C, J=8, OCH_2), 62.3 (dt, J=4.3, 28.6, OCH_2CF_2), 15.75 (d, 2 C, J=7, CH_3)	−83.3 (m, 3 F, CF_3), −124.4 (m, 2 F, CF_2)	−2.9	2991, 2916, 1279, (P=O), 1207, 1157, 1130, 1105 (P–O–CH_2R_F), 1032 (P–OEt), 985, 960, 868	Calc. $C_7H_{12}O_4F_5P$ 286.0393, found 286.0512 (error −41.5 ppm)
10	5.19 (dsep, 1 H, J=5.8, 6, CH), 4.2, (m, 2 H, OCH_2), 1.38 (t, 3 H, J=7, CH_3)	120.5 (q, 2 C, J=280, CF_3), 71.7 (dsep, 1 C, J=4, 35, CH), 65.2 (d, 2 C, J=8, OCH_2), 15.6 (d, 2 C, J=8, CH_3)	−73.5 (m, 6 F, CF_3)	−3.4	2920, 1385, 1269, (P=O), 1234, 1203, 1113 (P–O–CH_2R_F), 1038 (P–OEt), 887, 688	Calc. $C_7H_{11}O_4F_6P$ 307.0299, found 304.0213 (error 28.2 ppm)
11	4.46 (dt, 2 H, J=7.4, 13.2, OCH_2CF_3), 4.17 (m, 4 H, J=7, OCH_2), 1.37 (t, 6 H, J=7, CH_3)	116 (tq, 1 C, J=33, 287, CF_3), 112 (m, 1 C, CF_2), 107 (m, 1 C, CF_2), 64.7 (d, 2 C, J=6, OCH_2), 62.6 (dt, 1 C, J=6, 27, OCH_2CF_2), 15.82 (d, 2 C, J=6, CH_3)	−80 (m, 3 F, CF_3), −120.8 (m, 2 F, CF_2), −126.6 (m, 2 F, CH_2CF_2)	−2.8	2916, 2848, 1281 (P=O), 1232, 1186, 1132 (P–O–CH_2R_F), 1036 (P–OEt), 968, 926	Calc. $C_8H_{12}O_4F_7P$ 336.0361, found 336.0304 (error 17.1 ppm)
12	6.1 (tt, 1 H, J=5.3, 51.9, CF_2H), 4.47, (tdt, 2 H, J=1.3, 7.2, 17.4, OCH_2CF_2), 4.17 (dq, 4H, J=7, 7.3, OCH_2), 1.36 (dt, 6 H, J=1.1, 6.9, CH_3)	116 (m, 1 C, $CH_2CF_2CF_2$), 109.9 (m, 1 C, CF_2CF_2H), 114 (m, 1 C, CH_2CF_2), 107.5 (m, 1 C, CF_2H), 64.5 (d, 2 C, J=6.2, OCH_2), 62.7 (dt, 1 C, J=3.7, 27.3, OCH_2CF_2), 15.85 (d, 2 C, J=6.8 H, CH_3)	−120.4 (m, 2 F, CF_2CF_2H), −125 (m, 2 F, CF_2) −130 (m, 2 F, CH_2CF_2) −136.6 (m, 2 F, CF_2H)	−0.3	2991, 1279, (P=O), 1174, 1132 (P–O–CH_2R_F), 1038 (P–OEt), 987, 964, 904, 868, 806	Calc. $C_9H_{13}O_4F_8P$ 368.0424, found 368.0421 (error −0.6 ppm)

Further support for this pathway was provided by comparing reactions of dimethyl and diethyl (2,2,2-trifluoroethyl) phosphates with TMSBr. Monitoring by GC–MS established that the reaction of the dimethyl phosphate took place more rapidly than that of the diethyl phosphate, reflecting the greater ease of dealkylation of methoxy versus ethoxy groups[3]. A second attack by alkoxy oxygen of product **13** on TMSBr gave rise to small amounts of bis-silyl product **14**.

The alternative mechanism involving initial attack of phosphoryl oxygen on TMSBr to give phosphonium intermediate **16** can be ruled out. In this case, the bromide ion would be expected to attack the most electropositive carbon atom, namely the methylene carbon of the trifluoroethyl group, which would give dialkyl trimethylsilyl phosphate **17** with loss of 1-bromo-2,2,2-trifluoroethane. No evidence for either of these products was observed by analysis of reaction mixtures by GC–MS.

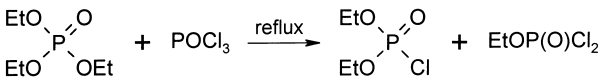


16 **17**

The mechanism of transesterification of unfluorinated alkyl esters of phosphorus with TMSBr involves the formation of phosphonium intermediates analogous to **16**. Silylation is a two-step process involving a fast reversible formation of phosphonium salt which decomposes in the rate-limiting step through dealkylation by bromide ion [15,17]. Our findings suggest that an alternative mechanism involving an oxonium intermediate operates in the transesterification of dialkyl fluoroalkyl phosphates with bromotrimethylsilane.

2.3. Reactivities of fluorinated and unfluorinated phosphates towards chlorinating agents

The comparative reactivities of triethyl phosphate and diethyl (2,2,2-trifluoroethyl) phosphate towards various chlorinating agents were examined. Neither compound reacted with oxalyl or thionyl chloride in chloroform under prolonged reflux. Triethyl phosphate was found to react very slowly with phosphorus oxychloride in refluxing chloroform to give a low conversion to diethyl chlorophosphate (5% yield after 8 h reflux, as determined by GC–MS).



Diethyl (2,2,2-trifluoroethyl) phosphate was less reactive than its unfluorinated counterpart and did not react at all with phosphorus oxychloride under identical conditions.

[3]Reactivity in the dealkylation process depends upon the size of the alkyl group. Competitive experiments on the dealkylation of dimethyl, diethyl and diisopropyl acylphosphonates with TMSBr indicated the relative reactivities to be 1:0.25:0.04 [16].

3. Experimental details

All reagents were of commercial quality. Anhydrous solvents were used for reactions: THF was distilled from sodium/benzophenone. NMR spectra were obtained on a Jeol Lambda 500 instrument (operating at 500 MHz for ^{1}H, 125 MHz for ^{13}C, 470 MHz for ^{19}F, and 202 MHz for ^{31}P spectra) as solutions in $CDCl_3$, with internal reference $SiMe_4$ for ^{1}H, external $CFCl_3$ for ^{19}F and external $(MeO)_3P$ (δ 140 ppm) for ^{31}P spectra. Data in Tables 2 and 3 are recorded as follows: chemical shifts in ppm from reference on the δ scale, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet and sep=septet), integration, coupling constant (Hz) and assignment. IR spectra were recorded as liquid films on a Nicolet SP210 instrument using Omnic software. Reaction mixtures were monitored by gas chromatography–mass spectrometry (GC–MS) using a Finnigan MAT GCQ instrument (chemical ionisation using methane as reagent gas). Analysis of pure products by high resolution mass spectrometry (HRMS) used a Micromass Autospec SQ Double Focusing Magnetic Sector instrument. Mode: +ve ion electron impact, magnet scan *m/z* 400 to 100 (seconds/decade), resolution 2900. Inlet: septum (160°C), 0.2 μl introduced. Source conditions: temperature 200°C, electron energy 70 eV, and accelerating voltage 8000 V. All reaction mixtures were stirred magnetically.

3.1. Synthesis of dialkyl fluoroalkyl phosphates

Method A: The fluoroalcohol (0.2 mol) and triethylamine (0.2 mol) in $CHCl_3$ (50 ml) were added dropwise over 2–3 h to the dialkyl phosphite (0.2 mol) and CCl_4 (0.2 mol) cooled to 0–5°C. When the addition was complete, a white precipitate of $Et_3N{\cdot}HCl$ had formed. The mixture was stirred for 2 h at 0–5°C and allowed to stand for 16 h at room temperature. The mixture was washed with water (2×25 ml), the organic layers combined, dried ($MgSO_4$), filtered and the solvent removed to leave an oil. This was distilled, initially at 12–15 mm Hg with gentle heating to remove any unreacted alcohol. The temperature was then increased and the vacuum adjusted to between 0.5–12 mm Hg depending on the boiling point of the product (Table 1).

Method B: A mixture of the fluoroalcohol (0.1 mol) and triethylamine (0.1 mol) was added dropwise to the dialkyl chlorophosphate (0.1 mol) in Et_2O (100 ml) cooled to 0–5°C (or at room temperature for compounds **4** and **12**). After addition the solution was stirred for 4 h and filtered. The filtrate was concentrated to an oil which was distilled according to Method A.

Method C: The fluoroalcohol (0.04 mol) in THF (30 ml) was added dropwise to a suspension of NaH (0.048 mol) in THF (30 ml) at room temperature (exothermic reaction). After addition the mixture was cooled to 0–5°C and to it was added dropwise a solution of dialkyl chlorophosphate

(0.04 mol) in THF (50 ml). After addition the mixture was allowed to warm to room temperature and left to stand for 16 h. The mixture was then treated carefully with water (50 ml) and extracted with $CHCl_3$ (3×50 ml). The organic extracts were combined, dried ($MgSO_4$) and the solvent removed to give an oil which was distilled according to Method A.

3.2. Reaction of phosphates with bromotrimethylsilane

TMSBr (10 mmol) was added by syringe to a solution of dialkyl fluoroalkyl phosphate (10 mmol) in $CHCl_3$ (10 ml) under argon at room temperature. Aliquots of the reaction mixture were analysed immediately after addition and at time intervals of 24 and 48 h.

3.3. Attempted reaction of phosphates with oxalyl or thionyl chlorides

Oxalyl or thionyl chloride (0.01 mmol) in $CHCl_3$ (10 ml) was added dropwise to a solution of trialkyl phosphate or dialkyl fluoroalkyl phosphate (0.01 mmol) in $CHCl_3$ (10 ml) at room temperature. The mixture was left for 2 h and analysed by GC–MS. It was then refluxed for 5 h and re-analysed by GC–MS.

3.4. Reaction of phosphates with phosphorus oxychloride

Phosphorus oxychloride (0.07 mmol) in $CHCl_3$ (50 ml) was added dropwise to a solution of dialkyl fluoroalkyl phosphate (0.07 mmol) in $CHCl_3$ (10 ml) at room temperature. After addition the mixture was refluxed for 4 h, analysed by GC–MS, refluxed for a further 4 h, and re-analysed by GC–MS.

4. Conclusion

Three methods have been developed which complement known synthetic routes to dialkyl fluoroalkyl phosphates (Section 1). Reaction of TMSBr with two fluoroalkyl phosphates revealed important information about their mechanism of interaction. Such reactions might provide a route to alkyl (fluoroalkyl) trimethylsilyl phosphates which may be useful intermediates to fluoroalkyl phosphorus compounds. The failure of dialkyl (2,2,2-trifluoroalkyl) phosphates to react with a variety of chlorinating agents highlights their inertness to certain electrophilic reagents.

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