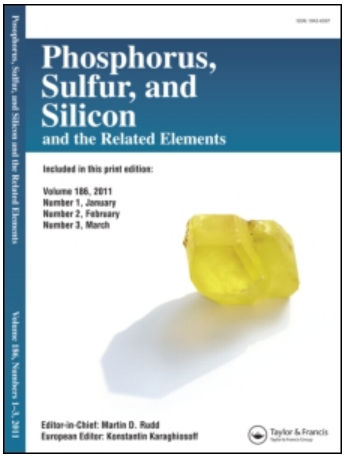

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THE THERMOLYTIC DECOMPOSITION OF ACYCLIC PHOSPHORANES

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THE THERMOLYTIC DECOMPOSITION OF ACYCLIC PHOSPHORANES

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The thermolytic decomposition of acyclic phosphoranes, $Ar_nP(OCH_2CF_3)_{5-n}$ in aprotic media has been shown by kinetic studies to proceed *via* rate-limiting ionization of the phosphoranes. Activation parameters, deuterium isotope effects, solvent effects and ρ-values (for n = 3 and n = 1) support this concept which is consistent with the observed rate-sequence of n = 3 > n = 2 > n = 1 > n = 0.

Key words: Phosphoranes, thermolysis, kinetics, mechanism.

INTRODUCTION

Acyclic alkoxyphosphoranes of the type $Ar_nP(OR)_{5-n}$ have been regarded as somewhat unstable species[1] but the advent of new synthetic methods, in particular the benzenesulphenate ester route (Equation 1) employing fluoroalkoxy groups[2] has enabled the isolation and complete characterisation of numerous molecules of this type. They are known to be susceptible to hydrolysis[3,4] but their thermal stability is evidenced by the fact that in some

$$\underset{(1)}{Ar_nP(OR)_{3-n}} + \underset{(2)}{2PhSOR'} \rightarrow \underset{(3)}{Ar_nP(OR)_{3-n}(OR')_2} + \underset{(4)}{Ph_2S_2} \qquad (1)$$

$$R' = \text{alkyl or fluoroalkyl}$$

cases they may be isolated by distillation. We now report the first kinetic study of the thermal decomposition of a range of acyclic phosphoranes. $Ar_nP(OCH_2CF_3)_{5-n}$ with n = 0–3.

RESULTS AND DISCUSSION

Each phosphorane was prepared by reaction of 2,2,2-trifluoroethoxybenzenesulphenate (2, R' = CH_2CF_3) with the appropriate tricoordinated phosphorus compound (**1**, R = CH_2CF_3) in mesitylene (for n = 3 or 2) and decalin (for n = 1 or 0) as solvents. The mixtures were then heated under N_2 in a thermostat bath and samples were taken at various time intervals for analysis by ^{31}P NMR. In each case the main phosphorus product (75–90%) was the oxide (**5**) corresponding to the phosphorane (**3**). In addition, however, at later stages of the thermolysis, varying amounts of tricoordinate phosphorus compounds (**1**, up to 7% for n = 3) and the

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TABLE I

^{31}P nmr data for tricoordinate phosphorus compounds (**1**), phosphoranes (**3**), oxides (**5**) and fluorophosphoranes (**6**) in C_7D_8 as solvent *vs* 85% H_3PO_4

	$\delta^{31}P$ (rel. to H_3PO_4)		R = CH_2CF_3		
n	(1)	(3)	(5)	(6)	$^1J_{PF}$ (Hz)
0	139.9	-76.9	-2.6	-76.8	762
1	166.7	-60.3	+20.6	-55.9	828
2	126.2	-45.8	+33.1	-42.3	748
3	-5.4	-59.2	+28.1	-58.6	630

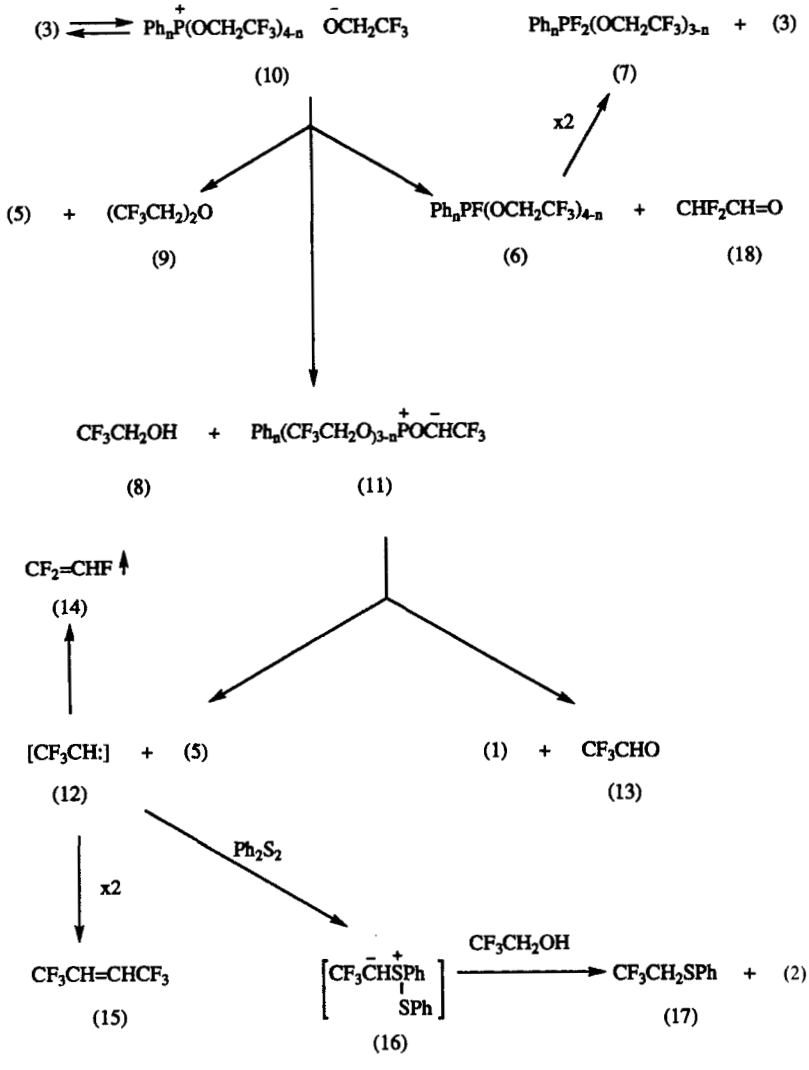
fluorophosphoranes (**6**, up to 15%) were observed.† The ^{31}P NMR shifts of compounds (**1**, **3**, **5** and **6**, Ar = Ph) are shown in Table I.

$$\underset{(3)}{Ar_nP(OCH_2CF_3)_{5-n}} \xrightarrow{\Delta} \underset{(5)}{Ar_nP(O)(OCH_2CF_3)_{3-n}} + (1) + \underset{(6)}{Ar_nPF(OCH_2CF_3)_{4-n}}$$

In one case (n = 0) it was possible to isolate the pure phosphorane, $P(OCH_2CF_3)_5$ by distillation. The major non-phosphorus containing product (ca. 90%) of the thermolysis of this phosphorane as determined by doping the ^{19}F NMR spectra with authentic samples was trifluoroethanol (**8**) together with hexafluorodiethyl ether (**9**, ca. 6%) and small quantities (<5%) of other, not fully identified fragments containing fluorine. In the presence of (**4**)—the by-product of the sulphenate ester reaction, the *rate* of thermolysis of (**3**, n = 0) remained the same but the *ratio* of (**8**) to (**9**) was reduced and a substantial quantity of a non-phosphorus containing product with δ ^{19}F = −67 (t, J_{FH} = 9.5 Hz) was observed which was assigned to $PhSCH_2CF_3$ (**17**) by comparison with the literature.[5] The minor non-phosphorus products included a ^{19}F signal at −81 (d, J_H = 3 Hz) which is consistent with CF_3CHO[6] and a doublet at −68.5 (J_H = 7.8 Hz) which may be due to $CF_3CH{=}CHCF_3$.[6]

The thermal decomposition may then be rationalised by Scheme I and although other routes may be envisaged to arrive at the products it is clear that the crucial intermediate is (**10**) leading by proton abstraction to (**11**) and the alcohol (**8**) followed by fragmentation to either the carbene (**12**)—the major route, or the aldehyde (**13**). The carbene can also undergo a known[7] rearrangement to the volatile alkene (**14**) which could be lost by evaporation, dimerise to (**15**) or react with Ph_2S_2 *via* (**16**) to form (**17**). Finally (**10**) may also rearrange through hydride transfer within the alkoxide ion to (**18**) and (**6**) which may disproportionate to (**3**) and (**7**). All of these reactions could be explained by homolytic cleavage of the P—O bond but the kinetic data presented below, which is the most important

†Small quantities (<2%) of $Ar_nPF_2(OCH_2CF_3)_{3-n}$ (**7**) for n = 1–3 were also detected by ^{19}F nmr presumably formed by disproportionation of (**6**).



SCHEME I

feature of the work, indicates heterolytic rather than homolytic decomposition of the phosphoranes.

The kinetics of each reaction were followed by ^{31}P NMR using the disappearance of phosphorane as the appropriate monitor.‡ First order kinetics were obeyed up to 90% reaction and the rate coefficients at a series of temperatures together with the resultant activation parameters are shown in Table II. It is clear from these data that the reaction rates follow the sequence $Ph_3P(OCH_2CF_3)_2 > Ph_2P(OCH_2CF_3)_3 > PhP(OCH_2CF_3)_4 > P(OCH_2CF_3)_5$ with an overall rate difference of 530,000

‡Response factors for both phosphorane and product oxide were determined in advance of the kinetic experiments.

TABLE II

Rate coefficients and activation parameters for the decomposition of (3) in hydrocarbon solvents

T/K (± 2)	$10^6 k_1/s^{-1}$	E_A (kJ mol^{-1})	$\Delta s^{\pm}$ (JK^{-1} mol^{-1}) @ 298 K
n = 3; solvent: mesitylene			
388	98 ± 4		
385	83 ± 3	127	-2
378	30 ± 1		
298 (calc)	6.5×10^{-4}		
n = 2; solvent: mesitylene			
408	104 ± 6		
403	94 ± 4		
401	66 ± 4	143	+22
396	40 ± 3		
393	31 ± 2		
388	12 ± 2		
298 (calc)	2.2×10^{-5}		
n = 1; solvent: decalin			
453	64 ± 2		
448	42 ± 2	171	+46
444	26 ± 3		
441	22 ± 1		
438	13 ± 1		
298 (calc)	4.1×10^{-9}		
n = 0; solvent: decalin			
455	47 ± 2		
448	21 ± 2	175	+47
444	16 ± 1		
298 (calc)	1.2×10^{-9}		

(= 33 kJ mole^{-1}) at 298 K. This is consistent with ionization as the rate limiting step with the slowest reaction corresponding to the least stable alkoxyphosphonium ion with four electron withdrawing trifluoroethoxy groups attached to phosphorus. Most of the free energy of activation appears as the enthalpy of reaction associated with cleavage of a phosphorus-oxygen bond and the increasingly positive activation entropies from n = 3 ($\Delta s^{\pm} = -2$ J mol^{-1} K^{-1}) to n = 0 ($\Delta s^{\pm} = 47$ J mol^{-1} K^{-1}) are consistent with this interpretation. If the thermolysis involved rate-limiting homolytic fission, a P—O bond would be broken in each case and one would not expect the enthalpy of activation to rise by 50 kJ mol^{-1} over the series from n = 3 to n = 0.

Since the principal decomposition route is *via* (**10**) it is possible that the rate determining step involves abstraction of a proton to form (**11**). In order to resolve this problem, two fully deuterated phosphoranes (**19**) and (**20**), were prepared and their rates of thermolysis were monitored relative to their protonated analogues

TABLE III

Deuterium isotope effects for the thermolysis of (3) with n = 3 and n = 0

Phosphorane	10^6k (s^{-1})	k_H / kD
$Ph_3P(OCH_2CF_3)_2$	46.4 +/- 1.0*	
		1.01 +/- 0.05
$Ph_3P(OCD_2CF_3)_2$	46.1 +/- 2.0*	
$P(OCH_2CF_3)_5$	3.63 +/- 0.11^S	
		1.18 +/- 0.04
$P(OCD_2CF_3)_5$	3.05 +/- 0.07^S	

* At 110 °C $ At 178 °C

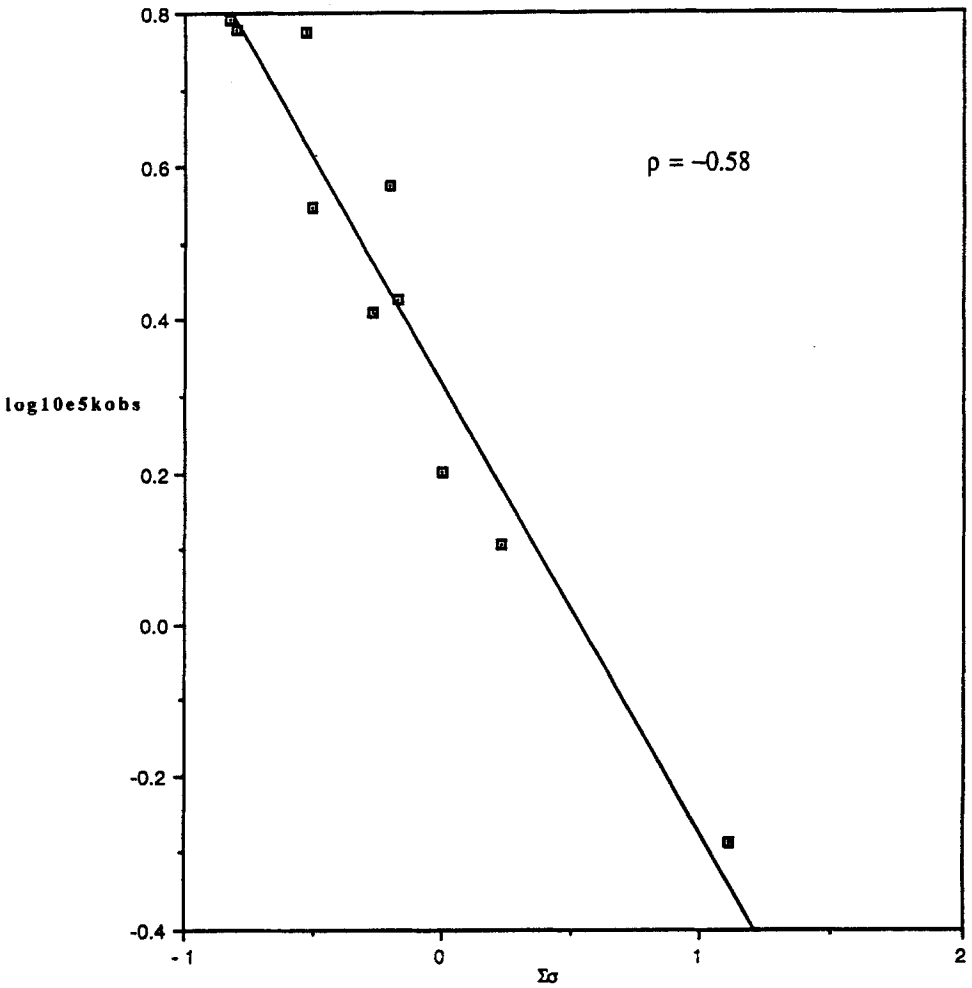


FIGURE 1 Hammett plot of log k_x/k_H *vs* $\Sigma\sigma$ for the thermolysis of (3, n = 3) at 125°C in mesitylene.

by ^{31}P NMR. The results (Table III) reveal k_H/k_D = 1.01 (±0.05) for (**19**) and 1.18 (±0.04) for (**20**) showing conclusively that there is no significant isotope effect and the rate-limiting step must therefore be the dissociation of the phosphoranes.

$Ph_3P(OCD_2CF_3)_2$ (**19**) $P(OCD_2CF_3)_5$ (**20**)

Hammett ρ-values were determined for the series with n = 3 and n = 1 by varying substituents in the aryl groups (Figures 1 and 2). The correlation in each case was with $\Sigma\sigma$[8,9] and by determining three ρ-values for n = 3 at three different temperatures (Table IV), an extrapolation enabled comparison of the ρ-values for n = 3 and n = 1 at 453 K.

Three points emerge from these data. In the first place, the negative ρ-values support the proposal of positive charge developing on phosphorus in the transition

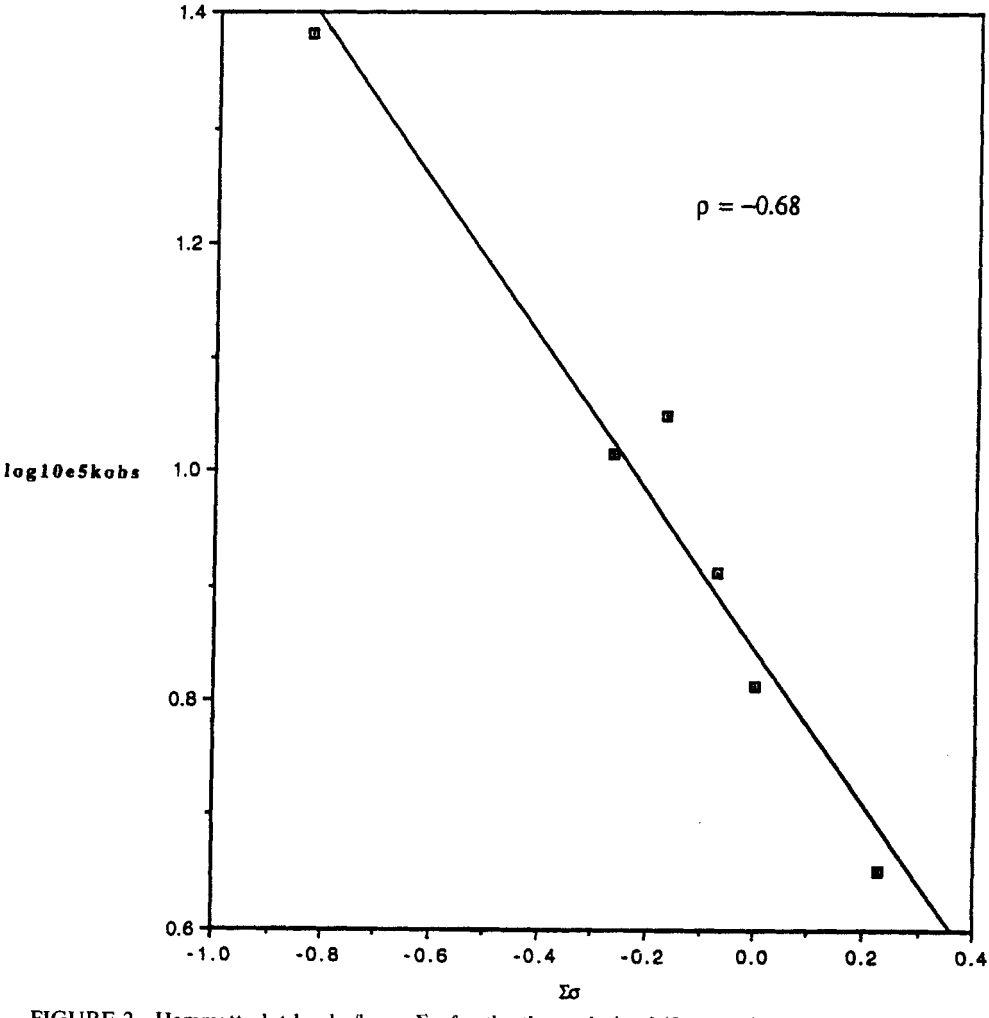


FIGURE 2 Hammett plot log k_X/k_H *vs* $\Sigma\sigma$ for the thermolysis of (**3**, n = 1) at 180°C in decalin.

TABLE IV

Hammett ρ-values for the thermolysis of (3, n = 3) at various temperatures

T (°C)	ρ	r
105	-0.58 ± 0.05	0.97
115	-0.53 ± 0.07	0.95
125	-0.49 ± 0.05	0.99

state. Secondly, the slower reaction (for n = 1) corresponds to the higher ρ-value (-0.67 *vs* -0.30 for n = 3) in line with the R.S.P.,[10,11] although the difference is small for a rate ratio at 298 K = 1.6×10^5 ($\equiv \delta\Delta G^{\neq}$ = 30 kJ mol^{-1}). Finally the magnitudes of the ρ-values point to only a low degree of positive charge developing on phosphorus which is analogous to the reaction of trico-ordinated phosphorus compounds with diethyl peroxide to form phosphoranes[8] and suggests that the transition states resemble ion-pairs (cf. Reference 2) rather than solvent-separated ions. In support of this hypothesis, the solvent effect for n = 3 between mesitylene (dielectric constant = 2.3) and 50:50 mesitylene-benzonitrile (*calculated* dielectric constant = 15.5) is a factor of only 1.8. This is again reminiscent of the peroxide reaction[8] and is not consistent with the development of a full positive charge on phosphorus.

EXPERIMENTAL

^{1}H, ^{19}F and ^{31} NMR spectra were recorded on Bruker HFX 90 or Bruker WM 250 instruments with TMS (^{1}H), $CFCl_3$ (^{19}F) and H_3PO_4 (^{31}P) as the reference signals in each case. Mass spectra were obtained through the University of London Intercollegiate Research Service operating from the School of Pharmacy, Brunswick Square, London.

The triarylphosphines (1, n = 3) were either available commercially or were prepared as described previously[8,9] and were characterised by m.p., ^{1}H and ^{31}P NMR. 2,2,2-Trifluoroethanol and d_3-trifluoroethanol were used as available commercially from Aldrich and Goss Scientific respectively.

Preparation of 2,2,2-trifluoroethyldiphenylphosphinite (1, *n = 2, Ar = Ph*)

A solution of 2,2,2-trifluoroethanol (6.9 g, 69 mmol) in THF (30 ml) was added, dropwise under nitrogen, over a period of 1 h to a stirred solution of diphenylphosphinous chloride (15.0 g, 68 mmol) and triethylamine (6.9 g, 68 mmol) in THF (120 ml) at −15°. The reaction mixture was allowed to warm to ambient and was stirred for a further 6 h. The precipitated amine hydrochloride was removed by filtration and the volatiles were removed under reduced pressure leaving 15.0 g (78%) of a pale yellow oil which was distilled through a 10 cm Vigreux column to give the product as a colourless oil of b.p. 97–98° @ 0.7 mm (lit.[2] 130° @ 2.5 mm). δ ^{31}P (C_6D_6) + 125.9 δ ^{1}H ($CDCl_3$) 4.15 (oct., $^3J_{PH}$ = 8.0 Hz, $^3J_{FH}$ = 8.0 Hz, 2 H) and 7.55 (m, 10 H), δ ^{19}F ($CDCl_3$/$CFCl_3$) −75.4 (sext., $^3J_{FH'}$ = 8.0 Hz, $^4J_{PF}$ = 5.9 Hz).

Preparation of bis-(2,2,2-trifluoroethyl)arylphosphonites (1, *n = 1*)

These were prepared from the corresponding arylphosphonous dichloride and a typical procedure for the phenylphosphonite is detailed below. Table V reports the yields, b.p. data, rmm values (by m.s.) and ^{31}P NMR shifts of the arylphosphonites.

A solution of 2,2,2-trifluoroethanol (13.35 g, 135 mmol) in THF (25 ml) was added, dropwise under nitrogen to a cooled (−10°), stirred solution of phenylphosphonous dichloride (11.70 g, 65 mmol) and triethylamine (13.50 g, 134 mmol) in THF (100 ml). The mixture was allowed to warm to ambient and

TABLE V

Yields, b.p.'s and ^{31}P n.m.r. chemical shifts of the series of bis-(2,2,2-trifluoroethyl) arylphosphonites

PHOSPHONITE	YIELD/%	BOILING POINT	$\delta^{31}P$ ($CDCl_3$)
X = H	65	63-63° @ 0.35 mm	+166.0[a]
X = *p*-Cl	69	71-72° @ 0.01 mm	+165.9
X = *m*-Me	64	55-56° @ 0.03 mm	+167.7
X = *p*-Me	64	55-56° @ 0.03 mm	+167.9
X = *p*-Me_2N	36	120-122° @ 0.9 mm	+170.4
X = *p*-MeO	59	95-99° @ 1 mm	+166.9[a]

[a]Solvent : C_6D_6

stirring was continued for a further 4 h. The triethylamine hydrochloride precipitate was removed by filtration and the volatiles were removed, under reduced pressure, from the filtrate leaving a yellow oil. This was distilled through a 20 cm, Vigreux column to yield 12.85 g (65%) of a colourless oil of b.p. 63–64° @ 0.35 mm (lit.[2] 48° @ 0.1 mm). δ ^{31}P (C_6D_6) + 166.0, δ ^1H ($CDCl_3$), 4.13 (m, 4 H) and 7.50 (m, 5 H), δ ^{19}F ($CDCl_3/CFCl_3$) −75.6 (sext., $^3J_{FH}$ = 8.5 Hz, $^4J_{PF}$ = 3.5 Hz).

Preparation of tris-(2,2,2-trifluoroethyl)phosphite

A mixture of 2,2,2-trifluoroethanol (15.3 g, 0.153 mol) and phosphorus trichloride (7.0 g, 0.051 mol) was stirred in a R.B. flask fitted with a reflux condensor under an atmosphere of nitrogen. Hydrogen chloride gas was expelled vigorously at the beginning of the reaction. The reaction vessel was heated to 80–90° for 4 h, cooled to ambient and allowed to stand for 14 h. The mixture was then distilled through a 20 cm Vigreux column to give 11.5 g (71%) of a light colourless oil of b.p. 65–70° @ 16 mm (lit.[13] 130–131° @ 743 mm). δ ^{31}P ($CDCl_3$) = 139.1, δ ^1H ($CDCl_3$) 4.24 (oct., $^3J_{PH}$ = 8.2 Hz, $^3J_{FH}$ = 8.2 Hz), δ ^{19}F ($CDCl_3/CFCl_3$) − 75.9 (sext., $^3J_{FH}$ = 8.2 Hz, $^4J_{PF}$ = 4.5 Hz).

Preparation of Tetracoordinate Oxides (**5**, *n = 0–3*)

A series of tetracoordinate oxides (**5**, n = 0–2) were prepared by oxidation of the respective tricoordinate using standard procedures.[14] Table VI quotes yields, b.p.'s and spectroscopic data for the three oxides. Triphenylphosphine oxide (n = 3) was obtained commercially (BDH).

Preparation of 2,2,2,2',2',2'-hexafluorodiethylether (**9**)

The compound was prepared by treatment of 2,2,2-trifluoroethyl tosylate with sodium 2,2,2-trifluoroethoxide.[15]

2,2,2-Trifluoroethyl Benzenesulphenate (**2**)

This compound was prepared from 2,2,2-trifluoroethanol and phenylsulphenyl chloride.[2] The same method using d-$_3$-trifluoroethanol gave 2,2,2-trifluoroethyl(d_2) benzene sulphenate, b.p. 102–105°/13 mm, with M^+ = 210 (calc. for $C_8H_5D_2F_3OS$ = 210). Found: C, 45.54; H = 3.32%; calc. C, 45.71, H (calc. as H + D), 3.36%.

Reactions of (**2**) *with* (**1**, *n = 0–3*)

(a) n = 1–3: A solution of the tricoordinated phosphorus nucleophile (0.48 mmol) in deuteriotoluene (1.5 ml) was added, dropwise with stirring at −78° to a solution of 2,2,2-trifluoroethyl benzenesulphenate (0.2 g, 0.96 mmol) in deuteriotoluene (1.5 ml). The mixture was allowed to warm to ambient and ^1H, ^{31}P and ^{19}F n.m.r. spectra were recorded which were consistent with the formation of a single product (Table VII).

TABLE VI

Yields, boiling points and spectroscopic data for the oxides (5, n = 0–2)

(5)	% Yield	b.p.[a]	δ^1H ($CDCl_3$)	δ_{31}P ($CDCl_3$)
n = 0	95	105-110° @ 12 mm (lit.[14] 186-189° @ 760 mm)	4.48 (oct. $^3J_{HF}$ =8, $^3J_{HP}$ = 8Hz)	-2.5
n = 1	92	120-130° @ 0.1 mm	4.54 (oct. $^3J_{HF}$ = 8Hz $^3J_{HP}$ = 8Hz, 4H) and 7.30-8.20 (m, 5H)	+21.3
n = 2	91	145-150° @ 0.2 mm	4.35 (oct., $^3J_{HF}$ = 8Hz, $^3J_{HP}$ = 8 Hz, 2H) and 7.35 - 8.25 (m, 10H)	+34.4

[a]Kugelrohr distillations

TABLE VII

Spectroscopic data for (3, R = CH_2CF_3, n = 0–3) and for $PhSP(OCH_2CF_3)_4$

PHOSPHORANE	δ^{31}P (C_7D_8)	δ^1H (C_7D_8)	δ^{19}F(C_7D_8)
$Ph_3P(OCH_2CF_3)_2$	-59.1	2.95 (oct. $^3J_{PH}$ = 4.5 Hz, $^3J_{FH}$ = 8.8Hz, 4H) and 7.10 - 8.35 (m, 15H)	-75.3 (t)
$Ph_2P(OCH_2CF_3)_3$	-44.5	3.80 (mound[a], 6H) and 7.20 - 8.10 (m, 10H)	-74.4 (mound[a], 2F) -75.4 (mound[a], 2F)
$PhP(OCH_2CF_3)_4$	-61.3	4.10 (oct., $^3J_{PH}$ = 5.0Hz, $^3J_{FH}$ = 8.4Hz, 8H) and 7.20 - 7.85 (m, 5H)	-75.2 (t)
$P(OCH_2CF_3)_5$	-77.2	4.22 (oct., $^3J_{PH}$ = 8.2Hz, $^3J_{FH}$ = 8.2Hz)	-75.7 (t)
$PhSP(OCH_2CF_3)_4$	-51.8	4.15 (oct, $^3J_{PH}$ = 8.2Hz, $^3J_{FH}$ = 8.2Hz, 8H) and 7.40 - 7.75 (m, 5H)	-75.3 (t)

[a]Broad peaks due to slow (on the n.m.r. time scale) ligand reorganisations [2]

(b) n = 0: A solution of tris-(2,2,2-trifluoroethyl)phosphite (0.157 g, 0.48 mmol) in deuteriotoluene (1.5 ml) was added, dropwise with stirring at −78° to a solution of 2,2,2-trifluoroethyl benzenesulphenate (0.2 g, 0.96 mmol) in deuteriotoluene (1.5 ml). The mixture was allowed to warm to ambient and was stirred for 12 h, when ^{1}H, ^{31}P and ^{19}F n.m.r. spectra were recorded which were consistent with the formation of a single product (Table VII).

TABLE VIII

^{31}P chemical shifts of a series of substituted bis-(2,2,2-trifluoroethoxy) trisarylphosphoranes (n = 3) and tetrakis-(2,2,2-trifluoroethoxy)arylphosphoranes (n = 1)

$(X^{1-3}C_6H_4)_3P(OCH_2CF_3)_2$	$\delta^{31}P$ (C_7D_8)	$XArP(OCH_2CF_3)_4$	$\delta^{31}P$ (Decalin)[a]
$X^1 = X^2 = X^3 = H$	-59.1	X = H	-60.2
$X^1 = X^2 = X^3 = p$-Cl	-59.8	X = *p*-Cl	-61.4
$X^1 = X^2 = X^3 = p$-Me	-59.3	X = *p*-MeO	-60.0
$X^1 = H, X^2 = X^3 = p$-MeO	-59.9	X = *m*-Me	-59.9
$X^1 = X^2 = X^3 = m$-Cl	-60.9	X = *p*-Me	-59.8
$X^1 = X^2 = H, X^3 = pMe_2N$	-59.2	X = *p*-Me_2N	-58.9
$X^1 = X^2 = X^3 = p$MeO	-60.2		
$X^1 = X^{-2} = H, X^{-3} = p$-Br	-59.1		
$X^1 = X^2 = H, X^3 = p$-MeO	-59.3	[a]External DMSO-d_6 lock.	
$X^1 = X^2 = H, X^3 = p$-Me	-59.2		
$X^1 = X^2 = X^3 =$ *p*-F	-60.4		
$X^1 = X^2 = X^3 =$ *m*-Me	-59.5		
$X^1 = X^2 = H, X^3 = o$-MeO	-54.5		

By varying the *m*- and *p*-substituents in the aryl groups attached to phosphorus a series of bis-(2,2,2-trifluoroethoxy)trisarylphosphoranes (**3**, n = 3) and tetrakis-(2,2,2-trifluoroethoxy)arylphosphoranes (**3**, n = 1) were prepared using the same procedures as for the parent compounds. The ^{31}P chemical shift of each material appears in Table VIII.

Thiophenyltetrakis-(2,2,2-trifluoroethoxy)phosphorane, $PhSP(OCH_2CF_3)_4$, and penta-(2,2,2-trifluoroethoxy)phosphorane, $P(OCH_3CF_3)_5$, were also synthesized and isolated on a preparative scale in 67% and 75% yields respectively using the method of Denney, b.p. 101–102° @ 1.1 mm (lit. 72° @ 0.15 mm)[2] and 55–56° @ 0.7 mm (lit. 44° @ 00.15 mm)[2] respectively.

REFERENCES

1. L. L. Chang, D. B. Denney, D. Z. Denney and R. J. Kazior, *J. Amer. Chem. Soc.*, **99**, 2293 (1977).
2. D. B. Denney, D. Z. Denney, P. J. Hammond and Yu-Pin Wong, *J. Amer. Chem. Soc.*, **103**, 1785 (1981).
3. a) W. C. Archie Jr. and F. H. Westheimer, *J. Amer. Chem. Soc.*, **95**, 5955 (1973); b) N. Lowther and C. D. Hall, *J. Chem. Soc., Chem. Commun.*, 1303 (1985).
4. A. Queen, A. E. Lemire and A. F. Janzen, *Internat. J. Chem. Kin.*, **13**, 411 (1981).
5. T. Nakai, K. Tanaka and N. Ishikawa, *J. Fluorine Chem.*, **9**, 89 (1977).
6. "Annual Reports on NMR Spectroscopy," Vol. 10b, Academic Press, London, 1980.
7. R. Fields and R. N. Haszeldine, *Proc. Chem. Soc.*, 22 (1960).
8. R. J. Lloyd, N. Lowther and C. D. Hall, *J. Chem. Soc., Perkin 2*, 245 (1985).
9. J. R. Lloyd, N. Lowther, G. Szabo and C. D. Hall, *J. Chem. Soc.*, 1813 (1985).
10. C. D. Johnson, *Chemical Reviews*, **75**, 755 (1975).
11. D. J. McLennan, *Tetrahedron*, 2331 (1978).
12. G. M. Kosalopoff and L. Maier, "Organic Phosphorus Compounds," Vol. 1, Wiley Interscience, New York, 1972.
13. L. C. Krogh, T. S. Reid and H. A. Brown, *J. Org. Chem.*, **19**, 1124 (1954).
14. G. M. Kosalopoff and L. Maier, "Organic Phosphorus Compounds," Vol. 3, Wiley Interscience, New York, 1972.
15. Pennsalt Chemicals Corp., B.P. 814, 493, CA, **54**, 1315.