

Received: December 15, 1976

ORGANOPHOSPHORUS CHEMISTRY. PART 18. POSSIBLE INTERVENTION  
OF A PHOSPHA-ALKENE IN THE REACTIONS OF A FLUOROALKYLPHOSPHINE  
WITH ALKOXIDES\*

R. N. HASZELDINE, D. R. TAYLOR and E. W. WHITE

Chemistry Department, University of Manchester Institute of  
Science and Technology, Manchester M60 1QD (Gt. Britain)

SUMMARY

Thermal reactions of phenylphosphine with tetrafluoroethylene and 1,1-difluoroethylene give, respectively, a mixture of phenyl-1,1,2,2-tetrafluoroethylphosphine and 1,2-bis-(phenylphosphino)tetrafluoroethane, and phenyl-2,2-difluoroethylphosphine. The phenyltetrafluoroethylphosphine reacts with an excess of ethanolic or methanolic alkoxide to give the corresponding alkyl phenyl-(E)-1-fluoro-2-alkoxyvinylphosphinite and minor amounts of the isomeric alkyl phenyl-(Z)-2-fluoro-2-alkoxyvinylphosphinite. The use of an equimolar proportion of sodium methoxide enables the intermediate products methyl phenyl-1,2,2-trifluoroethylphosphinite and methyl phenyl-(E)-1,2-difluorovinylphosphinite to be isolated: further reaction of these with methoxide yields the corresponding (E)-1-fluoro-2-methoxyvinylphosphinite. The reactions are discussed in terms of mechanisms which involve either an intermediate phospho-alkene or a hydride ion shift.

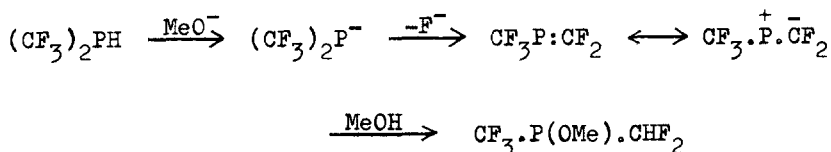
INTRODUCTION

Reactions between primary and secondary polyfluoroalkylphosphines and nucleophilic reagents such as amines and alkoxides have been postulated [2-4] to proceed via short-

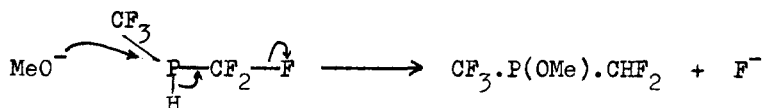
---

\* Part 17: Ref. [1].

lived intermediates termed phospho-alkenes,  $RP:CFR' \longleftrightarrow R\overset{+}{P}.CFR'$ , formed by dehydrofluorination of a  $-PH.CF<$  group. Subsequent addition to the supposed P:C bond can then give the isolated products, e.g.



An alternative to this elimination-addition sequence is a hydride ion shift mechanism in which migration of hydride from phosphorus to  $\alpha$ -carbon occurs during attack by the nucleophile upon phosphorus, e.g.



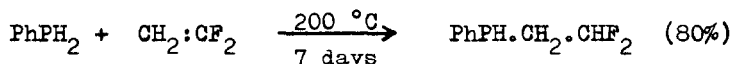
A similar hydride ion shift was invoked to explain the negligible incorporation of deuterium from solvent  $D_2O$  during the NaOD catalysed hydrolysis of chloromethylphosphinic acid to methylphosphonic acid [5], and was later postulated also to occur, albeit in competition with a phospho-alkene pathway, in reactions between methyl chloromethylphosphinate and Grignard reagents [6].

Reactions between phenyl-1,1,2,2-tetrafluoroethylphosphine and nucleophiles have now been studied to determine whether any evidence could be found of stabilisation of the phospho-alkene bond by an adjacent phenyl group. Related intermediates, e.g.  $PhP=O$  and  $PhP=S$ , have been chemically trapped [7], and recently three phospho-alkenes ( $CF_2:PH$ ,  $CH_2:PH$ , and  $CH_2:PCl$ ) were detected by microwave spectroscopic analysis of the products of pyrolysis of, for example,  $CF_3.PH_2$  at  $1000^\circ C$  [8].

## RESULTS AND DISCUSSION

The required precursor,  $PhPH.CF_2.CF_2H$ , was obtained by the thermally initiated addition of phenylphosphine to tetrafluoroethylene [9] in much improved yield (routinely over 80%).

Its formation was accompanied by low yields of 1,2-bis(phenylphosphino)tetrafluoroethane, but not by the previously reported by-product, phenyl-bis(1,1,2,2-tetrafluoroethyl)phosphine [9], which is presumably formed only when an excess of tetrafluoroethylene is used. Observation of the bis(phenylphosphino)ethane strongly favours a free-radical addition mechanism propagated by  $\text{PhPH}^\bullet$  radicals, a process analogous to the established mechanisms for addition of phosphine and dialkylphosphines to tetrafluoroethylene [10-12]. Consistent with this, but at odds with a mechanism involving nucleophilic addition of phenylphosphine, is our observation that phenylphosphine reacts thermally with 1,1-difluoroethylene to yield phenyl-2,2-difluoroethylphosphine, without detectable formation of the reverse adduct, phenyl-1,1-difluoroethylphosphine.



Reaction of Phenyl-1,1,2,2-tetrafluoroethylphosphine with an Excess of Alkoxide

Slow addition of the secondary phosphine to an excess of methanolic sodium methoxide led to a mildly exothermic reaction accompanied by deposition of sodium fluoride. Distillation of the organic material led to two fractions, both of which were found to contain mainly (> 90%) methyl phenyl-(E)-1-fluoro-2-methoxyvinylphosphinite (Ia) (74% yield). One of the contaminating by-products appears to be the related (Z)-2-fluoro-2-methoxyvinylphosphinite (IIa) (4%), but the more volatile third product (ca. 2%) was unidentified.

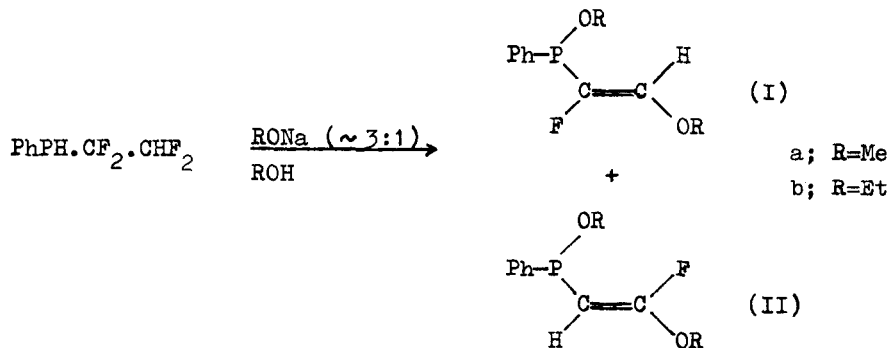


TABLE 1

N.m.r. Parameters of Unsaturated Products

Parameter <sup>a</sup>	Compound: (Ia) <sup>b</sup>	(Ib) <sup>c</sup>	(IV) <sup>d</sup>
$\delta_{\text{Ph}}$	-0.6m	-0.6m	-0.5m
$\delta_{\text{POR}}$	3.4dd	3.1dq, 5.7t	3.4dd
$\delta_{\text{:COR}}$	3.4s	3.1q, 5.7t	
$\delta_{\beta\text{H}}$	0.6dd	0.5dd	0.4ddd
$\delta_{\alpha\text{F}}$	72.4dd	72.4dd	69.9q
$\delta_{\beta\text{F}}$			59.4ddd
${}^2J_{\text{HF}}$			74.2
${}^3J_{\text{HF}}$	22.7	22.6	17.4
${}^3J_{\text{FF}}$			17.5
${}^2J_{\text{PF}}$	10.2	9.6	ca. 17
${}^3J_{\text{PF}}$			29.4
${}^3J_{\text{F}\beta\text{H}}$	6.0	6.0	4.2
${}^3J_{\text{FPOCH}}$	13.0	ca. 10	14.4

<sup>a</sup>Chemical shifts in p.p.m. (positive upfield);  $|J|$  in Hz.

<sup>b</sup>(E)-PhP(OMe).CF:CH.OMe, containing 5% (Z)-PhP(OMe).CH:CF.OMe which has  $\delta_{\beta\text{F}} = 83.8$  p.p.m., dd,  ${}^3J_{\text{HF}} = 24$ ,  ${}^3J_{\text{PF}} = 55$  Hz.

<sup>c</sup>(E)-PhP(OEt).CF:CH.OEt, containing 9% (Z)-PhP(OEt).CH:CF.OEt which has  $\delta_{\beta\text{F}} = 85.6$  p.p.m., dd,  ${}^3J_{\text{HF}} = 24$ ,  ${}^3J_{\text{PF}} = 64$  Hz.

<sup>d</sup>(E)-PhP(OMe).CF:CHF containing 50% PhP(OMe).CHF.CHF<sub>2</sub> (data in Table 2).

The structural assignment of (Ia) follows from its n.m.r. spectrum (Table 1). The disposition of the olefin's substituents is dictated by (i) the HC:CF coupling constant ( ${}^3J_{\text{HF}}$  22.7 Hz) which is too large for a cis coupling and too small for a

TABLE 2

N.m.r. Parameters of Saturated Products

Parameter <sup>a</sup>	PhPH.CF <sub>2</sub> .CHF <sub>2</sub> <sup>b</sup>	(PhPH.CF <sub>2</sub> ) <sub>2</sub> <sup>c</sup>	PhPH.CH <sub>2</sub> .CHF <sub>2</sub> <sup>d</sup>	(III) <sup>e</sup>
$\delta_P$	51dt	f	f	f
$\delta_{\underline{PH}}$	2.0dtt	1.9dtm	2.8dt	
$\delta_{Ph}$	-0.8m	-0.8m	-0.4m	-0.5m
$\delta_{Me}$				3.4dd
$\delta_{\alpha H}$			4.7m	f
$\delta_{\beta H}$	1.2ttd		1.1ttd	f
$\delta_{\alpha F}$	32.4d <sup>g</sup>	22.0m		140m
$\delta_{\beta F}$	56.4dm	22.0m	32.2d <sup>h</sup>	48.8m

<sup>a</sup>Chemical shifts in p.p.m. (positive upfield); moduli of spin-spin coupling constants in Hz (see footnotes).

<sup>b</sup> $^2J_{HF} = 53.8$ ,  $^3J_{\beta HF} = 4.6$ ,  $^3J_{HF} = 18.6$ ,  $^4J_{HF} = 3.0$ ,  $^2J_{PF} = 82.6$ ,

$^1J_{PH} = 224$ ,  $^3J_{PH} = 1.8$  Hz.

<sup>c</sup>In CCl<sub>4</sub> solution;  $J_{PH}$  ca. 228,  $J_t$  ca. 15.6 Hz.

<sup>d</sup> $^2J_{HF} = 56.4$ ,  $^1J_{PH} = 228$ ,  $^3J_{\alpha H\beta H} = 4.8$ ,  $^3J_{H\beta H} = 6.9$  Hz.

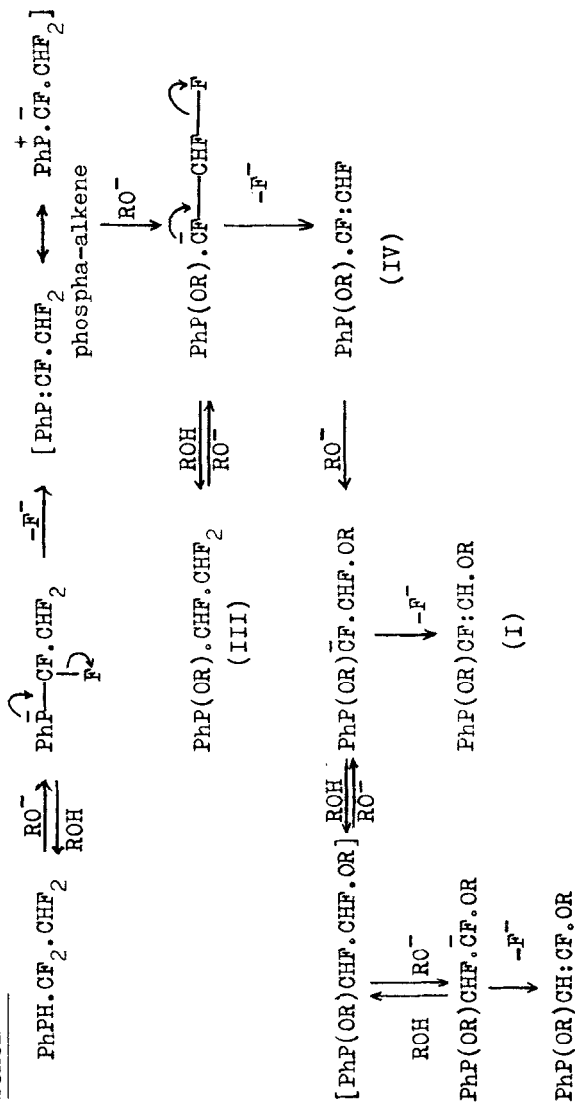
<sup>e</sup>PhP(OMe).CHF.CHF<sub>2</sub> containing 50% PhP(OMe).CF:CHF (data in Table 1); 94 MHz spectrum shows (III) to be 60:40 mixture of two diastereoisomers, the  $\alpha$ -F as two overlapping ddt,  $|J|/Hz$  ca. (minor diastereoisomer first):  $J_{\alpha F\beta H} = 9, 10$ ;  $J_{\alpha F\beta F} = 17, 18$ ;  $J_{\alpha F\alpha H} = 46, 47$ ;  $J_{\alpha FP} = 117, 103$ .

<sup>f</sup>Parameters not measured.

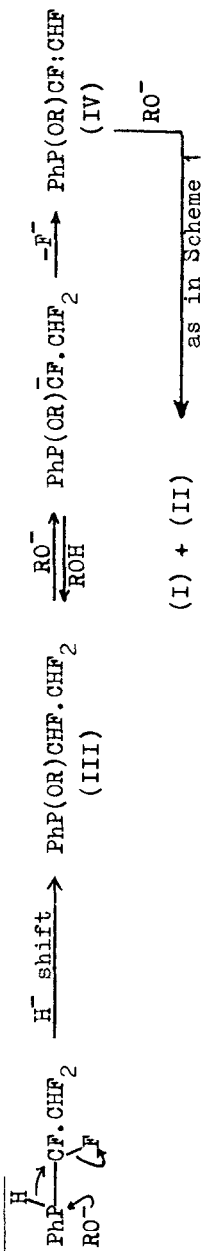
<sup>g</sup>AB type;  $J_{AB} = 298$  Hz, each portion as ddq,  $\delta_{AB} = 158$  Hz.

<sup>h</sup>AB type;  $J_{AB}$  ca. 280 Hz, not fully analysed.

Scheme 1



Scheme 2



geminal coupling [13,14], and (ii) the value of the PF coupling constant ( $^2J_{\text{PF}}$  10.2 Hz), which lies well outside the 53-84 Hz range associated with cis-FC:CP coupling [15,16]. Furthermore, the value of the HC:CP coupling constant ( $^3J_{\text{HP}}$  6 Hz) compares favourably with the value reported for the E-isomer of  $\text{Me}_2\text{P.CF:CH.CF}_2$  but is much smaller than that quoted for the corresponding Z-isomer [12].

Additional evidence in favour of (Ia), as opposed to any isomeric 1-H-2-F-vinylphosphinite, is provided by the result of an experiment in which phenyltetrafluoroethylphosphine was treated with an excess of sodium methoxide in methanol-O-d. The fluorovinylphosphinite obtained was found by mass spectrometry and n.m.r. to contain no deuterium. Routes to vinylphosphinites with a 1-proton [e.g., (IIa)] would require early and rapid exchange with MeOD at that position (see Schemes 1 and 2).

The 4% component in the main fraction of the phosphinite, detectable by  $^{19}\text{F}$  n.m.r. spectroscopy as a low intensity doublet of doublets, could not be removed or isolated but is taken to be an isomer of (Ia) on the basis of the elemental and mass analysis of the mixture. The n.m.r. data (Table 1) are consistent with (IIa); both a :CHF group and a cis-HC:CF geometry are excluded by the fluorine coupling constants observed (24 and 55 Hz), and the assignment of the smaller J-value to a trans-HC:CF element leads to the assignment of the other to a cis-PC:CF component, since it is too large for a geminal PCF arrangement [13-16]. Unfortunately it was not possible to determine whether this minor product incorporated deuterium in the MeONa-MeOD experiment.

Treatment of phenyltetrafluoroethylphosphine with a threefold excess of sodium ethoxide in anhydrous ethanol similarly gave ethyl phenyl-(E)-1-fluoro-2-ethoxyvinylphosphinite (Ib) (73%), readily identified by spectroscopic comparisons with (Ia). Two minor components were again detected, one of which appears to be (IIb) (6%) on the basis of  $^{19}\text{F}$  n.m.r. analysis (data in Table 1).

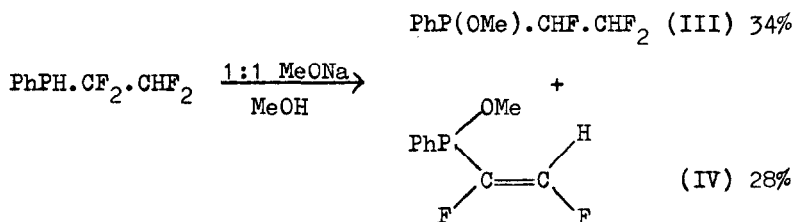
The formation of the observed products can be explained on the basis of either a mechanism involving an intermediate phospho-alkene (Scheme 1), or a pathway initiated by a hydride ion shift from phosphorus to  $\alpha$ -carbon (Scheme 2). Both routes necessitate the initial formation of the 1,2,2-trifluoroethylphosphinite (III) and its dehydrofluorination product (IV), which subsequently undergoes further reaction with alkoxide. Attempts were therefore made to isolate these intermediates using a deficiency of alkoxide.

Reaction of Phenyl-1,1,2,2-tetrafluoroethylphosphine with an Equimolar Proportion of Alkoxide

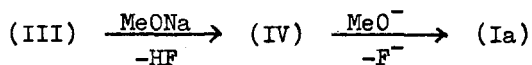
Using inverse addition to ensure that methoxide was never present in excess, the phenyltetrafluoroethylphosphine was converted by a 1:1 ratio of methanolic methoxide into a mixture of mainly two products which were identified without separation as the 1,2,2-trifluoroethylphosphinite (III) and the (E)-1,2-difluorovinylphosphinite (IV). Neither of the previously obtained products (Ia) and (IIa) were formed under these milder conditions.

The geometry of the vinyl group in (IV) is fixed by the value of  $^3J_{\text{FF}}$  (17.5 Hz), which is too small for a trans-coupling but is compatible with either a cis or a geminal arrangement [13,14]. However, the latter is excluded by the high observed coupling ascribed to :CHF ( $^2J_{\text{HF}}$  74 Hz), and a cis-FC:CF arrangement is therefore indicated. The 94 MHz  $^{19}\text{F}$  n.m.r. spectrum of the trifluoroethylphosphinite (III) (Table 2) reveals that a chiral centre is present, and in particular the CHF portion indicates that two diastereoisomers are present in roughly 60:40 proportions, an observation compatible only with a P.CHF.CHF<sub>2</sub> distribution of fluorines. After unsuccessful attempts to isolate pure samples of (III) and (IV), a sample of the mixture was treated with methanolic methoxide as a test of the mechanisms suggested.





The progress of their further reaction ultimately into essentially pure 1-fluoro-2-methoxyvinylphosphinite (Ia) was monitored by intermittent n.m.r. analysis of withdrawn samples, and the data obtained (Table 3) strongly suggest a stepwise process:



with the two steps occurring at approximately the same rate.

TABLE 3

Composition (mol %) of (I)/(III)/(IV) Mixtures<sup>a</sup>

Time/min	(III)	(IV)	(Ia)
0	50	50	0
20 <sup>b</sup>	31	53	16
90 <sup>c</sup>	27	49	24
160 <sup>d</sup>	0	0	100

<sup>a</sup> Determined by <sup>19</sup>F n.m.r. analysis.

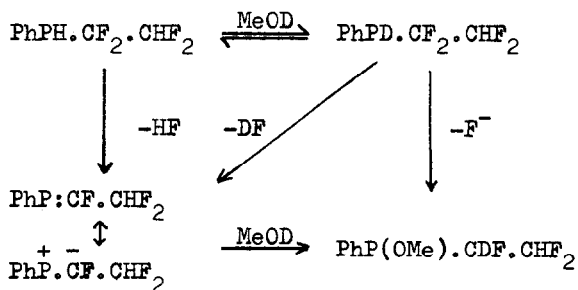
<sup>b</sup> At 0 °C.

<sup>c</sup> Further 60 min reflux, 10 min cooling.

<sup>d</sup> Additional MeONa added, further 60 min reflux, 10 min for evaporation to dryness.

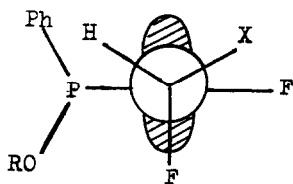
Mechanism of the Reaction

Proven formation of the intermediate products (III) and (IV) and the demonstration that their further treatment with alkoxide leads to (Ia), establishes that one or both of the pathways shown in Schemes 1-2 must be occurring. At first sight it would appear that treatment of the phosphine  $\text{PhPH.CF}_2.\text{CHF}_2$  with a deficiency of methoxide in methanol- $\text{O-d}$ , to test for any incorporation of deuterium at the  $\alpha$ -carbon atom of the trifluoroethylphosphinite (III), might discriminate between the two alternatives. However, earlier related experiments [17,18] had suggested that very rapid H for D exchange at phosphorus would almost certainly occur in the secondary phosphine under such conditions. For example, the half-life for H-D equilibration between bis(trifluoromethyl)phosphine and pure methanol- $\text{O-d}$  at 20 °C is ca. 5 min [17], and exchange is extremely rapid even between diethylphosphine and deuterium oxide [18]. Thus, any 1-D-1,2,2-trifluoroethylphosphinite detected in such an experiment could arise by either of the mechanistic pathways.

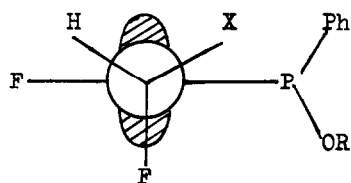


Nor does the striking stereospecificity of the reactions leading to (I) and (IV) offer a basis for selecting one pathway in preference to the other. Such stereospecificity is a common feature of vinylic substitutions which proceed via carbanions [19]. It presumably indicates that, of the two possible carbanion conformations (V-VI; X= F or OR), fluoride elimination occurs predominantly via (V), in which H and not X is placed in proximity of phosphorus and its substituent alkoxy and phenyl groups. Since the carbanion (V; X = F) can equally

well arise by alkoxide attack on the phospho-alkene  $\text{PhP:CF.CHF}_2$ , or by proton abstraction from (III) after a hydride ion shift, stereoselectivity could be expected with either mechanism.



(V)



(VI)

Thus whilst the formation of (III) and (IV) en route to (Ia) are fully consistent with Schemes 1 or 2, the evidence available does not yet provide a basis for distinction to be made between them.

## EXPERIMENTAL

Oxygen- and water-sensitive substances were manipulated under nitrogen, usually in a dry, oxygen-free, glove box vented directly to a fume chamber. Volatile compounds were stored and transferred using a conventional Pyrex vacuum system. N.m.r.: Perkin-Elmer R10, operated at 60 MHz for  $^1\text{H}$ , 24.29 MHz for  $^{31}\text{P}$ , and 56.46 MHz for  $^{19}\text{F}$ , Hitachi Perkin-Elmer R20A operated at 60 MHz for  $^1\text{H}$  and 56.46 MHz for  $^{19}\text{F}$ , and Varian HA100, operated at 100 MHz for  $^1\text{H}$  and 94.1 MHz for  $^{19}\text{F}$ , using pure liquid samples unless otherwise stated (chemical shifts quoted in p.p.m. rel. to external interchange samples of  $\text{C}_6\text{H}_6$  for  $^1\text{H}$ ,  $\text{CF}_3\text{CO}_2\text{H}$  for  $^{19}\text{F}$ , and 85%  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$ , positive values to high field of reference Mass spectrometry: A.E.I. MS902. Analytical g.l.c., when possible, was achieved for liquid samples using a Pye Model 104 chromatograph fitted with flame ionization detector and 2 m x 4.5 mm i.d. columns, and for gaseous samples using a Perkin-Elmer Model 116 chromatograph fitted with thermistor detectors and 7 m x 5 mm i.d. columns. Phenylphosphine, prepared on a

40-50 g scale in 80% yield by reduction of phenylphosphonous dichloride using lithium aluminium hydride in anhydrous ether [20] and purified by distillation at reduced pressure under  $N_2$ , was a colourless liquid, b.p. 40-41 °C at 10 mmHg (lit. [21] b.p. 41° at 11 mmHg); it was stored in sealed evacuated Pyrex ampoules (note: pyrophoric properties and nauseating odour).

Phenyl-1,1,2,2-tetrafluoroethylphosphine. - The method of Parshall *et al.* [9] was modified to enable 50 g quantities to be prepared safely and conveniently. A stainless steel autoclave (300 cm<sup>3</sup>) was provided with a removable but tight-fitting Pyrex liner vented through an anti-splash neck. In a typical experiment, phenylphosphine (29.3 g, 0.266 mol) and Terpene B polymerisation inhibitor (0.1 g) were placed in the liner under nitrogen, and the liner was firmly secured in the autoclave which was assembled and evacuated without admission of air. Tetrafluoroethylene (0.270 mol) was admitted, and the mixture kept in a rocking furnace at 150° for 10 h; final pressure 30 atm. Volatile products: tetrafluoroethylene (7% recovery), perfluorocyclobutane (5.7 mmol, 4% yield), and 1,1,2,2-tetrafluoroethane (7.7 mmol, 3%). The colourless liquid, removed and distilled under nitrogen blanket, gave phenylphosphine (2.42 g), a 27:73 mixture (1.17 g) of phenylphosphine (total recovery 9%) and phenyl-1,1,2,2-tetrafluoroethylphosphine (4 mmol), and finally pure phenyl-1,1,2,2-tetrafluoroethylphosphine (43.1 g, 0.205 mol, 84%) (Found: C, 46.3, H, 3.4%;  $M^+$ , 210. Calc. for  $C_8H_7F_4P$ : C, 45.7; H, 3.3%;  $M$ , 210) b.p. 67-69 °C at 10 mmHg (lit. [9] b.p. 28° at 0.5 mmHg) with the n.m.r. data in Table 2. The distillation residue, recrystallised from ethanol, afforded brilliant white plates of 1,2-bis(phenylphosphino)-tetrafluoroethane (3.42 g, 10.7 mmol, 4% yield on  $C_2F_4$  consumed) (Found: C, 52.6; H, 3.7; F, 23.7%;  $M^+$ , 318.  $C_{14}H_{12}F_4P_2$  requires C, 52.8; H, 3.8; F, 23.9%;  $M$ , 318) m.p. 60-61 °C,  $\lambda_{max}$  (mulls) at 3.24w, 3.27w, 4.30w (PH str.), 6.73w, 6.99m, 7.64w, 9.15s, 9.35m, 10.00w, 10.22w, 10.93w, 11.26w, 12.42m, 13.2m, 13.59s, 13.87m, and 14.45s  $\mu m$ , with the n.m.r. data in Table 2. In one experiment in which the scale was increased to 0.80 mol for each reagent, and in which no polymerisation inhibitor was present, an explosion

occurred after the 1-litre autoclave had been kept at 150° for 30 min., fracturing the 300 atm bursting disc. No reaction was detected when phenylphosphine and tetrafluoroethylene were irradiated in a sealed silica tube placed 10-15 cm from a 500 watt Hanovia U.V.S. lamp for 6 h at ca. 40 °C.

Reaction of Phenylphosphine with 1,1-Difluoroethylene.-

Negligible reaction occurred when 1,1-difluoroethylene and phenylphosphine were kept at 150 °C for 27 h. When 1,1-difluoroethylene (39 mmol) and phenylphosphine (4.25 g, 39 mmol) were kept in a Pyrex tube (250 cm<sup>3</sup>) at 200 °C for 7 days, 1,1-difluoroethylene (69%) was recovered and distillation of the liquid residue (4.71 g) (13 cm Vigreux column, N<sub>2</sub>) gave phenylphosphine (2.11 g), a mixture (0.42 g) shown by n.m.r. spectroscopy and g.l.c. (2 m SE30 at 150°) to consist of 69% phenylphosphine (total recovery 56%) and 31% phenyl-2,2-difluoroethylphosphine (0.13 g), and an evil-smelling liquid (1.55 g) identified spectroscopically as phenyl-2,2-difluoroethylphosphine (total yield 80% on olefin consumed) b.p. 85 °C at 10 mmHg (Found:  $M^+$ , 174. Calc. for C<sub>8</sub>H<sub>9</sub>F<sub>2</sub>P:  $M$ , 174);  $\lambda_{\max}$  (film) at 3.25w, 3.27w, 3.31w, 3.33w, 3.36w, 3.42w, 4.34m (PH str.), 6.74w, 6.95m, 7.08m, 7.22m, 7.30m, 7.40w, 8.08w, 8.40w, 9.01s, 9.63s, 9.91s, 10.02s, 10.88m, 11.79w, 13.51s, and 14.33s  $\mu\text{m}$ , n.m.r. data in Table 2.

Reactions of Phenyl-1,1,2,2-tetrafluoroethylphosphine.-(a)

With Methanol. No reaction occurred when phenyltetrafluoroethylphosphine was kept in refluxing methanol for 96 h under dry oxygen-free nitrogen.

(b) With an excess of sodium methoxide in methanol. Phenyl-1,1,2,2-tetrafluoroethylphosphine (16.1 g, 76.7 mmol) was added dropwise during 50 min to a vigorously stirred methanolic solution of sodium methoxide [from sodium (5.64 g, 240 mmol) and 50 cm<sup>3</sup> methanol]. A white precipitate formed and spontaneous reflux occurred: heat was supplied to maintain gentle reflux for 1 h after the addition. No gaseous products were detected in a

trap connected to the reaction flask. Methanol was removed at reduced pressure, the residue was extracted with diethyl ether (5 x 25 cm<sup>3</sup>) leaving a residue (9.4 g) containing ionic fluoride, and the extract was evaporated and then distilled under nitrogen at reduced pressure (15 cm Vigreux column) to give: (a) a fraction (0.61 g) b.r. 138-148° at 10 mmHg, shown by g.l.c. (2 m SE30 at 190°) to consist of a 93:7 mixture of methyl phenyl-(E)-1-fluoro-2-methoxyvinylphosphinite (Ia) identified by n.m.r. analysis, and an unidentified substance (i.r.  $\lambda_{\max}$  at 6.3  $\mu\text{m}$ ); (b) a fraction (12.3 g) b.p. 148-150° at 10 mmHg shown by n.m.r. analysis to consist of a 95:5 mixture of methyl phenyl-(E)-1-fluoro-2-methoxyvinylphosphinite (Ia) (yield 12.2 g, 57 mmol, 74%) and an isomer believed to be methyl phenyl-(Z)-2-fluoro-2-methoxyvinylphosphinite (IIa) (2.8 mmol, 4%); and (c) a brown tar (1.7 g) not investigated. Fraction (b) (Found: C, 56.0; H, 5.8; F, 8.4; P, 15.9%;  $\underline{M}^+$ , 214. Calc. for C<sub>10</sub>H<sub>12</sub>FO<sub>2</sub>P: C, 56.1; H, 5.6; F, 8.9; P, 15.7%;  $\underline{M}$ , 214),  $\lambda_{\max}$  (film) at 3.25m, 3.27m, 3.32m, 3.36m, 3.40s, 3.45m, 3.52m, 6.02s, 6.73m, 6.84m, 6.96s, 7.59m, 8.10s, 8.51m, 8.70s, 9.09s, 9.35w, 9.65s, 10.01m, 10.30s, 11.75w, 11.89w, 12.18m, 13.37s, 13.62s, and 14.29s  $\mu\text{m}$ , n.m.r. data in Table 1, could not be separated into pure components by preparative g.l.c.

(c) With an excess of sodium methoxide in methanol-0-d. Phenyl-tetrafluoroethylphosphine (5.05 g, 24 mmol) and a solution obtained by dissolving sodium (1.66 g, 73 mmol) in methanol-0-d (24 cm<sup>3</sup>), treated as described above, gave an ether-insoluble solid (2.82 g) and an ether-soluble oil which was fractionated as above to give (a) a 94:6 mixture (0.31 g) of methyl phenyl-(E)-1-fluoro-2-methoxyvinylphosphinite (Ia) and an unidentified substance; (b) a fraction (3.58 g) shown by i.r., n.m.r., and mass spectrometry to consist mainly (>98%, 75% yield) of the methoxyvinylphosphinite (Ia) (Found:  $\underline{M}^+$ , 214. Calc. for C<sub>10</sub>H<sub>12</sub>FO<sub>2</sub>P:  $\underline{M}$ , 214) containing negligible deuterium; and (c) a tarry residue (0.5 g).

(d) With an equimolar proportion of sodium methoxide in methanol.

A solution obtained by dissolving sodium (2.2 g, 95.6mmol) in anhydrous methanol (72 cm<sup>3</sup>) was added dropwise to phenyl-tetrafluoroethylphosphine (20 g, 95.2 mmol) with stirring at 0° over 2 h under nitrogen, and the solvent was then removed at low pressure. The residue was extracted with ether (7 x 25 cm<sup>3</sup>) leaving a white residue (4.1 g) containing fluoride ions, and the extract was evaporated and promptly distilled (15 cm Vigreux) to give: (a) phenyl-tetrafluoroethylphosphine (31%); (b) a fraction (5.87 g) b.p. 50-52° at 0.5 mmHg (Found: C, 50.5; H, 4.5%. Calc. for a 1:1 mixture of C<sub>9</sub>H<sub>10</sub>F<sub>3</sub>OP and C<sub>9</sub>H<sub>9</sub>F<sub>2</sub>OP: C, 51.0; H, 4.5%) unresolved on g.l.c. (2 m SE30 at 160-200°) but shown by n.m.r. (Tables 1-2) to consist of a 50:50 mixture of methyl phenyl-(E)-1,2-difluorovinylphosphinite (IV) [Found: (by m.s. analysis of the (III)/(IV) mixture)  $\underline{M}^+$ , 202. Calc. for C<sub>9</sub>H<sub>9</sub>F<sub>2</sub>OP:  $\underline{M}$ , 202], and methyl phenyl-1,2,2-trifluoroethylphosphinite (III) (Found:  $\underline{M}^+$ , 222. Calc. for C<sub>9</sub>H<sub>10</sub>F<sub>3</sub>OP:  $\underline{M}$ , 222); (c) a fraction (1.83 g) b.p. 52-54° at 0.5 mmHg shown as above to consist of a 38:62 mixture of the difluorovinylphosphinite (IV) and the trifluoroethylphosphinite (III); (d) a fraction (1.01 g) b.r. 54-72° at 0.5 mmHg, shown by n.m.r. and g.l.c. (2 m SE30 at 160-200°) to consist of a 27:67:6 mixture of (IV) (ca. 3.7 g, 28% on phosphine consumed), (III) (ca. 4.9 g, 34%) and unidentified material; and (e) a dark residue (3.4 g) not examined further. Fractions (b) - (d) were kept in sealed Pyrex tubes at -196°, since samples kept at ambient temperature became orange.

A sample of fraction (b) (1.99 g) was treated under nitrogen at 0° with a solution obtained from sodium (108 mg) in anhydrous methanol (3.5 cm<sup>3</sup>). After dropwise addition (20 min) methanol was removed, and the residue was shown by n.m.r. to consist of 53% difluorovinylphosphinite (IV), 31% trifluoroethylphosphinite (III), and 16% methyl phenyl-(E)-1-fluoro-2-methoxyvinylphosphinite (Ia). The n.m.r. sample and methanol (3.5 cm<sup>3</sup>) were returned to the reactor and kept at gentle reflux for 1 h. After cooling, the composition, determined as above, was found to be 49% (IV), 27% (III), and 24% (Ia). The sample and solvent were returned to the reactor to which was added a further solution from sodium (217 mg) and methanol (7 cm<sup>3</sup>). The mixture was stirred and gently

heated for 1 h, evaporated to dryness, extracted with ether (4 x 10 cm<sup>3</sup>) and the extract evaporated to yield almost pure methyl phenyl-(E)-1-fluoro-2-methoxyvinylphosphinite (Ia) (1.66 g, 83%) identified by i.r. and n.m.r. analysis.

(e) With an excess of ethanolic sodium ethoxide. Phenyl-tetrafluoroethylphosphine (13.0 g, 62 mmol) was added dropwise to a stirred solution obtained by dissolving sodium (190 mmol) in anhydrous ethanol (100 cm<sup>3</sup>); a white precipitate formed and heat was evolved. After the addition (35 min) gentle reflux was maintained for 1 h, the mixture then allowed to cool, and ethanol was removed at low pressure. The residue was extracted with ether (5 x 25 cm<sup>3</sup>), leaving a white residue (6.9 g) (fluoride), and the extract was evaporated and then distilled (Vigreux column) under nitrogen to give: (a) a fraction (2.16 g) b.p. 98-103° at 0.5 mmHg, shown by n.m.r. and g.l.c. (2 m SE30 at 200°) to consist of a 92:8 mixture of ethyl phenyl-(E)-1-fluoro-2-ethoxyvinylphosphinite (Ib) and an unidentified substance; (b) a fraction (9.85 g) b.p. 103-4° at 0.5 mmHg (Found: C, 59.8; H, 6.9%;  $\bar{M}_n^+$ , 242. C<sub>12</sub>H<sub>16</sub>FO<sub>2</sub>P requires C, 59.5; H, 6.6%;  $\bar{M}_n$ , 242)  $\lambda_{max}$  (film) at 3.25w, 3.27w, 3.36m, 3.40m, 3.46m, 6.04s, 6.75m, 7.19m, 7.32w, 7.58m, 7.72m, 8.33s, 8.77m, 9.17s, 9.35m, 9.57s, 9.75s, 9.90m, 10.81s, 11.05s, 11.76w, 12.58m, 13.42s, 13.70m, and 14.31s  $\mu$ m, unresolved by g.l.c. (2 m SE30 at 200°) but shown by n.m.r. (Table 1) to consist of a 91:9 mixture of ethyl phenyl-(E)-1-fluoro-2-ethoxyvinylphosphinite (Ib) (total 10.96g, 73%) and a substance believed to be ethyl phenyl-(Z)-2-fluoro-2-ethoxyvinylphosphinite (IIb) (0.89 g, 6%); and (c) a dark residue (1.89 g) not investigated further.

#### ACKNOWLEDGEMENTS

We thank Dr. M.G. Barlow, of this Department, for his assistance with the interpretation of the n.m.r. spectra.



## REFERENCES

- 1 D. Cooper, R. Fields, and R. N. Haszeldine, *J. Chem. Soc., Perkin I*, 702 (1975).
- 2 G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J. Chem. Soc.* 572 (1964).
- 3 H. Goldwhite, R. N. Haszeldine, and D. G. Rowsell, *J. Chem. Soc.*, 6875 (1965).
- 4 M. Green, R. N. Haszeldine, B. R. Iles, and D. G. Rowsell, *J. Chem. Soc.*, 6879 (1965).
- 5 C. E. Griffin, E. H. Uhing, and A. D. F. Toy, *J. Amer. Chem. Soc.*, 87, 4757 (1965).
- 6 H. Goldwhite and D. G. Rowsell, *J. Amer. Chem. Soc.*, 88, 3572 (1966).
- 7 M. Yoshifuji, S. Nakayama, R. Okazaki, and N. Inamoto, *J. Chem. Soc. Perkin I*, 2065 (1973); S. Nakayama, M. Yoshifuji, R. Okazaki, and N. Inamoto, *Chem. Comm.*, 1186 (1971).
- 8 M. J. Hopkinson, H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *Chem. Comm.*, 513 (1976).
- 9 G. W. Parshall, D. C. England, and R. V. Lindsey, *J. Amer. Chem. Soc.*, 81, 4801 (1959).
- 10 R. Brandon, R. N. Haszeldine, and P. J. Robinson, *J. Chem. Soc. Perkin II*, 1295 (1973).
- 11 R. Fields, R. N. Haszeldine, and J. Kirman, *J. Chem. Soc. (C)*, 197 (1970).
- 12 R. Fields, R. N. Haszeldine, and N. F. Wood, *J. Chem. Soc. (C)*, 1370 (1970).
- 13 J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Pergamon Press, Oxford, 1966, vol. 2; R. Fields, in E. J. Mooney (Editor), *Annual Reports of N.M.R. Spectroscopy*, Academic Press, New York, 1972, Vol. 5a, p. 99.
- 14 R. E. Banks, *Fluorocarbons and their Derivatives*, Macdonald, London, 2nd Edition, 1970, p. 231.
- 15 A. H. Cowley and M. W. Taylor, *J. Amer. Chem. Soc.*, 91, 1929 (1969).
- 16 P. Cooper, Ph. D. Thesis, U. M. I. S. T., 1969.

- 17 H. G. Higson, Ph. D. Thesis, U. M. I. S. T., 1966.
- 18 R. N. Haszeldine, D. R. Taylor, and E. W. White, unpublished.
- 19 Z. Rappoport, in V. Gold (Editor), *Advances in Physical Organic Chemistry*, 7, 1 (1969).
- 20 I. S. Fox, Ph. D. Thesis, U. M. I. S. T., 1964.
- 21 W. Kuchen and H. Buchwald, *Chem. Ber.*, 91, 2296 (1958).